

Formation of Silica-Containing Thrombolites: A Case Study of Visean Limestone in Fukushima Prefecture, Japan

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7 Abstract

8 The complex structural organization of microbialites and their mode of formation are
9 important indicators of the environmental conditions and microbial communities at the onset of
10 deposition, and have been the subject of extensive research. Thrombolites, a type of microbialite,
11 can possess structures containing silicon. The formation process of these structures is debated.
12 This study reports on thrombolites containing silica in Carboniferous (Visean) limestones of the
13 Tateishi Formation within the South Kitakami Belt, Japan, and discusses their formation processes.
14 The clotted texture of the thrombolites in the Tateishi Formation is characterized by the presence
15 of silica at the margins of the clots, and pyrite is present in some specimens. The formation of the
16 thrombolites can be explained by a process analogous to that proposed for silica concretions; i. e.,
17 the decomposition of organic matter, dissolution of carbonates, and precipitation of dissolved
18 silica as a result of a decrease in pH. The fact that pyrite, which is a byproduct of the anoxic
19 decomposition of organic matter by sulfate-reducing bacteria, was produced in association with
20 siliceous structures also supports the hypothesis that the siliceous layer was formed through the
21 decomposition of organic matter. Sclerosponges are known to occur in the Tateishi Formation,
22 and the siliceous fragments they contain are considered to have been the primary source of the
23 dissolved silica. These results indicate that at least some of the siliceous clotted textures observed
24 in microbialites are not primary structures, but rather the result of a combination of the primary
25 microbial fabric and early diagenesis. The fact that the formation process of silica layers, as
26 proposed in this study can provide a general explanation that does not require specific taxonomic
27 groups or unique environments will likely contribute to our understanding of the formation of
28 microbial rocks and early diagenesis throughout geological time.

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31 Keywords: Carboniferous, Concretion, Limestone, Microbialite, Tateishi Formation, Thrombolite.

1. Introduction

Microbialites are important sedimentary deposits that record the carbonate-forming processes associated with biological activity. The complex structural organization of microbialites and their mode of formation are regarded as important indicators of the environmental conditions and microbial ecosystems at the time of deposition (Bosak et al., 2013; Tang et al., 2013; Nomchong and Van Karendonk, 2020), and have been the subject of research for over a century. (Grey and Awramik, 2020). Thrombolites, which are a type of microbialite, are characterized by a microscopic to macroscopic clotted texture (Aitoken, 1967; Riding et al., 1991). This clotted texture is thought to form via the aggregation of microbial colonies, calcification associated with extracellular polymeric substances (EPSs), carbonate precipitation resulting from microbial photosynthesis, stromatolites that have grown within cavities, and dolomite formation associated with diagenesis (Burne and Moore, 1987; Riding, 1991; Shiraishi et al., 2017; Nomchong and Van Kranendonk, 2020; Li et al., 2024). Because clotted texture is formed by a combination of environmental and biological factors (Jahnert and Colins, 2012), its form and formation mechanisms are important for understanding carbonate-producing systems throughout geological time.

Thrombolites can contain silicified structures such as siliceous clotted textures and small spheres, and the formation processes of these features have been discussed in previous studies (Kah and Grotzinger, 1992; Wang et al., 2012; Zhang et al., 2019; Bosence and Gallois, 2022). However, uncertainties remain. Although sclerosponges, diatoms, and sedimentary quartz particles have been cited as the sources of silicon (Francis, 1982; Brehm et al., 2015; Bosence and Gallois, 2022), it remains unclear how they contributed to the formation of clotted textures. While research on the geobiological significance of microbialites continues to advance, the formation processes and genesis of thrombolites containing silicates in carbonate systems remain poorly understood.

This study examines partially silicified clotted textures and lamellar structures in Viséan limestone of the South Kitakami Belt in Japan, and describes their occurrence and petrographic characteristics. The results indicate that these siliceous structures resulted from early diagenesis associated with the decomposition of microbial organic matter. The formation processes of clotted textures and lamellar structures are discussed, along with the applicability of these processes to other siliceous structures in microbialites.

2. Geological setting

The Soma Paleozoic Strata in the Soma area of Fukushima Prefecture in northeastern Japan consist of bedrock that formed within a Paleozoic arc–trench system and overlying shallow-marine sedimentary rocks. The Soma Paleozoic Strata are exposed in northeastern Fukushima

Prefecture, in an area that is 20 km north–south and 6 km east–west (Fig. 1A). The Soma Paleozoic Strata are divided, from base to top, into the Matsugahira metamorphic rocks, the Upper Devonian Ainosawa Formation, the lower Carboniferous Mano and Tateishi formations, the lower Permian Uwagaya Formation, the middle Permian Oashi Formation, and the upper Permian Yumizorezawa Formation (Hanzawa, 1954; Sato, 1956; Yanagisawa et al., 1996; Suzuki et al., 2025). All of these rocks are marine strata, and while clastic rocks predominate, the Carboniferous Tateishi Formation is the only carbonate rock formation that yields fossils such as corals, brachiopods, and sclerosponges (e. g. Sato, 1956; Kato et al., 1987). The Tateishi Formation consists primarily of dark grey to black massive limestone (Yanagisawa et al., 1996) and, based on the species composition of rugose corals, is considered to include the upper Visean (Minato, 1955; Sato, 1956; Minato and Minoura, 1976; Kato, 1984; Yanagisawa et al., 1996). Sato (1956) listed the fusulinid fossils from the Tateishi Formation in his fossil index, and while some researchers suggest that their occurrence extends into the middle Carboniferous (Yanagisawa et al., 1996), this study focuses on an outcrop in which the aforementioned Visean corals occur.

The early Carboniferous Visean corresponds to the interglacial period between a series of extinction events spanning from the end-Devonian to the Tornaisian (Kaiser et al., 2016) and the Late Paleozoic Ice Age (Fielding et al., 2008; Isbell et al., 2012; Montañez and Poulsen, 2013). This stage is characterized by the final flourishing of Paleozoic reef-building organisms and the formation of extensive carbonate platforms. During a series of biological crises at the end-Devonian, the majority of Paleozoic reef-building organisms, including Paleozoic coral symbionts such as stromatoporoids (Vinn, 2017; Liang and Qiao, 2024), became extinct, and the carbonate production system underwent a major reorganization (Walleris, 1996; Webb, 2002; Shen and Qing, 2010; Kaiser et al., 2016). It has been suggested that, through this process, carbonate deposits of microbial origin became increasingly important, ranging from shallow-sea environments to the deep sea (e.g., Shen and Webb, 2008; Shen and Qing, 2010). The Visean was also marked by a gradual proliferation of organisms with hardened skeletons, such as rugose corals, crinoids, and bryozoans (e.g., Bancroft, 1987; Shi et al., 2021; Ausich et al., 2022), and the development of extensive carbonate platforms (Wright and Faulkner, 1990). The Visean carbonate depositional system is important in understanding the interactions between microbial activity and the reorganization of Paleozoic reef-building organisms.

