UNIVERSITY OF TARTU
INSTITUTE OF ECOLOGY AND EARTH SCIENCES
DEPARTMENT OF GEOLOGY

Sigrid Soomer

Paleoproterozoic spherulitic layers in Zaonega Formation, Karelia, northwestern Russia

MSc thesis

Supervisors: Kalle Kirsimäe
Aivo Lepland

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Contents

1. Introduction

Spherulitic sedimentary beds composed of spherical particles of different size and composition are peculiar features of the sedimentary successions. By definition the sedimentary spherulites are roughly spherical aggregates having radial internal structure or rounded particles made up of a thin, typically calcareous, layer covering a crystalline calcite core (Verrecchia et al. 1995).

Spherulitic particles found in sedimentary successions can be of different origin: early life forms (Javaux and Benzerara 2009; Sergeev 2009), aggregates produced by sedimentary processes like ooids (Sommers et al. 2000; Schröder et al. 2006) or hydrocarbon droplets created by oil migration (Mancuso et al. 1993), from volcanic eruptions (Brown et al. 2012; Brown et al. 2010), impact processes (Glass 2002; Cannon et al. 2010; Johnson and Melosh 2012; French and Koeberl 2010) or even meteoroid material itself (Harvey et al. 1998; van Ginneken et al. 2010). Occurrence and/or formation of spherulites in sedimentary beds provides, thus, information on sedimentary environments, early-to-late digenetic processes, and events beyond the sedimentary basins themselves.

About 2 Ga old Zaonega Formation organic-rich sediments in Onega basin, Karelia, Russia contain layer/lenses of spherical aggregates that were discovered in drillcores 13A and 12A of the Fennoscandian Arctic Russia-Drilling Early Earth Project (FAR—DEEP) in 2007. In autumn 2012 three additional cores were drilled in the same area under cooperation between Norwegian Geological Survey, University of Tartu, Tallinn University of Technology and Institute of Geology, Karelian Centre of Russian Academy of Sciences, and similar spherulitic aggregates were discovered in drillcore OnZap1.

Recently, these spherulitic beds were proposed to be of meteorite impact origin and the spherules to represent recrystallized ejected silicate glass droplets (Huber et al. 2014). Alternatively, a bacterial origin of these structures has been suggested (Medvedev et al. 2009), mainly because the existence of organic matter associated with spherical aggregates.

It is really important to learn to find and recognize impact spherule layers from Precambrian age because of much of the Earth’s crust from that period is now resorbed into the mantle and traces of impact /cratering is lost, only large to global impact ejecta /strewn fields may have locally preserved. It is also important that the age of this spherule layer is in the age close to the significant changes in Earth atmosphere, in evolution of life and ecosystems as a whole.

Studying spherule layers from this time could help to understand importance of meteorite impacts and its influence to evolution. Impact spherule layers have been investigated for a long time because this is not an easy task to classify globules in sedimentary beds to be impact spherules especially in sediments from Precambrian era. This thesis could be helpful to investigate and compare spherule layers this old since there has been efforts made to find certain characteristics for Precambrian spherule layers and learn what internal and external textures spherules can have and what it means (Simonson 2003).

The aims of this thesis are (1) to study the distribution, morphology, mineralogy and geochemistry of these spherical aggregates in drillcores 13A, 12A and OnZap1; (2) to describe and interpret the brecciated sedimentary beds containing the spherical aggregates and (3) to reveal the origin of the spherulitic aggregates considering different possible modes of formation.

2. Spherical aggregates in sedimentary rocks

There are several aggregates in rocks which have spherical morphology/ globular structure. Spherulites are found in igneous rocks characterized by a cluster of radiating acicular or lath-like crystals that form by crystallization under supercooling conditions where mineral nucleation is impeded (Gránásy et al. 2005). Most importantly, spherical textures are common in sedimentary rocks and may have very different origin ranging from spherical fossils of algae or bacteria to volcanic or impact lapilli.

2.1 Fossilized bacteria and algae

Possible life forms that have spherical morphology have been described from as early as 3 Ga time as small (<10 μm) solitary microfossils (Sergeev 2009). However, there are certain criteria which must be fulfilled for a globule to be described as a fossil (Javaux and Benzerara 2009). First it should be found in original (meta-)sedimentary context. Secondly, if spherules are fossilized remains these should be endogenous - enclosed within the minerals composing the rock or placed between the grains before cementation of the rock. Fossils should also be syngenetic - they must have occurred in the sediments prior to their diagenesis and lithification (Javaux and Benzerara 2009). The criteria for biogenity are mostly related to microstructures that are determined to be of biological morphology. This means that the morphology of the spherules has to be comparable to modern microorganisms or well documented fossils. Organic-walled microstructures which are well preserved in cherts and silicified sediments can show in 3D the cell lumina (originally cytoplasm-filled cell cavities) (Javaux and Benzerara 2009). Also, to determine spherical aggregate to be a fossil it should also be in biological size ranges (>0.01 μm^3) (Javaux and Benzerara 2009).

Another important criterion, if available and preserved, is the presence of organic carbon. For example, it is difficult to distinguish simple silica spheres representing moulds of bacterial cells from abiotic chemical precipitates, unless these silica spheres are hollow and contain traces of endogenous kerogen (Javaux and Benzerara 2009). Indicative feature for such fossil spheres containing carbonaceous materials is the isotopically light composition of the carbon, though some abiotic processes give similar values as well (McCollom and Seewald 2006). Also, morphologically the existence of membrane like outer rim, distinctive carbonaceous cell wall, is an important feature. These cell wall features could be replaced by pyrite, iron oxides, silica, calcite or phosphate according to environment where it was fossilized (Javaux and Benzerara 2009). However, because of its complexity, when distinction between abiogenic or biogenic origin is considered, so called falsification approach is used meaning that the biogenic origin is considered as the last option (Brasier 1992).

2.2 Ooids

Another common spherical forms in sedimentary rocks are ooids. These are spherical to ovoid grains, consisting of one or more regular concentric lamellae composed of authigenic mineral aggregate (calcite, Fe-oxides, etc.) around a nucleus which usually is a carbonate mineral particle or quartz grain. Sediment composed of ooids is referred to as an oolite (Tucker 1990). Ancient ooids are usually composed of calcite but might have originally been aragonite. Ooids can be dissolved out completely leaving holes which can be filled with secondary calcite cement. Some ancient ooids in rocks have micritic texture. Primary calcite ooids typically have radial texture of wedge-shaped fibrous crystals, with an extinction cross under crossed polars (Tucker 1990).

Paleoproterozoic ooids have been described in Canada, Gunflint Formation where calcitic ooids still show faint lamination covering the inside blocky calcite, often twinned while some were recrystallized to fibrous calcite crystal aggregates (Sommers et al. 2000). Under both plane-polarized and crossed-polarized light some ooids show yellow-brown coloration but some are colorless (Sommers et al. 2000).

2.3 Hydrocarbon migration

Black globules composed of carbon have been described on veins of conglomerates (Mancuso et al. 1993). These are lithified pyrobitumen droplets that form 1-10 mm sized variable (kidney, round to discoid and elongated) shaped droplets. These blebs are the result of natural migration and maturation of Precambrian petroleum (Mancuso et al. 1993).

2.4 Accretionary lapilli

Accretionary lapilli settle from the cloud of volcanic eruption or from the impact plume (Johnson and Melosh 2014). Accretionary lapilli are roughly spherical and are composed of accreted fine-grained material from the turbulent and volatile rich cloud of ash. These particles can vary in size, from a centimeter to smaller than a millimeter (Brown et al. 2012).

Brown et al. (2010) have classified volcanic accretionary lapilli into five morphological types, which have rim or concentric rims and some have no rim at all. The main indicator for lapillus is its composition dominated by fine (volcanic) ash. The center and rim could be composed of different sized ash particles but it should be distinguishably "grainy" when seeing through microscope (Brown et al. 2010) though recrystallization may significantly hamper the observation in ancient lapilli.

Lapilli type particles can also form in meteorite impact processes. Accretionary impact lapilli are morphologically similar to volcanic lapilli showing roughly spherical shape and being composed of accreted fine-grained material (Johnson and Melosh 2014). Impact lapilli, unlike impact spherules, are mechanical aggregates rather than melt droplets (Simonson and Glass 2004). Formation of accretionary impact lapilli has been described as a process taking place in turbulent density currents, similar to the formation of volcanic lapilli (Branney and Brown 2011; Knauth et al. 2005). However, lapilli are found in the impact regolith on the Moon (Mckay and Morrison 1971) where in the absence of an atmosphere or volatiles the turbulent density currents cannot form (Wilson 2009). On the other hand, modeling study by Jonson and Melosh (2014) shows that accretionary impact lapilli form during the ejection process where molten silicate acts as the binding agent for lapilli formation. This suggests that accretionary impact lapilli can form on any rocky body, even those that contain no water and have no atmosphere (Johnson and Melosh 2014).

2.5 Meteorite ablation debris

Spherical aggregates could also represent meteorite ablation debris, material that melts and is swept off from meteorites during its passage through Earth's atmosphere (Harvey et al. 1998). These are usually confirmed by its specific chemical composition that should be similar to some meteorite group, which is then considered to be the original abraded body. However, originally glassy ablation debris is easily weathered and therefore might be difficult to find exact match to certain meteorite group (van Ginneken et al. 2010; Harvey et al. 1998). Moreover, such particles have been mostly found in glacier ice and it is unclear how dense the population of spherules would be in sedimentary strata. Van Ginneken et al. (2010) even suggests that material found could be concentrated by rolling into traps on lower parts of ice.

Taylor (1991) have described these as cosmic spherules measuring 0.025-2 mm in diameter and being a product of melting of incoming planetary dust and large objects. He claimed these mainly being composed of olivine (Taylor and Brownlee 1991).

2.6 Impact spherules

Impact spherules are melt droplets that form from rock melt and vapor cloud created by an impact event. There are two different types of spherules by their origin. First type is formed by condensation in the vapor plume and second type represent dispersed and ejected melt particles. Formation of either types depends on pressure and temperature within the ejecta cloud (Johnson and Melosh 2012).