3. Lithostratigraphy of the studied section

Field surveys were conducted in the areas surrounding Tateishi in Minamisoma City, Fukushima Prefecture, which is the type locality of the Tateishi Formation (Fig. 1B). In this area, limestone of the Tateishi Formation is exposed over an area that extends 2 km east–west and 1 km north–south, into the southeast of the Mano dam. In this study, the lithostratigraphy and

lithology were recorded in an outcrop that is 100 m wide and 200 m high facing the south side of the Mano River (Fig. 1C). The limestone strikes N20°W–N20°E, dips 20°–40°N, with a total thickness in the outcrop of ~200 m (Fig. 2). The surveyed section consists mainly of light grey to grey limestone, that is thickly stratified into layers of ~1 m thickness, with a layer of mudstone (~3 m thick) in the middle of the section. The interval extending from 10 to 35 m from the base of the section consists of dark grey to black limestone that is thinly layered with bed thicknesses of 10–40 cm. With the exception of the bottom 5 m of the section, the limestone contains coral fossils and a dark-coloured clotted texture, and both the abundance of coral fossils and the development of the dark-coloured clotted texture vary through the section. Both the coral fossils and the clotted texture protrude slightly from the surrounding limestone and are clearly visible on weathered surfaces (Fig. 3A). Area of clotted texture are sparse in the light grey to grey limestone, but more common in the dark grey to black layered limestone.

Rocks formed by microorganisms can be classified into three types based on their characteristics: stromatolites (laminated), thrombolites (clotted), and leiolites (structureless) (Kennard and James, 1986; Schmid, 1996; Dupraz and Strasser, 1999; Lenfelder and Schmid, 2000). As described below, most of the limestone in the examined section consists primarily of micrite, peloids, and calcimicrobes. Because the texture contains numerous areas of clotted texture ranging in diameter from several millimetres to >10 cm, it is classified as thrombolite. The definitions of terms referring to “clotted texture” vary slightly among researchers. In this paper, the term “mesoclots” (Kennard and James, 1986; Shapiro, 2000) is used to refer to areas of clotted texture ranging in size from 1 mm to ~10 cm; i. e., from areas of clotted texture in thin section to those large enough to be observed with the naked eye.

No distinct sedimentary structures other than bedding are observed throughout the outcrop. Furthermore, the coral fossils occur sparsely and have a range of orientations, and no in situ reef structure has been identified. The bedding planes of the dark grey to black layered limestone are undulating, with wavelengths of 20–40 cm. In addition, thin, lamellar structures oriented parallel to bedding planes occur in limestone (Fig. 3B). These structures consist of one to several layers of sheet-like material, each no thicker than 5 mm. These structures are easily recognizable because they protrude from the surrounding surface on weathered faces, but they have poor lateral continuity a few to ~20 cm. They are thicker and more distinct than the laminae structure of stromatolites, and less numerous. In this study, 71 rock specimens were collected to examine these structures and mesoclots.

Approximately 500 thin sections and 25 polished sections were prepared from the limestone samples collected from this section, and observations were made of the limestone constituents and texture. The limestone that forms thrombolites consists of mesoclots and bio-pel-micrite/wackestone or floatstone. It contains bioparticles such as calcimicrobes, foraminifera,

crinoid ossicles, corals, and brachiopods, as well as abundant peloids. The matrix consists of micrite or locally sparite and occasional angular to subrounded quartz particles of ~100 µm in size. Among the biological specimens, sections of coral observed in thin sections reveal a layer composed of microcrystals, with a maximum width of about 500 µm, formed on the surface of the fossil. The boundary between this thin layer and the coral is indistinct and irregular, and the inward migration of the layer appears to have involved the dissolution of the coral fossil. Several species of calcimicrobe have been identified in the section, and they exist in the substrate either as individuals or in colonies. Bioparticles, micrite and peroids are also the components of the mesoclots, which contain large numbers of calcimicrobes that have aggregated into clusters. The grey limestone comprising the bottom 5 m of the studied section is a calcareous sandstone that contains very fine to medium-sand-sized grains of calcite grains. The grains are subrounded to well-rounded, and the rock is sorted. This limestone does not contain biogenic fragments, such as calcimicrobes.

4. Calcimicrobes and microbialite structures

4.1. Calcimicrobes

The thin sections contain the calcimicrobes, *Girvanella* Nicholson and Etheridge 1878, *Phacelophyton* Bian and Zhou 1990, *Frustulata*-like calsimicrobe and *Aphralysia* cf. *carbonia* Garwood 1914 (fig 4A–E).

Girvanella, which appears as elongate and gently curved calcareous tubes, occurs throughout the biomicrite. The sheath does not branch and has a uniform diameter, with a maximum length of ~500 µm. *Girvanella* is classified into parallel adherent types and grain adherent types, based on its growth form. Parallel adherent types have a tube with a diameter of 30–50 µm, do not grow in densely packed clusters and extend nearly parallel to bedding planes. The sheaths are not perfectly parallel, but bend irregularly. Grain adherent types are small, with a diameter of 20–30 µm, and are densely packed in the direction perpendicular to bedding planes, being particularly dense on the surfaces of coral fossils and small mesoclots. Sheaths similar to *Girvanella*, with a diameter of 20–30 µm, exist within the structures of the mesoclots (Fig 4A and B).

Phacelophyton comprises elongate subcircular sparite tubes that are straight to gently curved and 2–5 mm in diameter. The sheath contains sections where it branches at a sharp angle. The relatively thick microcrystalline layered wall exhibits a distinct sheath structure with a diameter of 20–50 µm (Fig 4C).

Aphralysia cf. *carbonaria*, which consists of clusters of foamy structures, is rare in the biomicrite. The clusters are subcircular to irregular in shape, >1 cm in size, and filled with peloids and micrite (Fig 4D).

Frustulata-like calcimicrobes, which have calcareous plates with irregular bends and

branches, tend to occur within the mesoclots. The skeleton consists of microcrystalline calcite, is layered, and is 50–100 μm wide. Regularly ramified and acute apical forms are observed locally (Fig 4E).

4.2. Mesoclots and EPMA analysis

To determine the constituent materials and elemental distribution of the thrombolites, observations and analyses were first conducted using polished and thin sections of mesoclots. Mesoclots were clearly identifiable in the polished sections, and reflected light microscopy of the polished sections revealed that ~25% of the mesoclots contain multiple pyrite crystals (diameter 10–30 μm) at their peripheries (Fig. 5). The pyrite grains are concentrated in some samples and are particularly prominent in the black limestone. The interiors of mesoclots consist of calcimicrobes, other biological fragments, peloids, micrite, and sparite. The mesoclots have a distinct outer margin, and irregular shape. The margins of the mesoclots consist of microcrystalline material, but it is not possible to distinguish the margins from the rest of the mesoclots or to determine the composition of the microcrystalline material.