Individual droplets of melted target rock are generally produced during the early stages of cratering and are immediately ejected at high velocities from the developing crater, often to regional or even global distances. Such particles are therefore rare in the proximal ejecta deposits associated with the crater itself (French and Koeberl 2010). Typically, most of ejecta material falls within the radius of one diameter of the final crater, material that falls further, the high velocity ejecta, creates the distal layer of spherules which is formed early in the cratering process when energy densities are high enough to expel material at velocities comparable to the impact velocity (Johnson and Melosh 2012). Any ejecta deposited >5 crater radii from the rim of the crater is considered distal and <5 crater radii as proximal (Simonson and Glass 2004).

Impact spherules are not necessarily perfectly round. Simonson and Glass (2004) had pointed out that larger spherules tend to be less spherical in shape and lie on a continuum of fluidal shapes referred to as splash forms, and show different textures internally. Ovoids are the commonest shape after spheres, lesser numbers of spherules have fluidal-aerodynamic shapes such as teardrops and dumbbells. Simonson and Glass (2004) point out that in Phanerozoic spherule layers, more than 50% of the glass occurs as fragments rather than whole splash forms inside about 30 to 50 crater diameters.

Impact spherules can be classified by characteristic textural features. Intact, unaltered, impact spherules consisting entirely of glass are referred as microtektites and microkrystites are spherules containing primary crystallites (Glass and Burns 1988), tough this distinction is difficult to apply to geologically older layers in which crystals and/or glass can be replaced by secondary phases (Simonson and Glass 2004). Microtektites can have devitrification textures of glass which are described as sheaf-shaped fibrous crystals growing radially inwards or less often acicular randomly oriented fibrous crystals form a crust over spherule or fills its inner part (Lofgren 1971).

What differs the impact spherules from other spherule types is that they are known to form the marker beds that extend to the vastest areas in comparison with other processes that form spherical aggregates (Simonson and Glass 2004).

3. Geological background

The Paleoproterozoic Zaonega Formation in the Onega Basin is located in the south-eastern part of the Archean Karelian craton in NW Russia (Figure 1). Onega Basin is filled with a sequence of green-schist metamorphic-grade volcano-sedimentary rocks unconformably lying on Archean granites and gneisses.

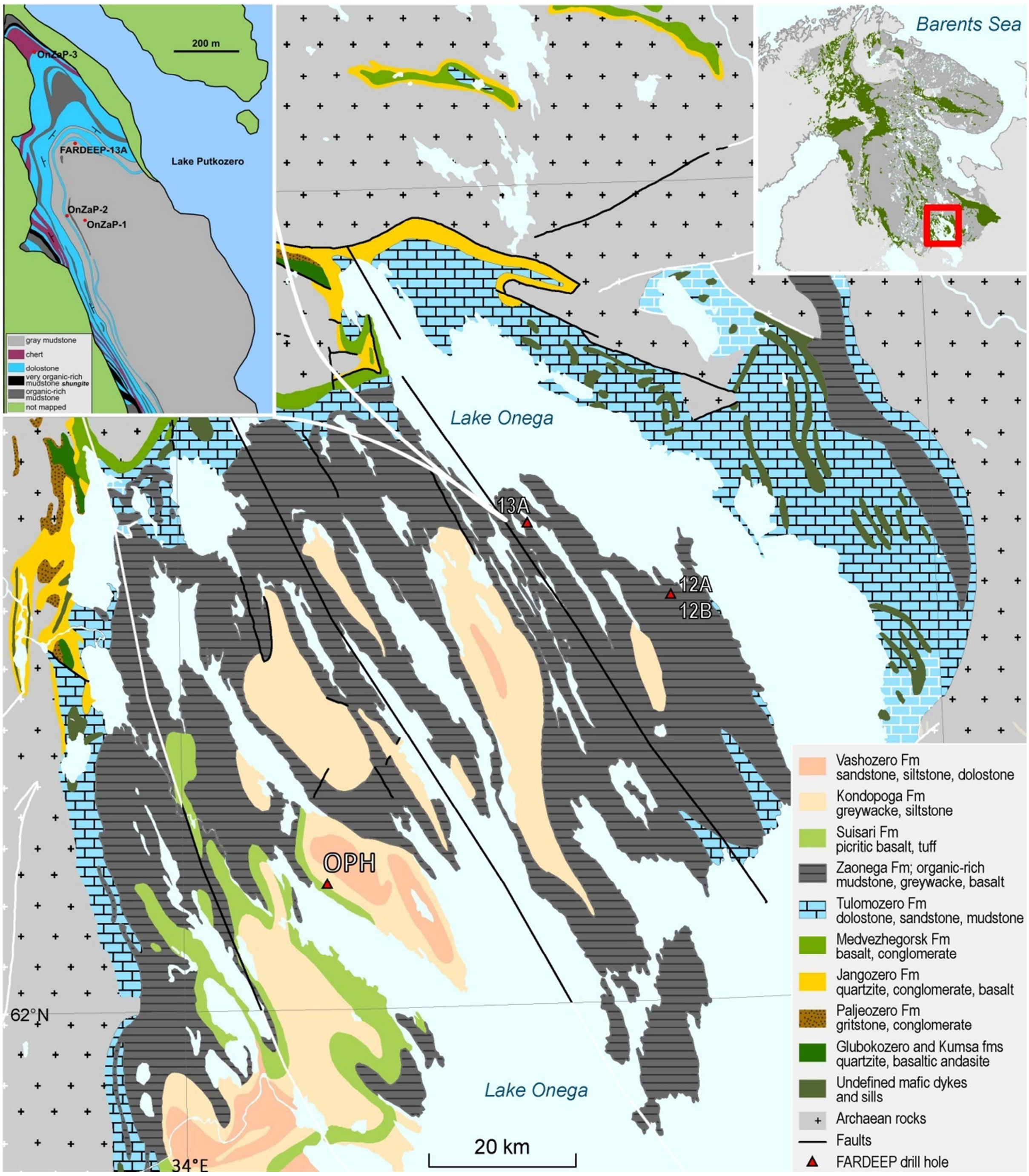

Figure 1. Map of Onega basin and location of studied drillcores . Modified after Črne et al. (2013a) and Lepland et al. (2013)

The Paleoproterozoic rocks of the Onega Basin are subdivided into four super-horizons - the Sarioli, Jatuli, Ludicovi and Kalevi. The Ludicovian is subdivided into two lithostratigraphical units: the lower Zaonega Formation and the upper Suisari Formation (Melezhik et al. 1999; Melezhik et al. 2012). Zaonega Formation is several hundreds of meters thick and composed of alternating siliciclastic rocks, limestones, dolostones, cherts, mafic tuffs and basalt flows, and intrusive gabbroic sills (Črne et al. 2013a). The Zaonega sequence occurs above the Tulomozero Formation dominated by carbonate rocks with positive carbon isotope signature known as Lomagundi-Jatuli excursion (Karhu and Holland 1996; Melezhik et al. 1999). Suisari Formation composed of basalt flows and gabbroic sills overlies the Zaonega Formation (Črne, et al. 2013b).

The sedimentary rocks of the Zaonega Formation are characterized by high content of organic carbon reaching >40 wt% in organic-rich mudstones and up to 90% in pyrobitumen veins (Melezhik et al. 1999; Medvedev et al. 2009). The carbonaceous material occurs as autochtonous kerogen residues and allochtonous pyrobitumen representing migrated hydrocarbons (oil) (Črne et al. 2013b). Zaonega Formation represents probably one of the earliest significant petroleum deposits on Earth (Črne et al. 2013b; Melezhik et al. 1999). Organic-rich mudstone and dolomite beds contain several phosphorous-rich layers in upper part of the Zaonega Formation (Lepland et al. 2013).

The age of the Zaonega Formation is constrained by the underlying Burakovka Pluton dated at 2449 ± 1 Ma (Amelin et al. 1995) and 1969 ± 18 Ma Re-Os isochron age from the overlying Suisari Formation (Puchtel et al. 1999). Ages of different units in the Onega Basin suggest the Zaonega Fm is younger than ca. 2060 Ma (Hannah et al. 2008; Ovchinnikova et al. 2007).

The spherule layer in Zaonega Formation sediments was first found in drillcores 12A and 13A that were drilled in 2007 during Fennoscandian Arctic Russia-Drilling Early Earth Project of the International Continental Drilling Program (ICDP FAR—DEEP) in Palaeoproterozoic Onega Basin, Karelia, Russia (Črne et al. 2013b; Črne et al. 2013a; Huber et al. 2014).

Drillhole 13A (62°35′21″N, 34°55′38″E) in the northeastern part of Onega basin 100 m east from locality of shungite in Shunga Village and 12A (62°29′41″N, 35°17′20″E) 25 km southeast from 13A. Drillhole 12A objective was to obtain a ca. 500 m-long section through an unroofed organosiliceous diapir, encased in a thick succession of organic-rich shales of the lower to middle part of the Zaonega Formation, the unit that records the initiation of the

Shunga Event. Drillhole 13A was targeted at the ca. 120 m-deep stratified organic-rich shungite deposits of the middle-upper part of the Zaonega Formation, the interval that stratigraphically spans the acme of the Shunga Event. Spherule layer is represented by three intervals in drillcore 13A and some spherules have been found on the upper section of 12A (Huber et al. 2014).

4. Material and methods

Material studied here was sampled (a) in cores 13A and 12a of the FAR-DEEP drilling program, (b) OPH (geophysical parametric drillhole) made by Institute of Geology, Karelian Centre of Russian Academy of Sciences near to town Kondopoga and three drill cores - OnZap1 (62°35′13.2″N, 34°55′51.6″E), OnZap2 (62°35′13″N, 34°55′48″E) and OnZap-3 (62°35′31.2″N, 34°55′40.8″E) were made in vicinity of the Shunga outcrop.

Structures and textures of the intervals supposedly bearing spherulitic particles were described in detail and logged at the Norwegian Geological Survey (NGU) with a help by Martin Klug using Innov-X Delta professional handheld XRF unit in MiningPlusMode which takes measurements with two beams; 40 and 10 keV. Each of the spectra is subjected to modeling where the software assumes that certain elements are present in the sample and iteratively fits a model to the data. Abundances of Ti, Mn, Cr, V, Fe, Co, Ni, Cu, Zn, As, Zr, Mo, Ag, Cd, Sn, Sb, W, Pb, Bi, Mg, Al, Si, P, S, Ca, Cl and K were measured. XRF logging was carried out with step length 0.5 cm and 30 seconds exposure time for each beam.

To investigate mineralogy and morphology of spherules polished slabs and thin-sections were made in intervals where spherules were identified in cores 13A, 12A, OnZap1 and from OPH drill cores. Petrographic study was performed by means of optical microscope and scanning electron microscope (SEM) analysis. For optical microscopy Leica DM2500P polarization microscope equipped with Leica DFC495 digital camera was used. SEM imaging of uncoated and carbon coated samples was done using a ZEISS EVO MA15 SEM. The images were captured by backscattered electron (BSE) mode and chemical characterization by elemental mapping of the samples was performed with Oxford AZTEC-MAX energy-dispersive spectroscopy (EDS) attached to SEM.

Selected samples from core 13A were prepared for focused–ion beam transmission electron microscopy (FIB-TEM) investigation to study spherule edges, especially recrystallization features. Sample preparation was made by Anja Schreiber at Podstam GeoForschungsZentrum and TEM measurements were carried out by Richard Wirth with the author participation.

5. Results

5.1 Distribution and lithology of the spherule beds

Spherules were earlier described in cores 13A and 12A (Črne et.al. 2013a; Črne et.al. 2013b; Huber et al. 2014), and were found in core OnZap1. Also, in OPH core spherule-like features were observed. The core 13A contained two intervals with brecciated beds containing spherules that are described in detail.

Drillcore 13A

About 240 m deep drillcore 13A contains mainly sedimentary rocks and mafic lava flows that represent the upper part of Zaonega Formation (Črne et.al. 2013a). Spherule layers are found at depths 26.51 to 27.69 m and 66.83 to 67.33 m and few spherules have been also found at depth 71.10 m (Huber et al. 2014) in the dolostone-chert member (Črne et.al. 2013a). The setting of spherule intervals is complicated – the lower interval of spherules is located within a brecciated dolostone and spherules seem to be injected between clasts.

The upper spherule layer starts at 26.52 m depth and continues until the depth 27.64 m. Layer starts with 7 cm bed where few sparsely distributed spherules are situated in chert containing a clast of dolostone (Figure 2a, b). At depth 26.58 m there is dense layer of spherules until the depth 26.71 m. Layer does not form sharp boundaries and has a fluidal structure (Figure 2a, c). This spherulitic interval is situated between chert beds. The distinct layer of spherules is followed by 3 cm thick bed where spherules are sparsely distributed within a chert (Figure 2a). Both chert beds contain some light calcite crystals in, probably as the result of dolomitization.

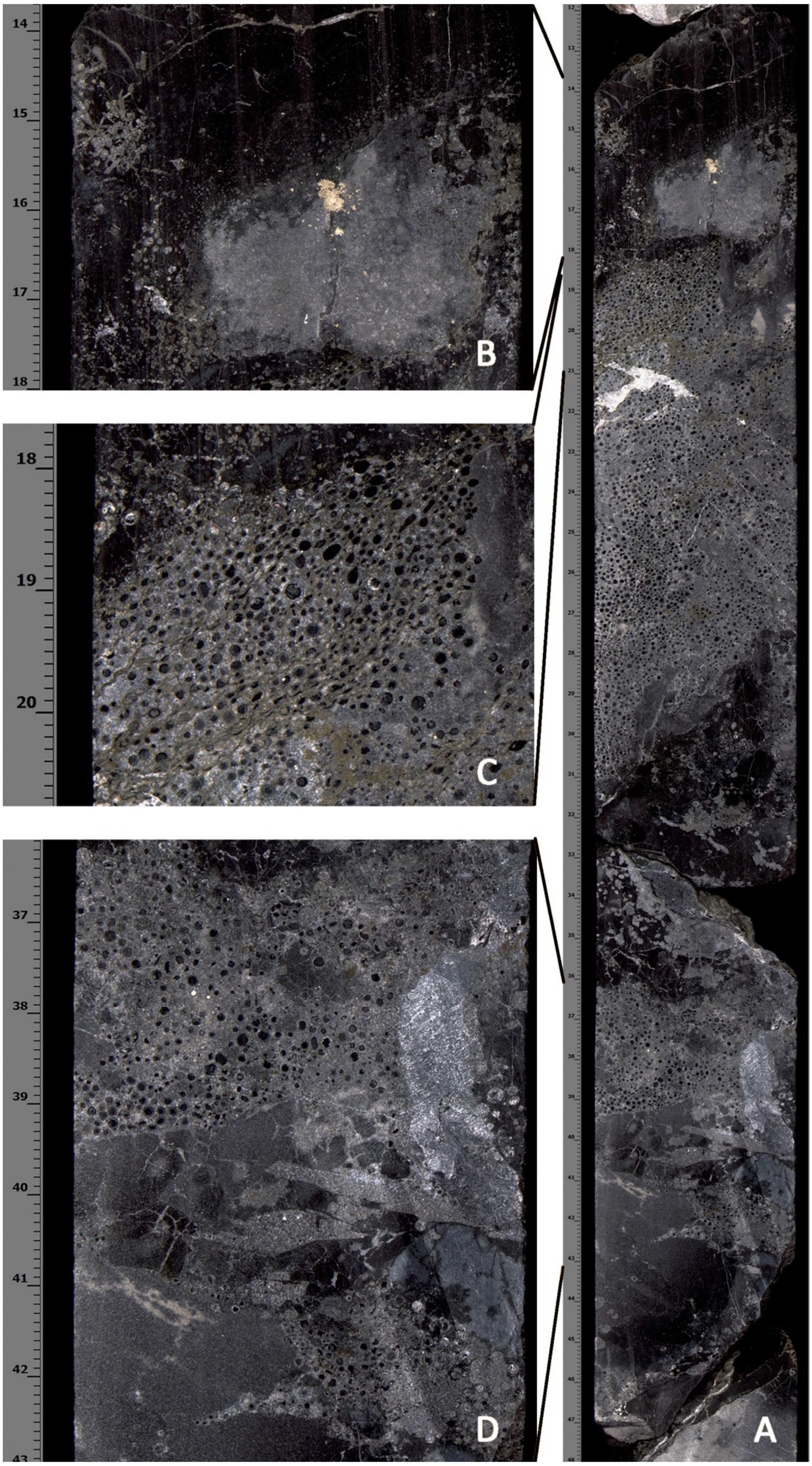

Figure 2. Drill core 13A upper interval of spherules (A) at depth 26.52-26.86 m, (B) close look at the light spherules in chert from the beginning of the interval, (C) fluidal texture of spherules in calcitic matrix, (D) interval where several brecciation episodes can be described and spherules are forming matrix between dolomite clasts.

This interval continues with 3.5 cm thick spherule layer which is evidently intruded between dolomite clasts (Figure 2a, d). The dolomitic breccia below this spherule layer contains angular intraclasts (0.5x2 cm) which possibly suggests several brecciation episodes.

At the depth 26.8 m the spherules are contained in veins between clasts, sometimes intruding into cracks in these clasts (Figure 3). Brecciated dolomite interval is additionally intruded by mudstone vein at 26.86-26.89 m (46-49 cm in Figure 2a and 4a) depth interval. Under that, white colored round shape 4-2 mm-sized dolomite aggregates resembling cauliflower structures are found (Figure 4a). Light dolomitic matrix between spherules continues to 26.94 m depth. At the depth 26.94-26.97 m (54-57cm on Figure 4a) spherules surround clast which edges are partly sharp and partly gradual suggesting that sediment had been still plastic (semiconsolidated) while spherules invaded. There are areas/clasts where spherules smoothly grade into the dolomite clast.

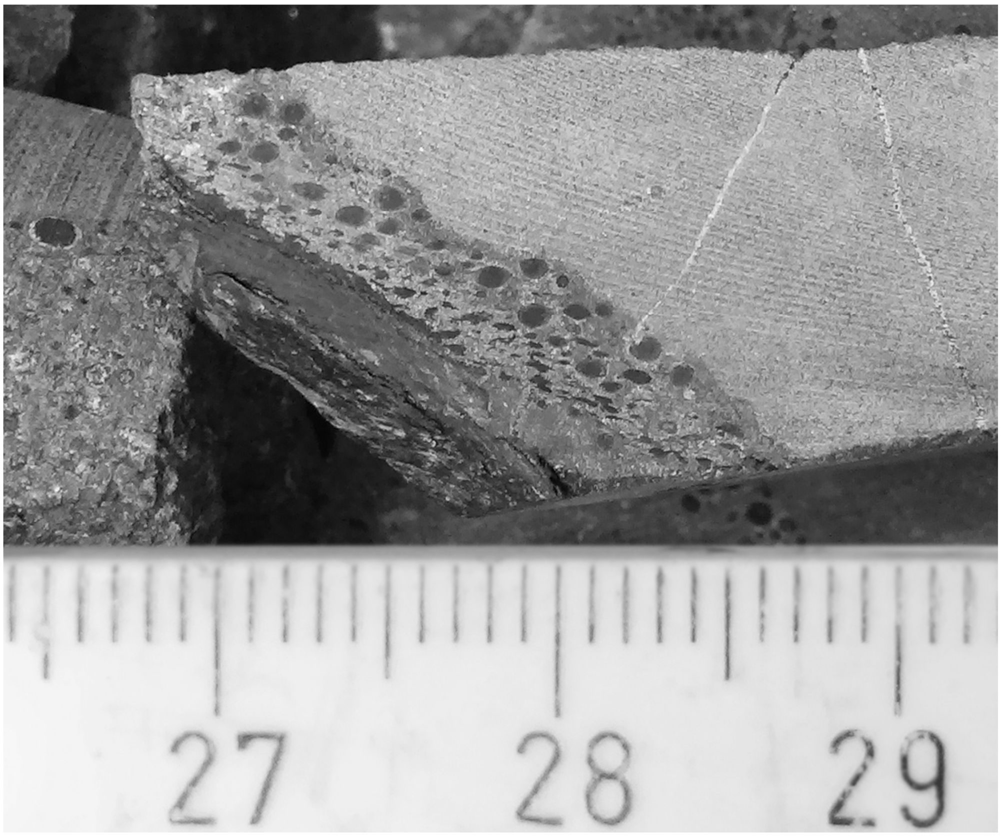

Figure 3. Spherule bearing matrix near mudstone vein where spherules are gone through plastic deformation

Figure 4. Part from depth 26.84 m – 27.64 m (A) cauliflower textures and dense distribution of spherules is (B) becoming more as a matrix between large dolostone clasts sometimes dissolved into these and (C) quantity of spherules is less downcore

At depth 26.99-27.08 m (58-68 cm on Figure 4a) spherule-clast mixture contains white quartz veins and wedge-shaped intrusions. Under that continues brecciated dolostone with a matrix containing spherules that sometimes are filling cracks in clasts (Figure 4b, c). At depth 27.16-27.26 m ca. 9-10 cm thick intrusion of mudstone cuts the brecciated interval (Figure 4b). It is interesting that spherules seem to follow the mudstone intrusion. The deformed, but not crushed spherules suggest that mudstone was intruded at very low rate so that instead of brittle deformation plastic deformation occurred (Figures 3, 9a).