To examine the mesoclots in detail, 17 thin sections containing mesoclots of ~1–30 mm were polished to #6000, coated with platinum, and analysed using an electron probe microanalyzer (EPMA; JXA-8530F). The analysis focused on the periphery, the centre, and the transect from the periphery to the centre of the mesoclots. Measurements were taken within areas of $600 \times 600 \mu\text{m}$, $1 \times 1 \text{ mm}$, and $5 \times 5 \text{ mm}$ using beam diameters of 1.0, 1.5, and 5.0 μm , respectively. EPMA analysis confirmed that in all of the mesoclots, the central portion contains a high concentration of Ca, while the peripheral regions consist of a Si-rich microcrystalline material (Fig. 6). The high Si concentration occurs in a layer that is <3 mm thick. In the central parts of the mesoclots, calcimicrobe fossils and micrite are often rich in Ca, and scarce Si-rich biological fragments and Si-rich aggregates also occur. There is a gradual decrease in Ca content and an increase in Si content from the centre to the periphery of mesoclots. The outermost Si-rich parts of the mesoclots, contain pyrite crystals that are ~30 μm in size (Fig. 7). The S and Fe contents are low in the central parts of the mesoclots and high in the Si-rich zones. The P contents are low in both the central and peripheral regions of the mesoclots, with a maximum concentration ~5%. The bio-pel-micrite in the limestone matrix surrounding the mesoclots is poor in Si and rich in Ca, and the boundary between this material and the mesoclots is clearly defined on elemental maps. In some samples, Al and Mg coexist within the same phase in both the matrix and the mesoclots, and Mg occurs in scattered clusters (Fig. 8).

4.3. EPMA analysis of lamellar structures and the surfaces of coral fossils

The lamellar structure consists of microcrystals, and a microcrystalline layer with a maximum

width of 500 μm occurs on the surface of the coral fossils. EPMA analysis was performed to determine the constituent materials of these structures and the distribution of elements within them as done for the mesoclots. The analysis targeted the upper part of the surface structure and the surface of coral fossils, with measurements taken over areas of $500 \times 500 \mu\text{m}$ and $600 \times 600 \mu\text{m}$ in size using a beam diameter of 1 μm (Figs. 9 and 10). The microcrystalline phase that constitutes the lamellar structure is rich in Si and consists of alternating layers rich in Ca. Although both layers are microcrystalline and their mineralogical differences are indistinguishable in thin section, EPMA elemental maps clearly reveal compositional contrasts between them. The Si-rich layers are $\sim 100 \mu\text{m}$ thick and show high Si counts, whereas the Ca-rich layers exhibit elevated Ca counts and contain micrite. The boundary with the surrounding limestone matrix is distinct, and no specific particles or structures are observed in the microcrystalline phase other than the Si-rich crystals. The microcrystalline layer on surface of coral fossils is enriched in Si. Although the boundary with the substrate is distinct, the boundary between the coral fossil and the silica layer is indistinct. The coral fossils are characterized primarily by Ca, with Si being limited to the surface.

5. Discussion

5.1. Peloids and micrite in the Tateishi Formation

The limestone of the Tateishi Formation is poor in macrofossils, and it is difficult to explain the formation of the limestone based solely on the corals reported in previous studies. As noted above, from a macro-scale perspective, microorganisms and thrombolites contribute to limestone formation. In addition, microorganisms also contribute to the formation of peloids and micrite, which are the main constituents of the limestone of the Tateishi Formation. Although the origins of peloids are diverse, many are thought to involve microorganisms (e.g., El Ayyat, 2015; Zhou and Pratt, 2019; Guanming et al., 2025). Guanming et al. (2025) defined microbial peloids as rounded particles of 30–120 μm in size, with indistinct edges and no internal structure. Since peloids lack embedded rock fragments or distinct boundaries, can be clearly distinguished from intraclasts, and have not been affected by transport or redeposition, they are described as the products of microbial activity and metabolism (Sun and Wright, 1989; Folk and Chafetz, 2000; Riding and Tomás, 2006; Boulvain, 2007; Zhou and Pratt, 2019; Guanming et al., 2025).

Similarly, the peloids of the Tateishi Formation lack distinct margins and show no internal structure, suggesting that their origin was associated with microbial activity. Micrite has three distinct origins: formation in response to changes in water chemistry (automicrite), originating from organic skeletons (allomicrite), and formation after carbonate deposition (pseudomicrite) (Frügel, 1982). The Tateishi Formation contains organisms with calcareous skeletons, such as corals, foraminifera, and brachiopods, and it includes allomicrite. In general, the fragmentation

of biogenic skeletons is interpreted to result from mechanical erosion by water currents and waves, or from maceration, whereby the skeleton breaks down as its constituent organic matter is leached away (Alexandersson, 1979). However, given the abundance of calcimicrobes in the Tateishi Formation, the focus here is on microbial boring. Although microbial erosion proceeds through biochemical dissolution and therefore does not directly affect the production of calcareous mud, it is thought to enhance the process of grain size reduction by reducing the structural durability of a wide range of particle sizes, from skeletal material to calcareous sand (Okimura et al., 1995). In particular, *Girvanella* can bore into carbonate particles (Huang et al., 2019), and it should be considered whether boring occurred in the Tateishi Formation, which is rich in calcimicrobes including *Girvanella*.

Pratt (2001) suggested that *Girvanella*-like calcimicrobes are the source of a significant amount of calcareous mud in marine ecosystems; consequently, calcimicrobes, as well as bioskeletons, can be considered the primary source of the micrite in the Tateishi Formation. Furthermore, it is believed that *Girvanella* carried out photosynthesis and that its metabolism triggered carbonate precipitation (Chafetz, 1986; Folk and Chafetz, 2000; Yan et al., 2019; Luo et al., 2021). Accordingly, micrite and peloids in the Tateishi Formation are inferred to have been formed through microbial activity.

Microbe-dominated reefs increase in number following extinction events (Kiessling, 2002). Microbe-dominated reefs made up ~50% of the total reefs during the early Carboniferous, which is the highest value recorded since the Early Ordovician (Adachi et al., 2012), when reef-building organisms with skeletons first appeared during the Paleozoic (Kiessling, 2002). The limestone of the Tateishi Formation also represents a depositional environment that closely reflects Visean and Mississippian settings, and it is considered that not only corals but also calcimicrobes thrived in this setting. There have been no reports of calcimicrobes in the Carboniferous limestone of the South Kitakami Belt, possibly because of the focus on macrofossils (e.g., Kawamura and Kawamura, 1989; Ehiro, 2017). The microbialites in the Tateishi limestone will likely provide important insights into the depositional environment of the South Kitakami Belt as a model case for the Visean.