In the lower part of the spherule containing interval the dolomite clasts become bigger and are better defined. Veins of the spherule containing matrix between clasts become thinner and contain less spherules and more calcitic material (Figure 4c). The deepest occurrence of spherules in this interval are found at the depth 27.64 m.

Core 13A continues with ca. 40 cm without any signs of spherules in dolostone nor in intrusive mudstone bed.

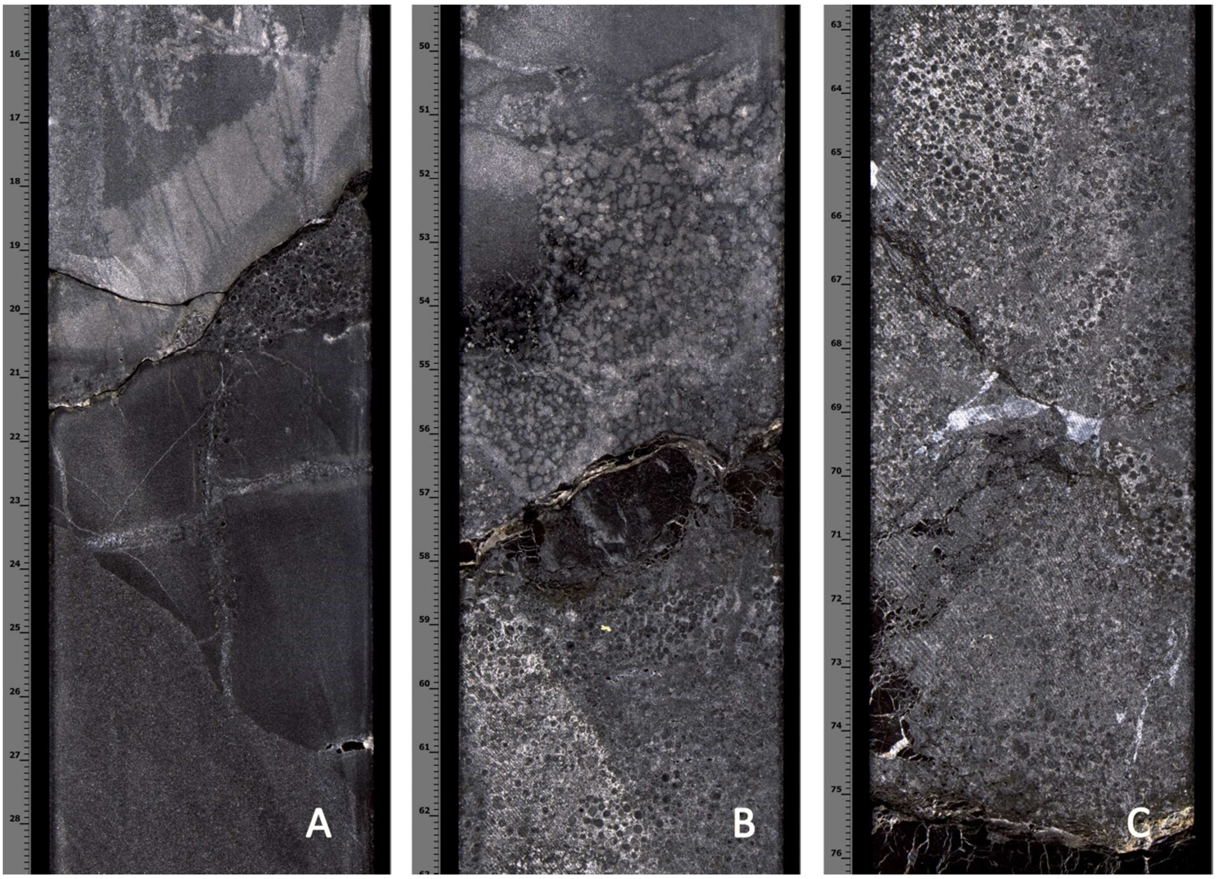

Figure 5. Lower interval of spherules in core 13A 66.84 m- 67.61 m, (A) First dark gray brecciated dolomite clast with spherules in matrix, (B) Cauliflower structures again and spherule interval in light gray calcitic matrix that continues to (C) and ends in bituminous vein.

Lower interval of spherules from core 13A starts at 66.84 m depth. Spherules occur similar to the upper interval in brecciated dolostone section. At the beginning of second interval one peculiar ca. 8 cm in diameter darker fine grained dolostone clast seems to be embedded into coarse grained dolostone. The clast itself is brecciated and contains spherule matrix (Figure 5a). It is followed by 30 cm dolostone interval which at the upper part intruded with black bituminous veinlets that contain pyrobitumen globules. Dolomite clast contain light colored dolomite areas ca. 2-5 mm in diameter that resemble "cauliflower" shape aggregates (Figure 5b). Spherules are found again at depth 67.42 m and are contained mostly in light gray matrix and does not show brecciation in 17 cm interval of spherules (figure 5b, c). At the depth 71.1 m a cluster of few spherules are found again (Figure 6).

Figure 6. Cluster of spherules described in core 13A in depth 71.1 m

Drill core 12A

Sparsely distributed spherules were found also in the beginning of core 12A at depth 3.97-4.54 m, which is correlated with the lower interval of spherules from core 13A (Črne et al. 2013b). Interval contains small, ca. 2 cm diameter light gray dolomite clasts with a dolomite-clay matrix containing spherules (Figure 7). Pyritizised rims around spherules have been oxidized. Cavities and veins are filled with calcite crystals. Spherule interval is followed by mudstones and then dolostone consisting phosphate granules.

OnZap1

From core OnZap1 spherule bearing interval begins at depth 42.77 m and covers 58 cm ending at 43.55 m. Distribution and structure of the spherule containing interval is similar to that in the upper spherulite layers in 13A core. Spherules are present in the carbonate-clay matrix between brecciated dolostone unit that is intruded by light calcite veins in its lower part. First interval ca. 4 cm, under Ca-phosphate rich bed mixes with spherules followed by 6 cm dolomite clast followed by ca. 3 cm spherule bed that is intruded by 1-0.5 cm wide white calcite veins (Figure 8a). Next spherule bed starts 5 cm below latter and covers 5 cm (Figure 8b) then 24 cm interval does not contain any spherules but only light gray dolomite clasts with a matrix of shattered dolomite and few darker areas that seem to be silicified (Figure 8b bottom). Under the dolomite layer the 12 cm-thick spherule bed is brecciated and spherules with calcite-clay matter form a matrix between dolomite clasts 2-3 cm in size (Figure 8c). Spherule interval ends with a mudstone bed. Core continues down-core with dolostone intruded by numerous sub-millimeter size light veinlets as well as bituminous intrusions.

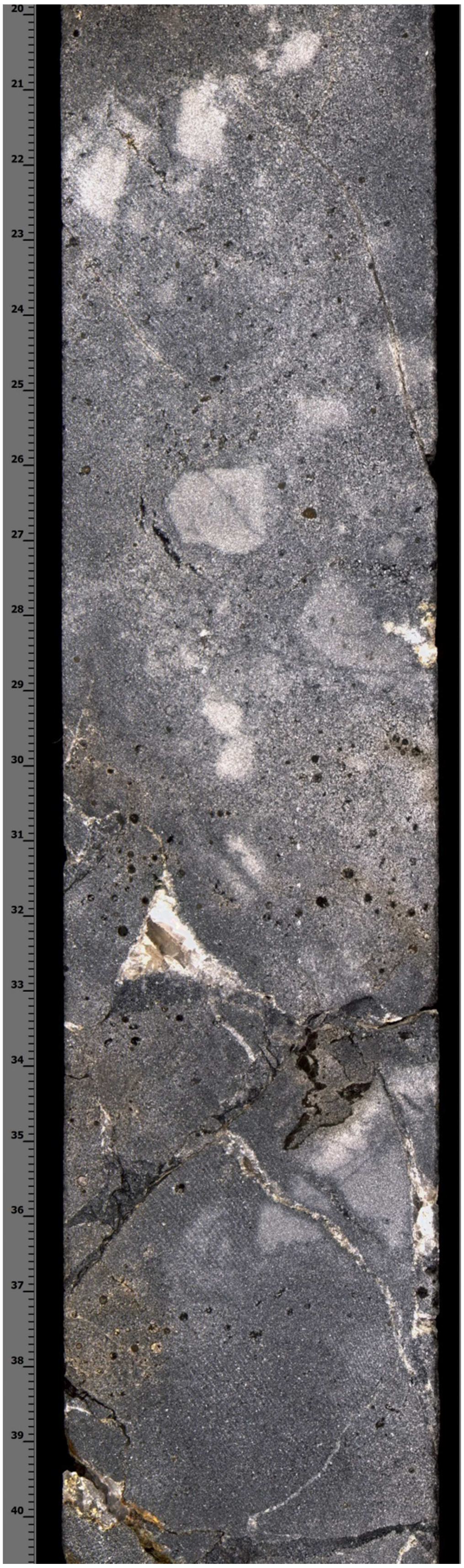

Figure 7. Sparsely located spherules in core 12A.