5.2. Sources of Silica

The origin and formation process of silica in thrombolites are debated. The sources of silicon in carbonate rocks are generally considered to be diatoms, sedimentary quartz grains, and sclerosponges (e.g., Wang et al., 2012; Bosence and Gallois, 2022). Of these, diatoms appeared in the fossil record during the early Jurassic (Rothpletz, 1896, 1900) or, according to molecular phylogeny, between the late Permian and Middle Jurassic (Sorhannus, 2007); thus, they are excluded from consideration in the present case. Although some reports suggest that mesoclots

coated with silicate-containing carbonates are formed by the EPS structures of calcified cyanobacteria and algae, the silicate layer is only a few microns thick because it originates from EPSs, and it occurs as a continuous capsule because it accumulates over multiple generations (Zhang et al., 2019).

In the Tateishi Formation, there is an uneven distribution of Si, which is concentrated extensively on the surfaces and planar structures of mesoclots to a thickness of ~3 mm, thereby complicating interpretations of silicate based on EPS structures. Brehm et al. (2015) reported experimental results showing that microbial communities within biofilms cause the dissolution of sedimentary quartz particles, and Bosence and Gallois (2022) invoked this result to explain the origin of silica in thrombolite. Although there are no reports of tuffaceous facies in the Tateishi Formation, the matrix contains a small number of quartz grains, and elemental analysis shows that, depending on the sample, the formation contains Mg and Al. Therefore, it is possible that silicified materials, such as clay minerals and volcanic clasts, were introduced to the sediment and served as a source of silicon. On the other hand, *Chaetetes* sp. occurs in the Tateishi Formation (Kato et al., 1987), indicating the presence of a sponge-rich habitat. Although the presence of siliceous skeletal elements in *Chaetetes* sp. cannot be confirmed (e. g. Gray, 1980; Sánchez-Beristain et al., 2012), its occurrence suggests that siliceous sponges were likely present, and the dissolution of their skeletal fragments may have provided a primary source of dissolved silica. This interpretation is supported by the elemental distribution data of the present study, which shows silicon-rich biofragments interpreted as remnants of siliceous fragments. Since pore water is silica-unsaturated, biogenic opal dissolves over time (Cappellen et al., 2002), and it is thought that siliceous fragments could also have served as a source of silica. The concentration of silica in the pore water of sediments increases significantly over time (e.g., Schink and Guinasso, 1975), and this could contribute to the formation of siliceous material.

5.3. Formation of the Silica Layer

Here we consider the formation process of the silicon-rich layer that borders the mesoclots. Thrombolites are generally interpreted to have formed through biogenic construction, erosion, encrustation, internal deposition, and early calcite cementation (Ginsburg and Schroeder, 1973; Bosence, 1984; Bosence and Gallois, 2022). Consequently, thrombolites have a non-uniform internal structure (e.g., Riding, 2000; Pache et al., 2001) and often contain silicate-rich textures (e.g., Kah and Grotzinger, 1992; Wang et al., 2012; Bosence and Gallois, 2022). Zhang et al. (2019) reported mesoclots covered by siliceous carbonate, minerals and interpret the silica in the mesoclots to have resulted from the distinctive EPS structures of the calcified cyanobacteria/algae *Epiphyton*. However, since such silica layers are only a few microns thick and had disappeared by the Cretaceous (Barattolo, 1990), it is difficult to explain all silicate structures based solely on

EPSs.

If we consider the mesoclots of the present study to be silicified structures in carbonate sediment, they can be considered a type of silica concretion, despite their range of shapes. The term “concretion” refers to a spherical rock mass in sedimentary rock, and such features occur across all time periods and regions (Bates and Jackson, 1987). The formation processes of concretions, particularly carbonate concretions, have been elucidated in recent studies (Yoshida et al., 2015, 2018, 2020). Whether carbonate, silica, or iron-dominated, concretions form rapidly as a result of changes in the pH of the pore water between biogenic material and its surroundings (Yoshida et al., 2015, 2018, 2020, 2021; Shirono et al., 2021). According to Yoshida et al. (2021), silica precipitation occurs because the solubility of silica is reduced by decrease in pore water pH resulting from the decomposition of organic matter. Since the solubility of silica in water decreases significantly at pH <9.5 (Alexander et al., 1954), a decrease in pH affects the precipitation of silica. Precipitated silica fills both existing pores and those formed by the dissolution of carbonates, thereby blocking the supply of acid and dissolved silica as well as diffusion driven by concentration gradients (Yoshida et al., 2021). As a result, a distinct chemical boundary ultimately forms between the sediment and the precipitate (Yoshida et al., 2021). Within microbial communities, a decrease in pH and the chemical dissolution of calcareous material are associated with increases in dissolved organic carbon and organic acids (Monty, 1976; Dupraz et al., 2009). The mesoclots of the Tateishi Formation contain abundant calcimicrobes, and it is considered that these microorganisms were the primary source of organic matter.

The occurrence of pyrite scattered across the surface of mesoclots also indicates the decomposition of organic matter. In anaerobic environments, sulfate-reducing bacteria obtain energy by degrading organic matter and reducing SO_4^{2-} (e.g., Postgate, 1984). Pyrite is formed when H_2S , a byproduct of anaerobic activity, reacts with Fe^{2+} and subsequently with FeS , which is a product of the initial reaction (e.g., Berner, 1970). The pyrite of the present study occurs within structural boundaries and is sealed within silica, which would have preventing it from receiving H_2S and Fe^{2+} ; thus, it seems difficult to explain the formation of the pyrite. This discrepancy between the sealed condition of the pyrite and its formation can likely be explained by the formation of a precipitation front where silica becomes supersaturated and by the diffusion of silica driven by chemical concentration gradients (Bojanowski and Clarkson, 2012; Yoshida et al., 2021).

In summary, the boundary between the silica and the limestone matrix resulted from silica diffusion and precipitation, and the front of organic matter decomposition was located closer to the centre of the mesoclots than the boundary currently observed. It is considered that the area where pyrite is distributed was not initially sealed off by silica but was in a “semi-buried” state, receiving H_2S from organic matter and Fe^{2+} from sediments. It cannot be definitively stated that

the actual depositional environment was the extremely reducing environment assumed for pyrite formation, and it is difficult to explain pyrite formation solely through the reaction between FeS and H₂S. Therefore, it is thought that the reaction between FeS and the elemental sulfur formed by the oxidation of H₂S was also one of the pathways leading to the formation of pyrite (e.g., Wilkin and Barnes, 1996; Rickard, 1997). Even if the reaction began as aerobic respiration, once the oxygen was consumed, it would have transitioned to anaerobic respiration, thereby providing a sufficient explanation for the origin of the pyrite. Furthermore, the metabolic processes of bacteria such as sulfate-reducing bacteria, nitrogen-fixing bacteria, and methanogens under anaerobic conditions result in higher HCO₃ levels, leading to the supersaturation and precipitation of calcium carbonate (e.g., Roberts and Whelan, 1975; Suess, 1979). Since the pH decreases with the precipitation of calcium carbonate, it is possible that a silica layer formed while producing minute amounts of carbonate even under anaerobic conditions.

The same formation process applies to the coral fossils in the Tateishi Formation that have a silica layer on their surface. In summary, this layer is explained by the decomposition of organic matter, the dissolution of carbonates, and the precipitation of silica. Although no pyrite deposits were observed, the boundary between the coral fossils and the silica layer is quite indistinct, and since erosion of the silica layer into the coral fossils is evident, it is concluded that carbonate dissolution occurred, at least on the surface of the coral fossils.

The lamellar structures of the Tateishi Formation are also characterized by high contents of silicon, and their formation can be explained in the same way as for the mesoclots. Kuma et al. (2019) and Yoshida et al. (2021) proposed that the bedded chert of the Green River Formation in the USA resulted from the decomposition of organic matter—, as derived from algae that were uniformly distributed within the sediment—, and the precipitation of silica due to pH reactions. Although no algae have been identified to date that are uniformly distributed within the Tateishi Formation, the horizontal diffusion rate of silica in fine layered sediments should be higher than the vertical diffusion rate (Yoshida et al., 2021), and it is reasonable to assume that if algae or similar organisms were to grow in a thin, dense layer on the sediment surface, they could be formed through a similar process to that which produced bedded chert of the Green River Formation.

5.4. Significance of Siliceous Layers in Microbialites

The mesoclots with silica layers in the Tateishi Formation were not formed by siliceous microorganisms. Instead, they are interpreted to have formed secondarily as a result of diagenesis during the early stages of burial, from dense aggregates of calcimicrobes (Fig. 11), as follows (1) Matrix and “calcimicrobes” exist, and particularly dense concentrations of microorganisms form the framework that gives rise to mesoclots. (2) Mesoclots form complex structures as a result of

erosion and damage. (3) As the matrix accumulates, the mesoclots become buried. (4) With the oxidation of organic matter of microbial origin, the saturation of calcium carbonate decreases, causing carbonates to dissolve. (5) As the decomposition of organic matter progresses, Ca in the pore water becomes depleted due to the formation of carbonate minerals, causing the pH to drop. As a result, dissolved silicon precipitates in the pores, forming a silicate-rich structure. Although such organic oxidation may initially occur aerobically, in the final stages of organic oxidation when oxygen has been consumed, anaerobic oxidation becomes the predominant process, and pyrite crystals are formed from hydrogen sulfide produced by sulfate-reducing bacteria. As a result, mesoclots are formed with characteristic surface deposits of silica and pyrite. In summary, silicified mesoclots are not primary structures but are interpreted to have formed through the early diagenesis of carbonate microbialites.

The formation of the silica layers in the Tateishi Formation does not require specific taxonomic groups or extremely specialized environments. Furthermore, whether the shape of the layers is irregular or planar, their origin can be explained in terms of the original organic matter and dissolved silica. This generality should aid in understanding carbonate rocks containing thrombolites or other siliceous structures that contain silica, regardless of age or region.

6. Conclusion

The Visean stage of the early Carboniferous was a period of flourishing reef-building organisms, and previous research on the Tateishi Formation has focused primarily on coral fossils. The present study focused on the microscale and revealed that the limestone of the Tateishi Formation consists of thrombolites composed of calcimicrobes, microbial peloids, micrite, and mesoclots. It is considered that microbial activity played an important role in the formation of the carbonates of the Tateishi Formation. The silicon in mesoclots is concentrated at the outer edges and is associated with pyrite. This characteristic is not due to the structure of the original microorganisms, but can be explained by the dissolution of carbonates and the precipitation of silicon associated with the early decomposition of organic matter following burial. Therefore, structures with silica-rich rims in microbialites do not necessarily represent primary microbial calcification, but may be the result of a combination of a primary microbial fabric and early diagenesis.

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Captions

Figure 1. Maps showing (A) the location of the South Kitakami Belt and the Soma area, (B) the surveyed geology of the study area and distribution of the South Kitakami Belt, and (C) a route map of the study area. The green star in (B) indicates the area shown in (C).

Figure 2. Columnar section of the eastern part of the Tateishi Formation.

Figure 3 (A) Outcrop section containing mesoclots. (B) Sheet-like structure (TILS-21). Scale bar is 2 cm.

Figure 4. (A) & (B) *Girvanella*. (C) *Phacelophyton* sp. (D) *Aphralysia* cf. *carbonaria*. (E) Frustulata-like calcimicrobe. Scale bar is 0.5 mm for (A) to (D) and 2 mm for (E).

Figure 5. (A) Polished surface containing mesoclots (TILS-27; scale bar is 5 cm). (B) Close-up of the polished surface containing mesoclots (scale bar is 0.5 cm)

Figure 6. EPMA analysis results (TILS-27) for a thin section containing mesoclots (scale bar is 2 mm) and the area outlined in the figure.