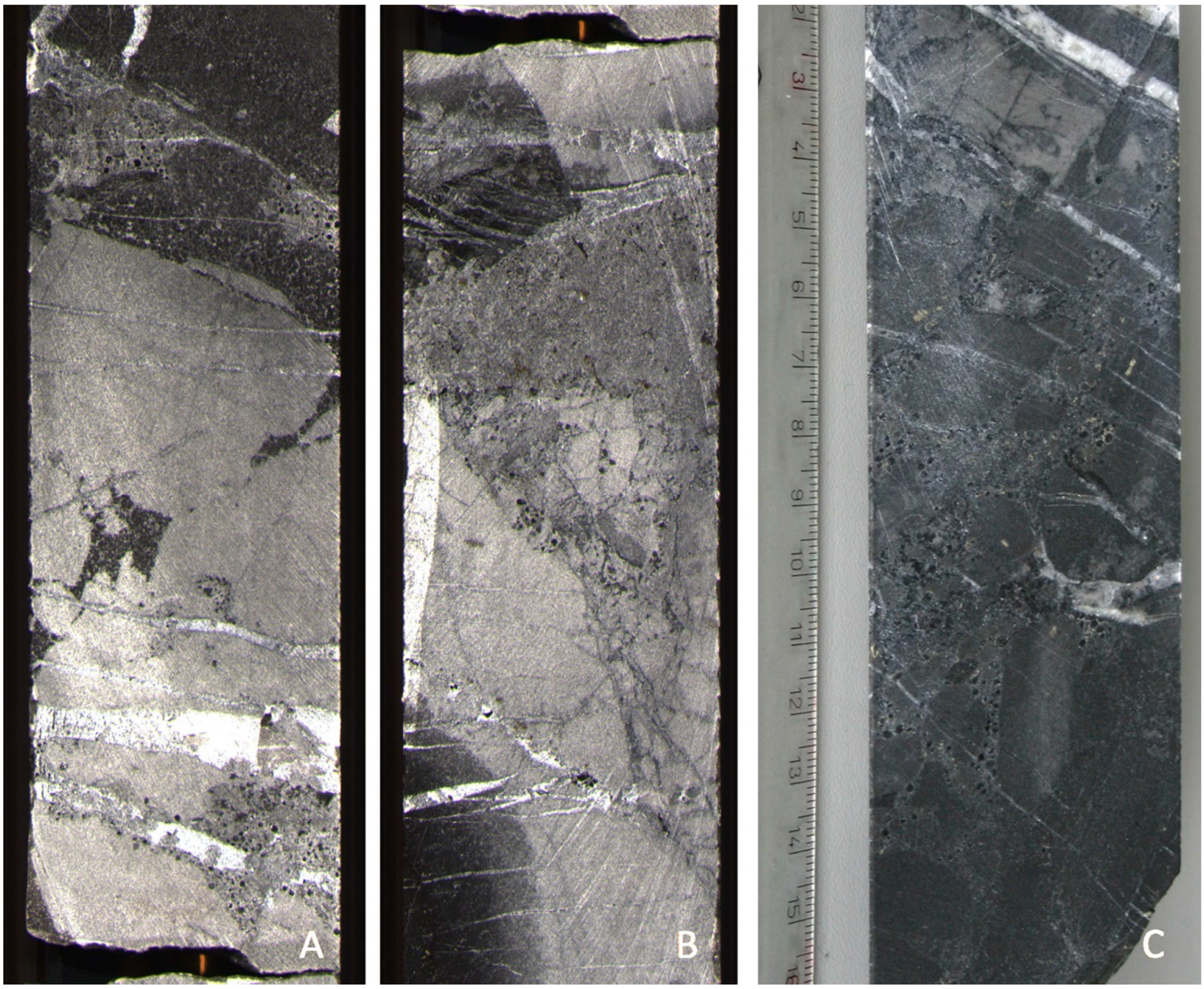

Figure 8. Spherule interval from core OnZap1 where (A) spherules are in veins between dolomite clasts, (B) are intruded into cracks in brecciated edges of clast and (C) form matrix between 1-2 cm clasts being secondarily intruded with calcite veinlets. Note that slab C has polished surface and thus seems darker in color

OnZap2

OnZap 2 core is situated ca. 500 m to the SW direction and opens principally the same interval as in core OnZap1. However, spherules were not discovered in this core. Interval that corresponds to spherule beds in core OnZap1 is represented by monolithic massive dolostone (ca 8-9 m) with some cauliflower-like features at the few meters of the beginning of the interval. It is interesting that the same features occur in other drill cores between spherule beds as well. The dolomite interval in this part of the core is placed between chert layers.

OPH -parametric drillhole

In OPH core interval that tentatively was suggested to correspond to mudstone-dolostone-(chert) section in Shunga was inspected for spherule beds. Studied interval is composed of dolomite which is intruded by pyrobitumen veins (Figure 9). At a depth 1083.65 m few spherule-like forms were detected and were sampled for further petrographic study.

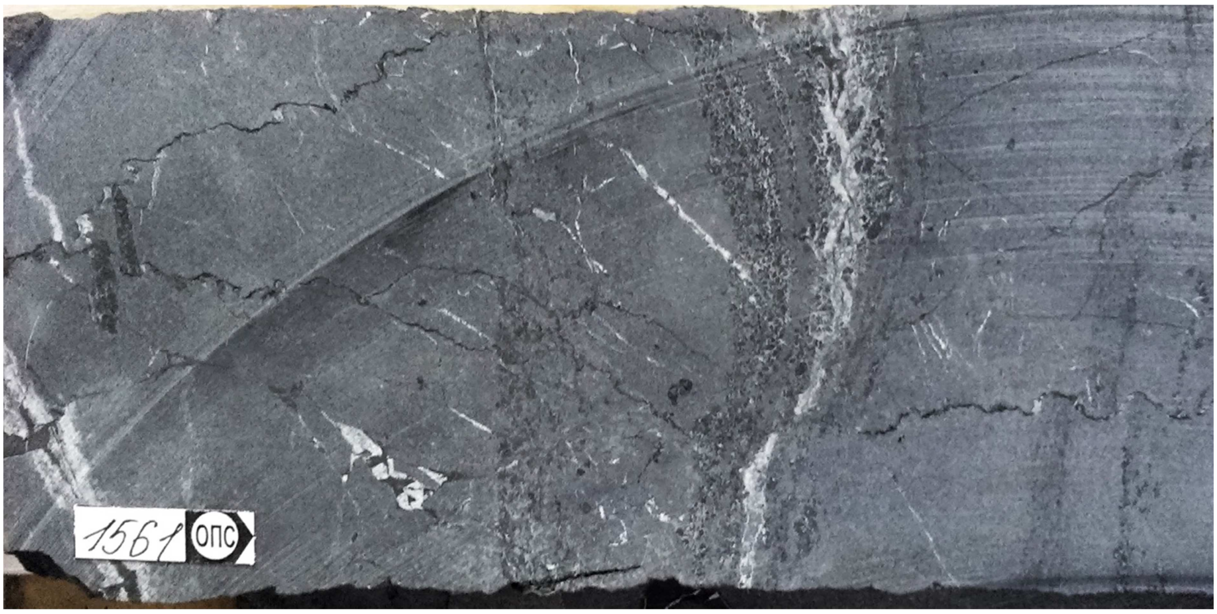

Figure 9. One slab from OPH core that shows globular black texture in veins between dolostone.

5.2 Petrography and mineralogical /chemical composition of spherules

Spherules found in Zaonega Formation are in size between 0.2-2 mm, both round and elongated forms are presented as well as dumbbell and teardrop shapes (Figure 10) characteristic to ballistic transport of molten rock droplets (French and Koeberl 2010). Most have visible rims and scalloping edges around central vesicle are common (Figure 10, 12).

Under crossed polars some rims show inwards growing crystallization (Figure 12a,b,c) whereas in some spherules the rim material is monolithic/blocky in appearance. Central part of spherules is composed of calcite, phlogopite or sometimes carbon, pyrite or even phosphate (See Table 1). Phlogopite occurs in spherules as crystallites or more massive blocky aggregates. Rim material varies as well. It is composed of calcite, phlogopite sometimes thin or diffused pyrite layer occurs in rim. At some intervals Ca-phosphate crystallization on rims occurs.

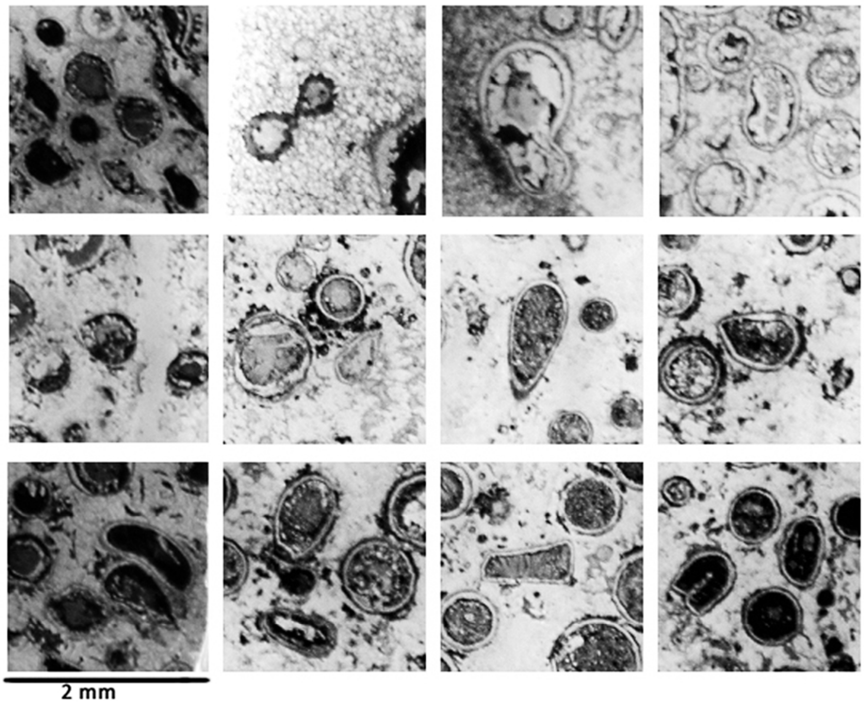

Figure 10. Examples of several shapes of spherules found in core13A and OnZap1.