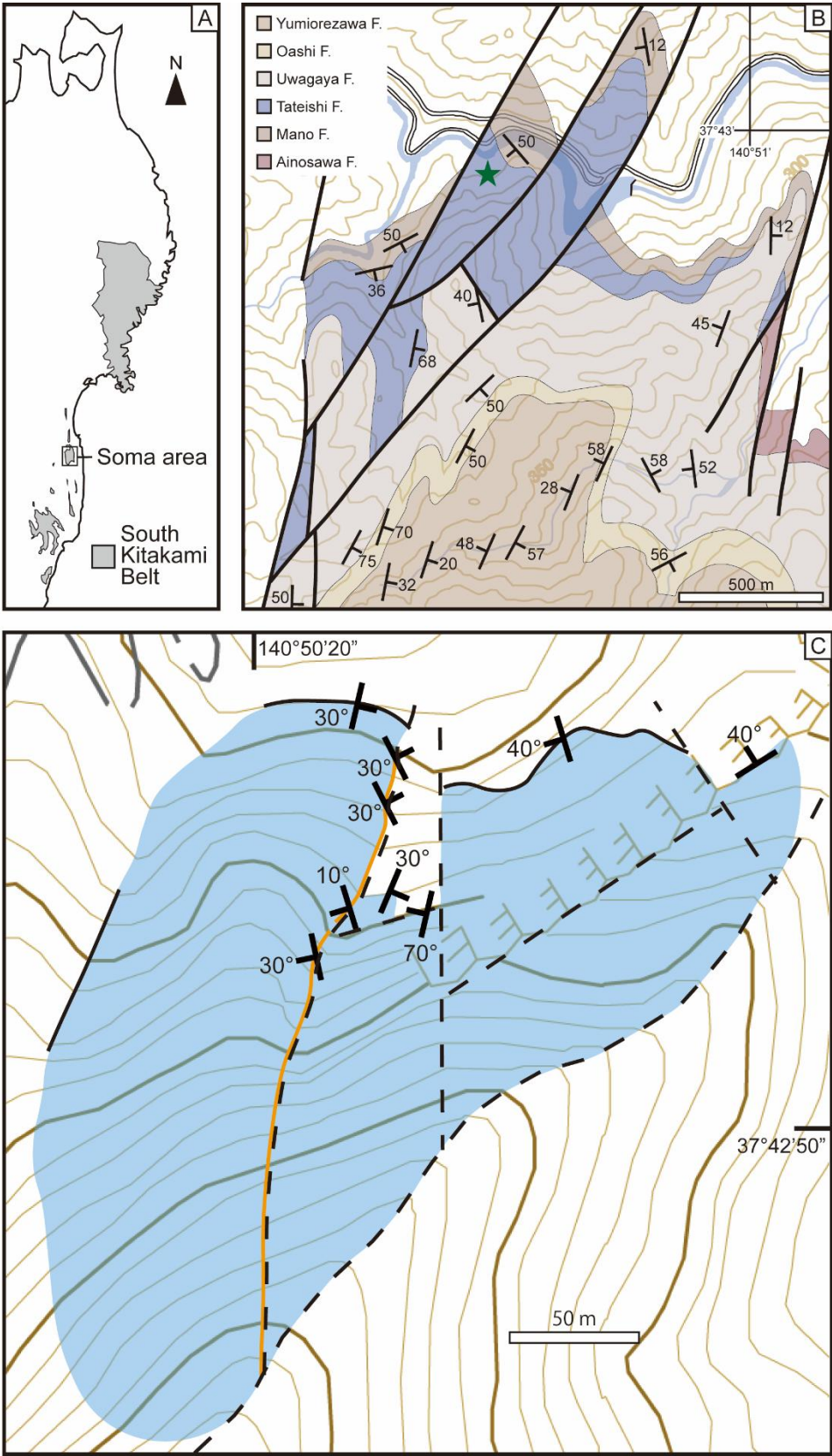
Figure 7. EPMA analysis results for the margins of mesoclots (TILS-27).

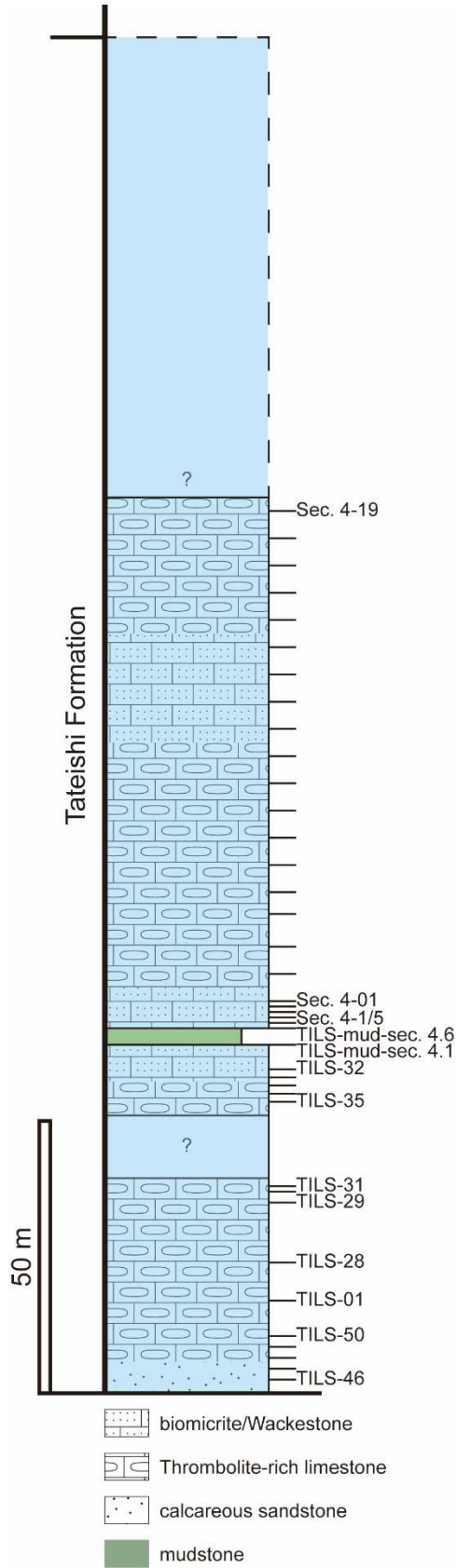
Figure 8. EPMA analysis results of the peripheral regions of mesoclots in a layer containing Al and Mg (TILS-09).

Figure 9. EPMA analysis results (TILS-21) for a thin section containing a sheet-like structure (scale bar is 1 mm) and the area enclosed by the rectangle.

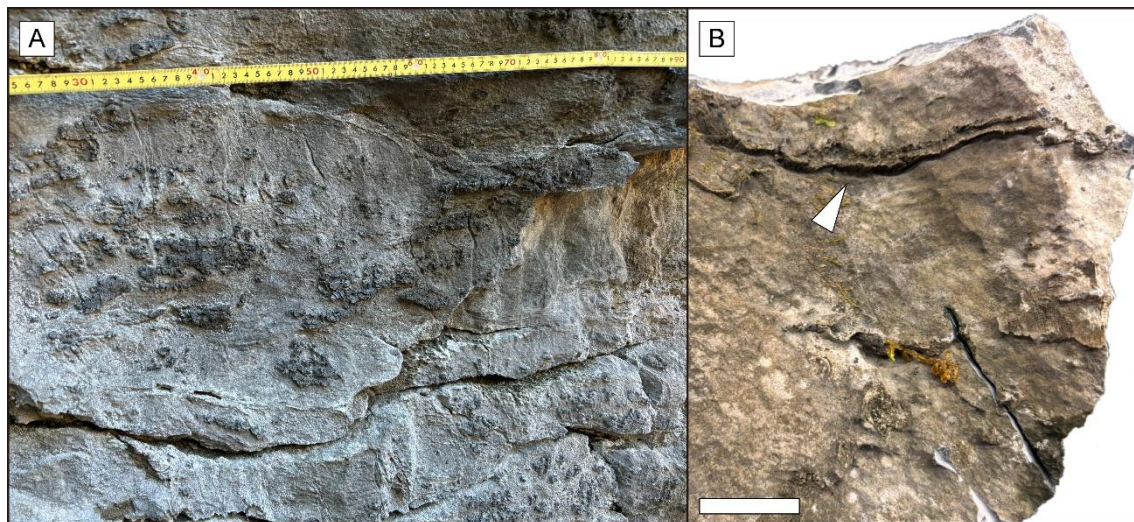
Figure 10. Thin section containing coral fossils (scale bar is 1 mm) and EPMA analysis results for the area outlined by the rectangles (TILS-21).