It is important to remember that all these spherules are recrystallized. Intrusions and fluids alternated the rock have influence on composition of spherules. For example it can be seen in Core 13A at depth 27.26 m where spherules in dolomite have a clear white rim and halo extending into the rock (see figure 4b at 86 cm). It also appears that spherules in dark/ black chert are light gray and often do not show clear rim (in 13A 16-17 cm and 27.5-32.5 cm and 39 cm, 41.1 cm, 45.7 cm) while spherules in lighter gray matrix (calcite) are dark/black inside and usually have a rim (Figure 2). Also on figure 12a it is evident that spherules near carbon rich mudstone vein have carbon in their composition while few cm away these are without black fill.

13A and 12A

Spherules are chemically quite different though similar features are observed within the same interval (Table 1). Rim material of spherules is usually different of the material filling the inner parts of the spherule. The most varying spherules were found in the upper interval of core 13A. Spherules are mainly of phlogopite composition with two signatures - Al-rich and one Mg-rich variety. Also, these spherules are in contact with phosphatic cement/matrix that forms rims on spherule cores as well (See table 1). Few spherules had intermittent layers composed of phosphate and phyllosilicate (Figure 12e). In a thinsection prepared of the spherule bed at 26.51 m depth also silica (quartz) was found to partly fill inner parts of the spherules. In this sample also a spherule containing Ca-phosphate aggregates was found (Figure 11). Also, rare calcite fillings were observed. In some cases rim has additional carbon layering which were investigated by FIB-TEM analysis. Thin carbon layering could occur much often than it can be seen by SEM analysis.

As it can be seen on Figure 12a spherules near carbon-rich mudstone vein have gained some extra carbon into their composition as well. Also it is clear that mudstone vein is secondary compared with the spherule bed itself as spherules on the edge are deformed (Figures 12, 3).

The lower section of spherules in core 13A could be divided into two parts as well. Spherules in the darker dolomite clast (Figures 5a, 13a) have a different composition and are characterized by high abundance of the organic matter. In veins of the dark clast the organic matter occurs inside the spherules and fills space between blocky calcite crystallites (Figure 13a) whereas rims are composed of phlogopite. At the end of lower interval organic matter occurred rarely in rims sometimes mixed with phlogopite, sometimes giving distinct thin layer.

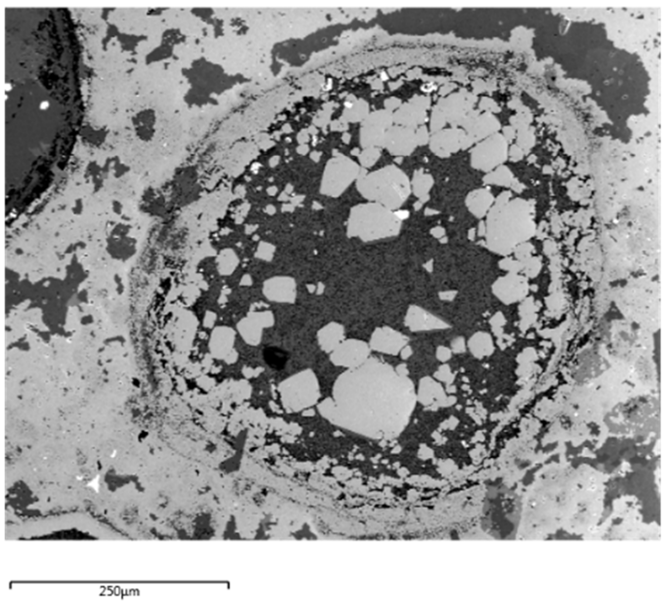

Figure 11. BSE image of spherule filled with Ca-phosphate (white angular) and phlogopite (gray)

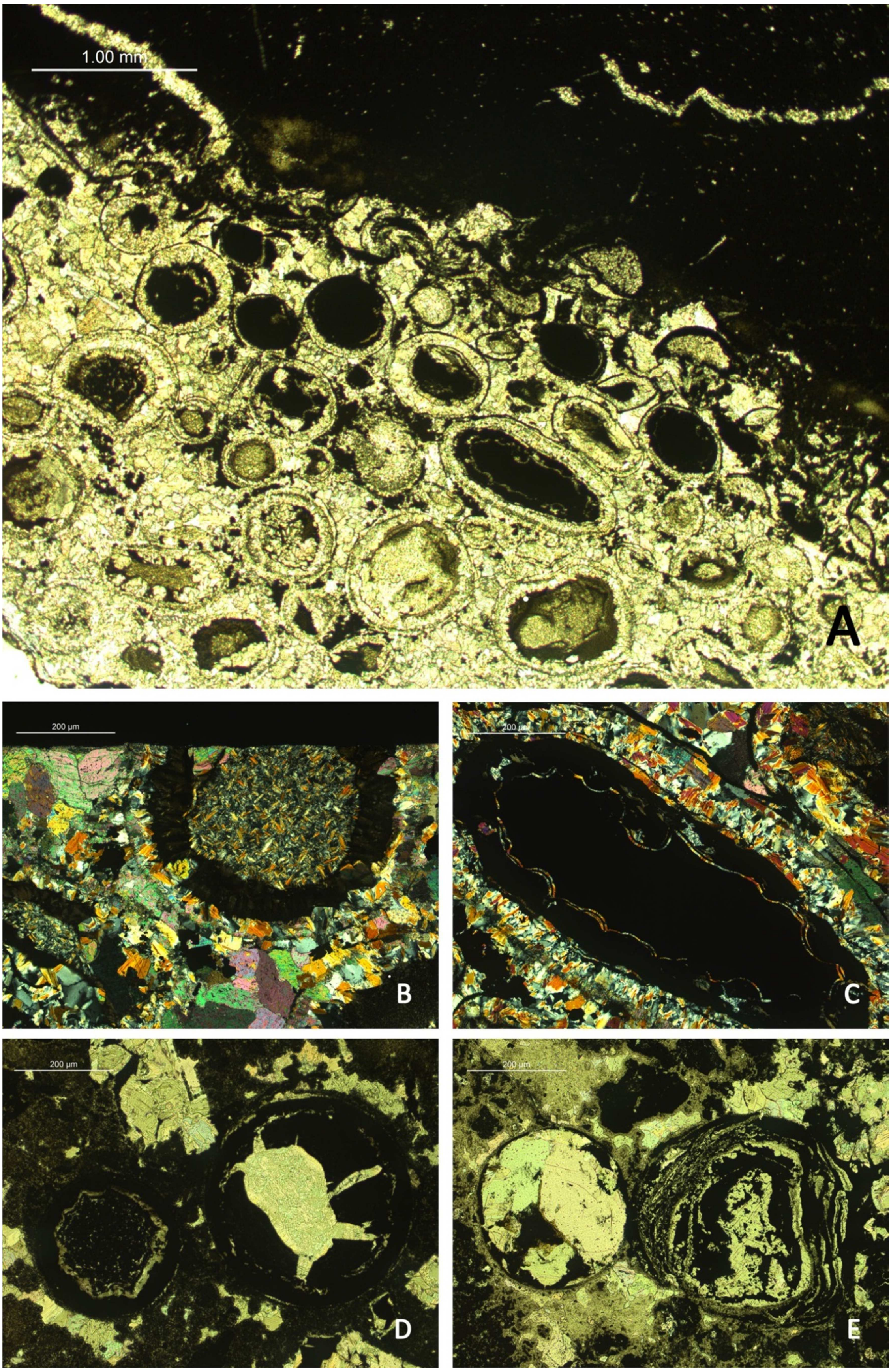

Figure 12. Spherules from core 13A upper section, (A) Several shapes of spherules near carbon-rich mudstone vein, plain polars; (B) Fibrous crystals filling the vesicle in the spherule, crossed polars; (C) elongated spherule with a rim of inward radiating crystals and scalloped edge vesicle in the middle, crossed polars; (D) carbon (black) and quarz (light) filled spherule, plain polars; (E) blocky calcite filled spherule on the left and ooid-like spherule with intermittent phosphatized rims, plain polars.

In the second spherule interval in the lower section of core 13A spherules are much more homogenous in composition than these were in upper interval (Figure 13b). Most of the spherules are composed of blocky calcite and rim material is phlogopite type phyllosilicate. Some diffuse pyrite rims were observed and in some rare samples carbon material was contained inside the spherules.

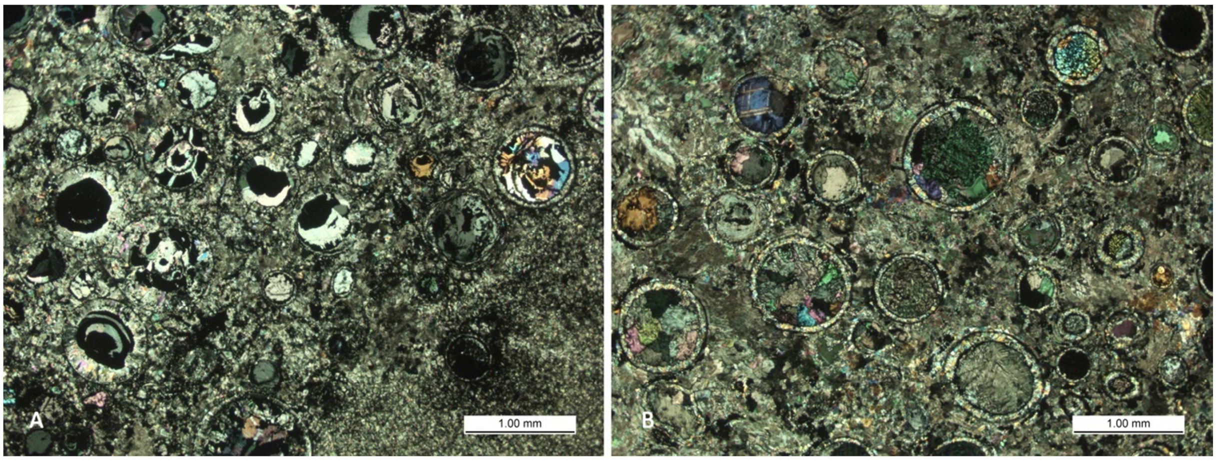

Figure 13. Spherules from lower part of core 13A. A) carbon filled spherules from clast at depth 66.83 m and B) Homogenous calcite filled spherules with thin phlogopite rim from depth 67.21 m, both crossed polars.

OnZap1

Core OnZap1 has spherules distributed between several beds in ca. 0.5 m interval where upper interval in depth 42.77 m contains Ca-phosphate cement between spherules and spherules have thin rim of Ca-phosphate as well (Figure 15b, Table 1). Composition of spherules in the middle bed at depth of 42.87 m is quite homogenous - inner parts are composed mainly of phyllosilicate mineral phase, rims are composed of calcite, rarely an additional rim composed of pyrite crystals occurs. Spherules are found in dolostone–phlogopite matrix with single or clusters of pyrite crystals (Figure 14). The lower bed of spherules in depth 43.46 m is intruded by quartz veinlets and even spherules are sometimes silicified (Figure 15a).

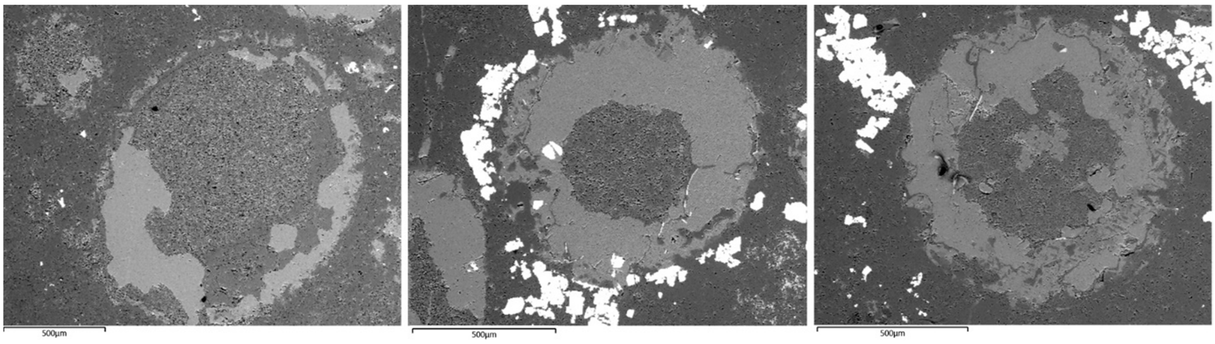

Figure 14. BSE image of spherules from core OnZap1. Pyrite appears white, calcite light homogenous gray, uneven gray is phlogopite and the darkest gray is dolomite

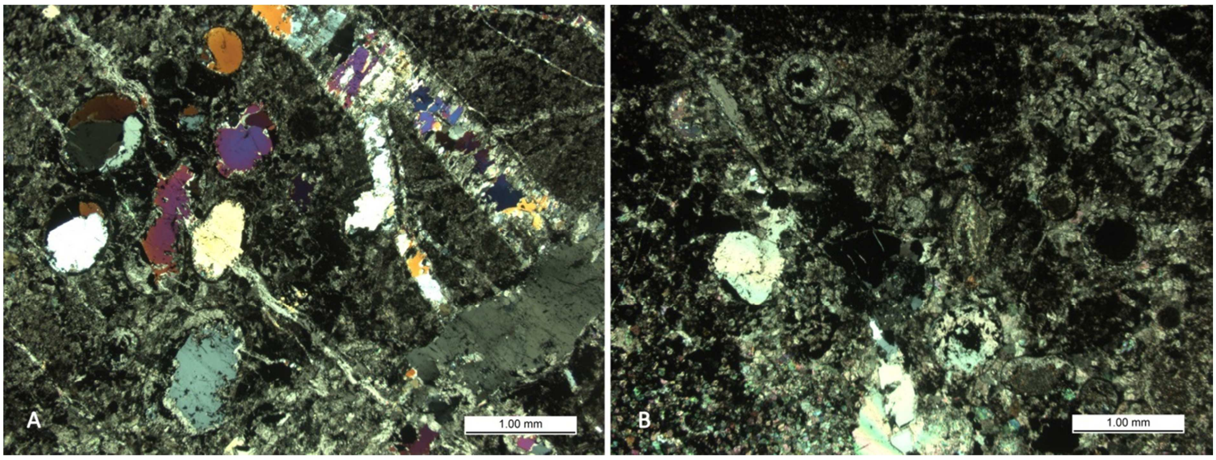

Figure 15 . Spherules in OnZap1 core from A) the last bed of spherules and B) spherules at the beginning of intervall .

OPH spherule-like particles

From OPH core 5 samples were taken but from only one sample two spherule-like objects were found (Figure 16 a, b). These are 0.2 mm in diameter and one has calcite rim and other are composed of blocky calcite but have no continuous rim. Most of spherical features observed in this core were bituminous globules filling the cracks in dolostone (Figures 9; 16c, d). These do not have any distinctive rim and are composed of carbon material.

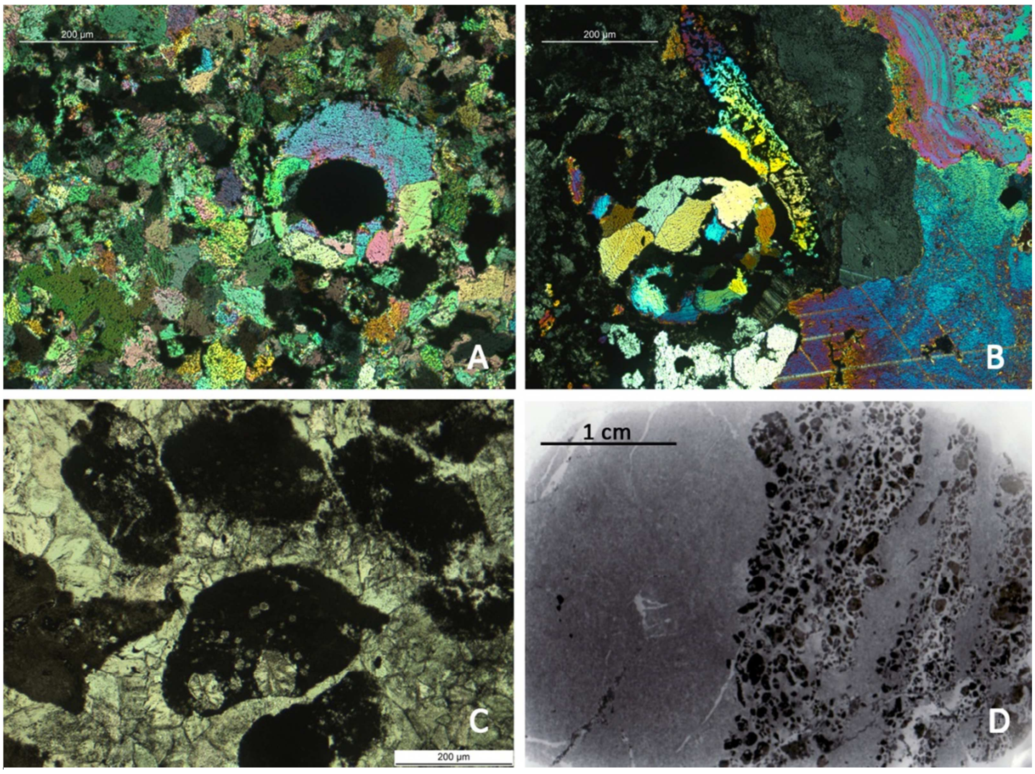

Figure 16. (A,B) Spherule-like particles in OPH core, crossed polars, (C) plain polars picture of pyrobitumen droplets that fill the cracks in dolostone and (D) picture of thin section showing veins filled with pyrobitumen droplets (see also figure 9.)

FIB-TEM characterization of the spherule rims

Rim areas of the phosphatised spherules at 26,73 m and 26,51 m depth in core 13A were characterized by FIB-TEM analysis that shows on both cases that Ca-phosphate mineral apatite inside the phlogopitized carbon rich rim wall is massive (Figure 17a, b) but outside the rim wall it is porous and shows some dissolution margins (Figure 17c). The carbon material in the rim has a tendency to be oriented near phosphate but it is totally amorphous beyond (Figure 17 d, e). Also, the Ca-phosphate grains in the matrix between spherules have rims of graphitized lamellae which has been described as marker to metamorphic changes up to temperatures of 700 °C (Buseck and Beyssac 2014). However, van Zuilen et al. (2012) has described these as mineral induced graphite films, because the oriented graphite sheets are only near edges of sharp bordered phosphate crystals. Much lower metamorphic temperature is also suggested by a TiO_2 micrograin that by lattice parameters is anatase (Figure 18), mineral which is not stable at temperatures above 400 °C (Smith 2009).