Figure 11. Formation of mesoclots containing silicates on their surfaces





726 Fig 3



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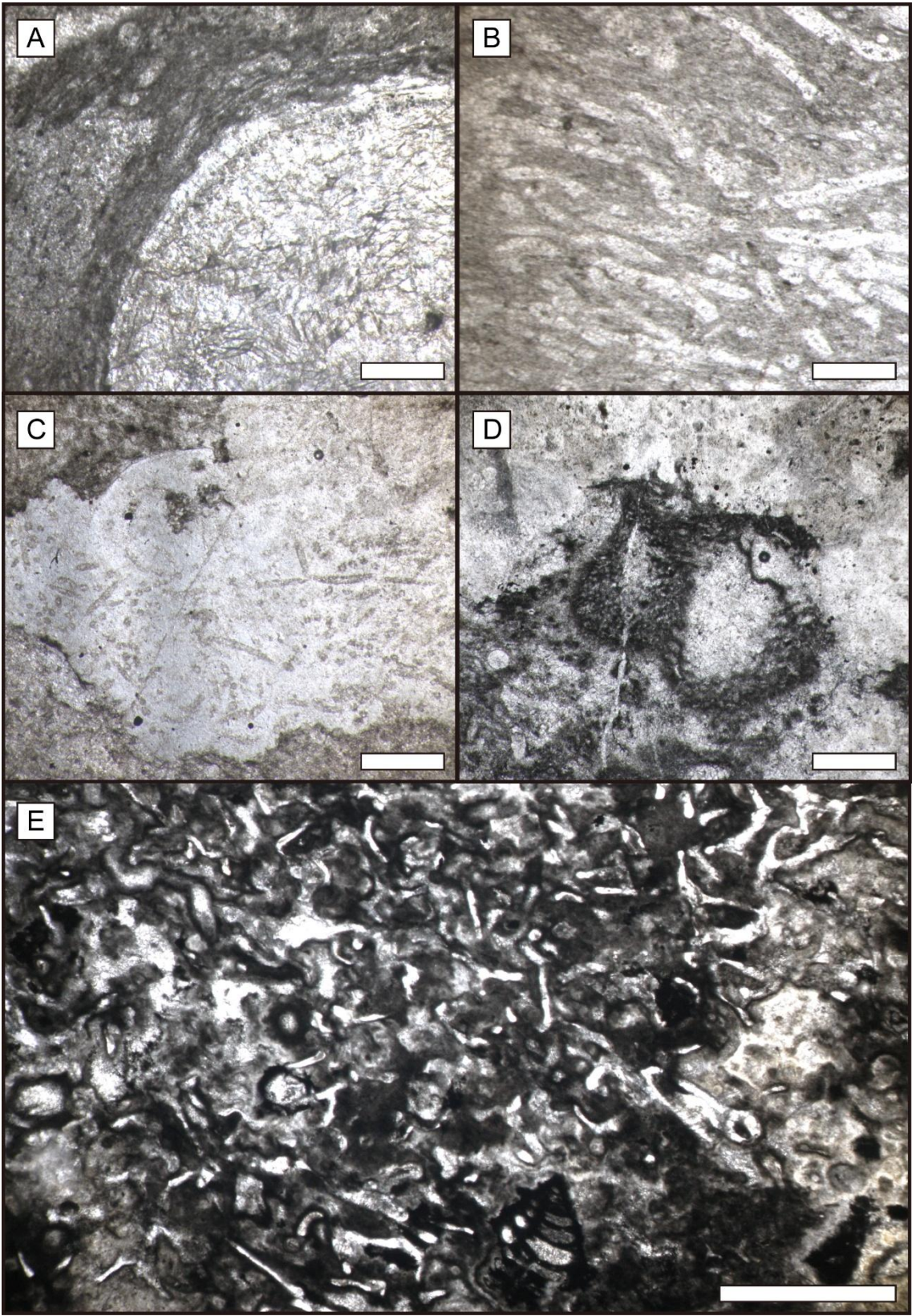


Fig 5

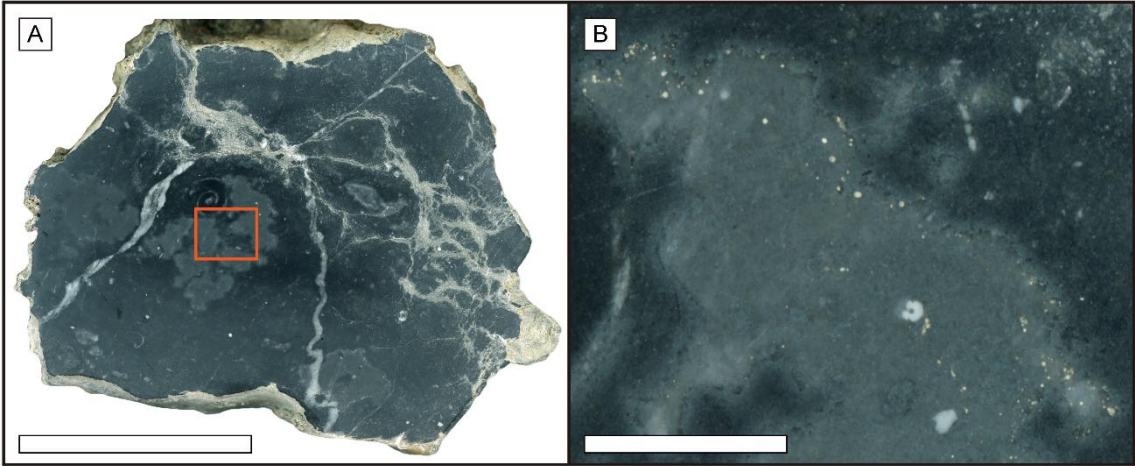
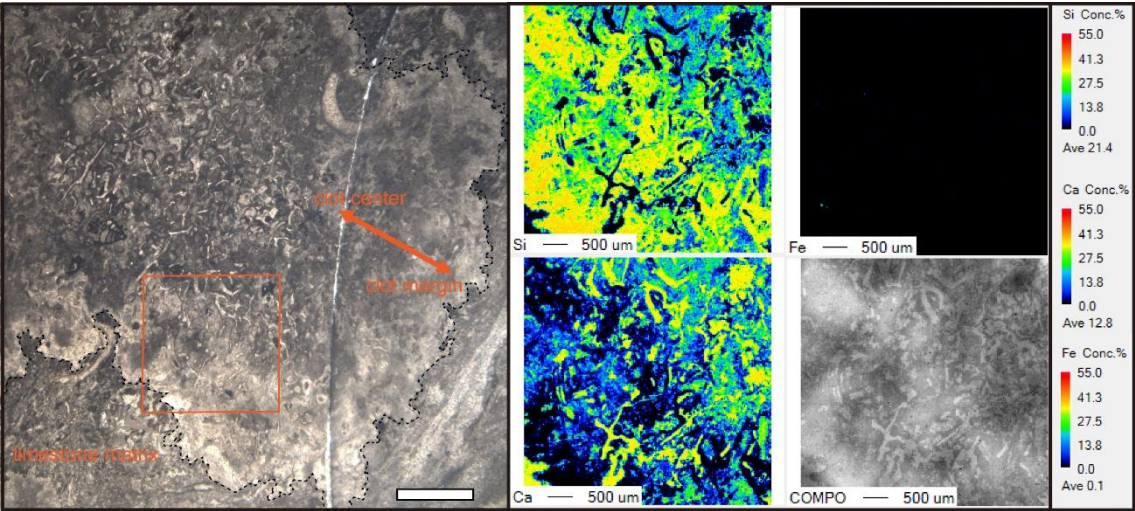
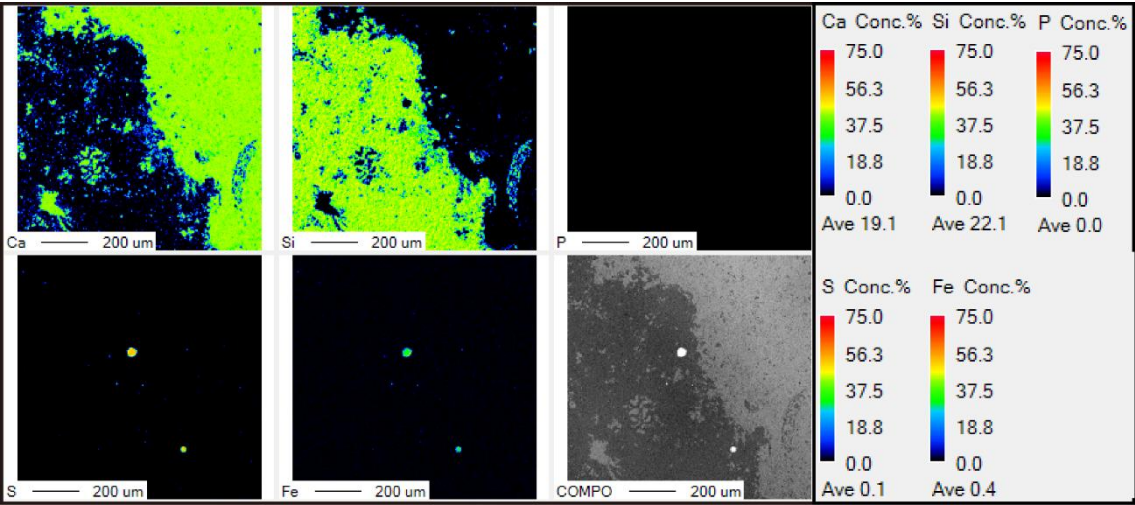