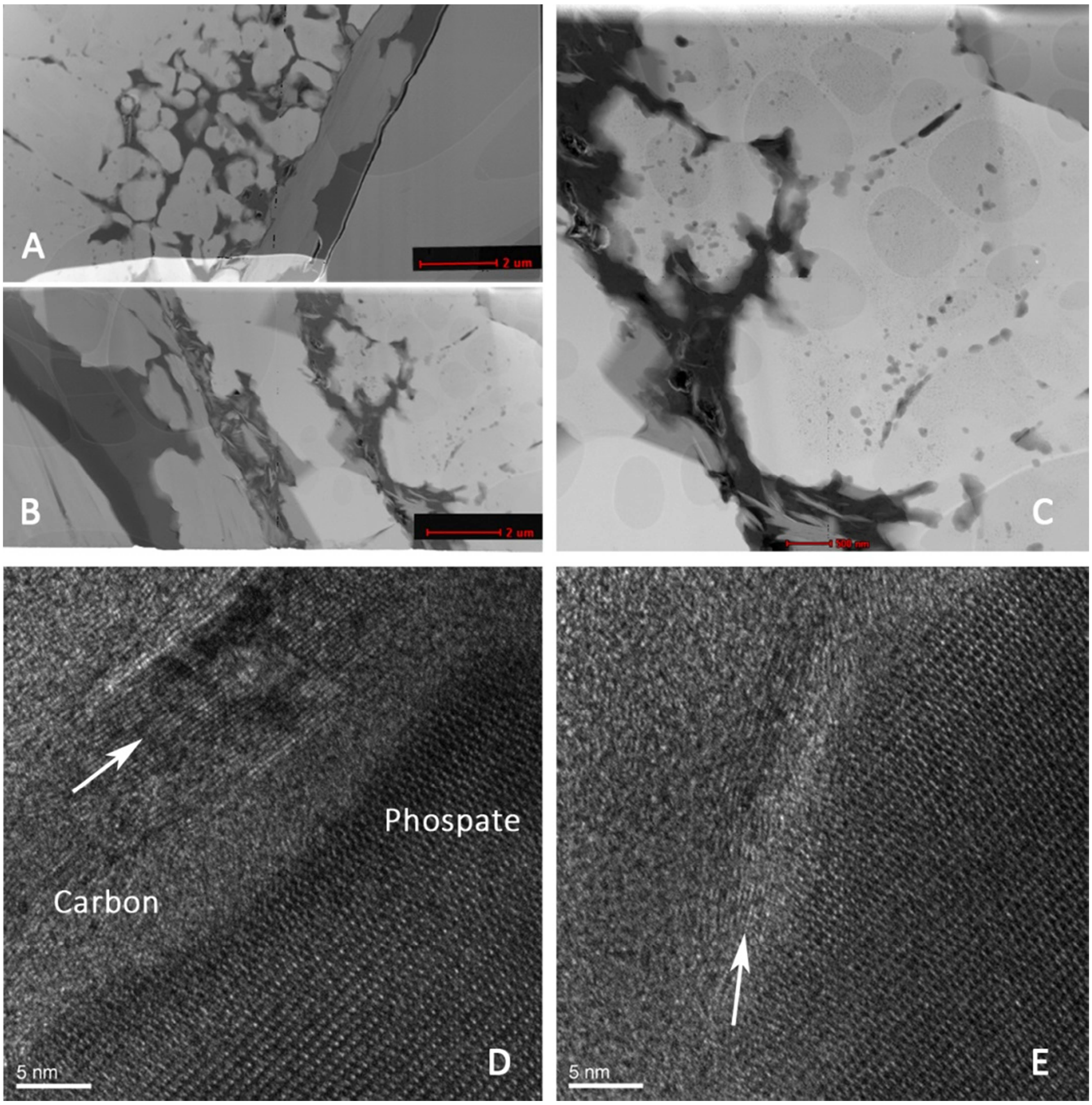

Figure 17. FIB-TEM images of spherule rims from core 13A upper interval. (A) porous Ca-phosphate on the rim of a spherule (white), (B) and (C) Porous Ca-Phosphate on the rim of a spherule though inside the layer of phlogopite (dark-gray lamellae) it becomes massive, (D) and (E) HREM images of oriented carbon (graphite) shown with arrows near the edge of Ca-phosphate.

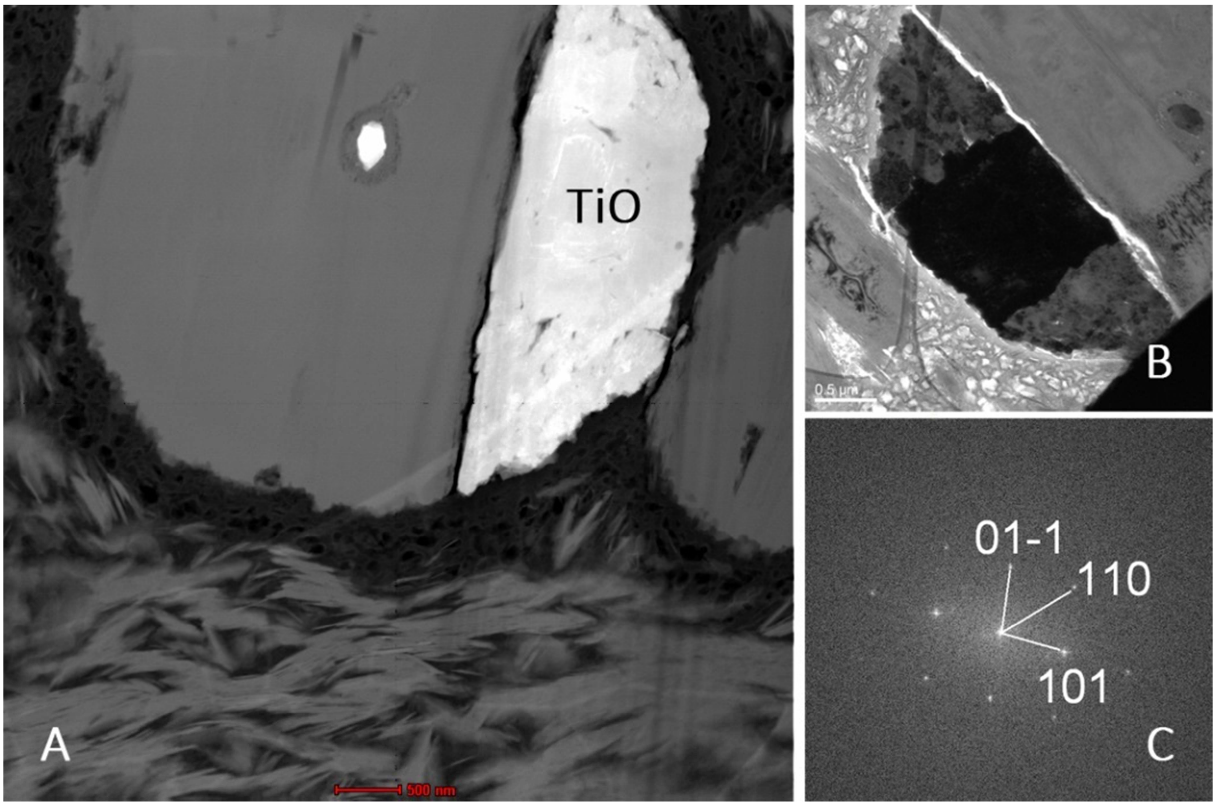

Figure 18. TiO_2 grain in a vesicle inside spherule (A), (B) brightfield image of the same TiO_2 grain, (C) Lattice planes of TiO_2 grain that is anatase, FFT of HREM

6. Discussion

Spherical aggregates in the Paleoporterozoic Zaonega formation closely resemble impact induced distal ejecta material though this is not easy to confirm. The most straightforward confirmation of impact origin and involvement of the meteoritic material would be the increased abundances in Ir and other PGE elements in spherules (French and Koeberl 2010). The actual amount of impactor material mixed into impact crater rocks is generally small, typically less than 1 wt%. Therefore critical elements that could confirm meteoritic origin occur in very small quantities at sub-ppm levels. The main element characteristic to meteoritic material is iridium. Its concentration exceeding 1–2 ppb is considered as indicating involvement of extraterrestrial material. Usually abundances of other siderophile elements are measured as well to see if these elements occurrences follow a meteoritic (e.g., chondritic) distribution pattern, rather than a terrestrial. This is done because slight Ir enrichments (up to a few hundred ppt) can also be produced by terrestrial processes, such as hydrothermal activity or the incorporation of ultramafic rocks. Typically, the use of such small enrichments as meteorite impact indicators is considered questionable (French and Koeberl 2010).

Ir and abundances of some PGE's from 13A and 12A were measured by Huber et al. (2014) but the maximum amount for Ir was found 0.75 ppb from only one sample while average was 0.2 ppb (Huber et al. 2014). Ir concentration that certainly refers to extraterrestrial material is 1-2 ppb (French and Koeberl 2010). Moreover, though Ir abundances measured in Huber et al. (2014) are elevated compared with average composition of the volcanic rocks in Zaonega Formation, it must be considered that sedimentary sequence in Zaonega formation including brecciated dolomites bearing spherules have been altered by hydrothermal fluids which may give the slight elevation of Ir in these sediments.

Also, it is thought that Precambrian Earth crust had different composition than today. Earth had mostly covered with oceanic crust (basalts) therefore the average composition of the crust was more mafic having elevated concentration of PGE elements (Simonson and Harnik 2000).

Therefore, unless a distinctly higher Ir concentration is confirmed in Zaonega spherule beds, the only important feature by which we could establish the origin of these spherules is the morphology.

Though proposed earlier (e.g. Medevedev et al. 2009) it is evident from studied material that the biogenic origin of these features is the least probable. Spherules are not constituents of the original sediment and are rather injected during brecciation of sediments. Uniform and biologically possible sizes of the spherules as well as organic carbon associated with some of the spherule types seems to favor the biogenic origin though observed aerodynamic shapes, devitrification/crystallization features, and variation of inner structures do not support biogenic criteria. Also FIB-TEM analysis of spherule rim did not reveal resemblance to organic cell wall. Organic matter found in and around spherules is not an original degraded biomass of a fossil, but is most probably related to the widespread pyrobitumen migration in Zaonega Formation sediments (Melezhik et al. 1999). Pyrobitumen droplets form also spherule-like particles as found in OPH drillcore (Figure 16c,d). In the core the C-rich spherule-like features are concentrated next to organic-rich mudstone intrusions, which were probably the source of bituminous material. Also there is a spherule layer described in Ketilidian orogen, South Greenland where spherules contain carbon material in their composition and it is thought to be a result of hydrocarbon migration as well (Chadwick et al. 2001).

Though described spherules could morphologically resemble to meteorite ablation debris or cosmic spherules then the thickness of spherule bearing bed is too much for ablation debris and cosmic spherules contain Fe-Ni contents or stony spherules contain olivine (Taylor and Brownlee 1991), which have not been found in studied spherules.

Another explanation could be that described particles are ooids (Figure 12e). Indeed couple of spherules resemble morphologically the ooid-like aggregates, but most of the studied spherules are not (Figure 12a, b, c, d; 13; 14; 15). Similarly, concentric rims in some spherules found in Zaonega Formation could suggest that these spherical aggregates are volcanic lapilli (Brown et al. 2012). However, there is no indication for ignimbrite/remnants of recrystallized volcanic ash in same interval with spherules, even though the area has been tectonically active (Melezhik et al. 2012). Furthermore, to consider these spherules to be volcanic or impact lapilli these should have agglomerated fine-grained texture which has not been found either. Additionally, the central cement filled vesicle is not always in the middle in studied spherules like it should be in case of lapilli and ooids (Simonson 2003).

Simonson (2003) has suggested four criteria to follow when classifying spherical forms to impact spherules. First, a predominance of highly spherical grains, second, occurrence of splash forms, third, rims consisting of radial-fibrous crystals that grow inward, and fourth, presence of a vesicle filled with cement that is not in the middle (