Fig 6



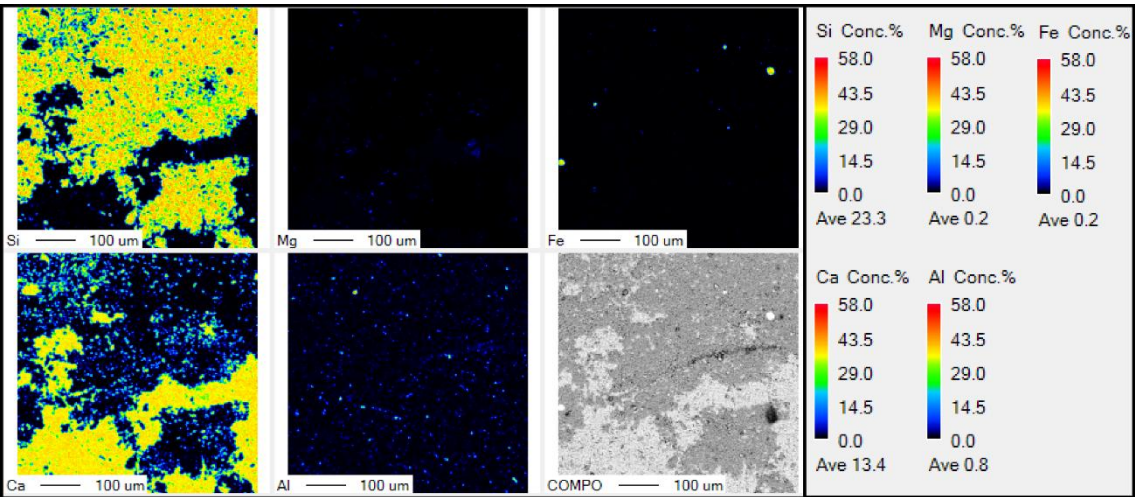
739 Fig 7



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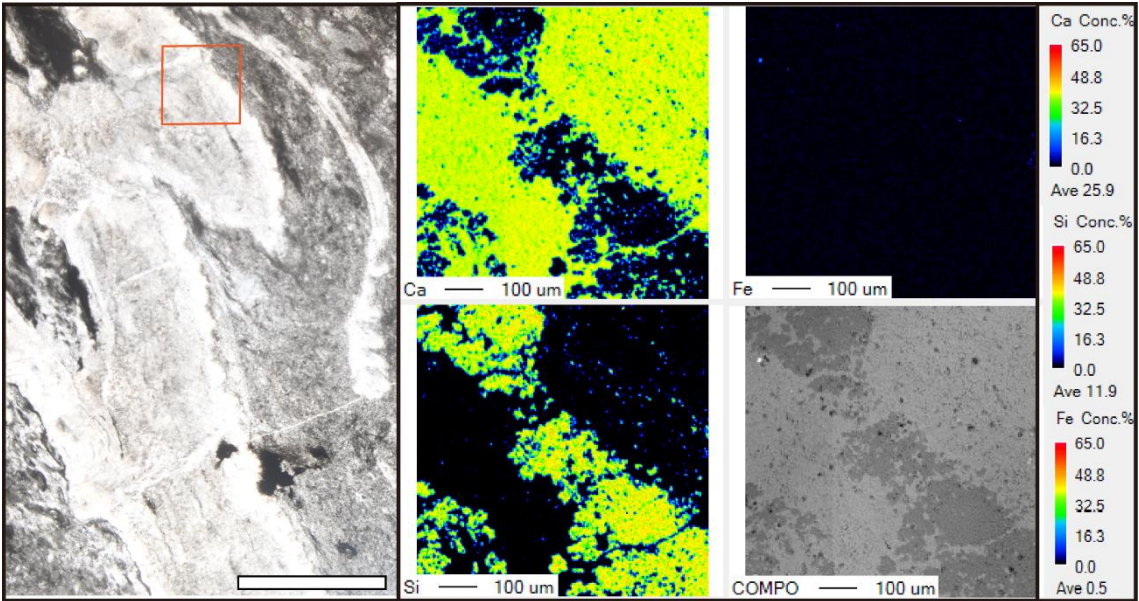
742 Fig 8



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745 Fig 9



749 Fig 10

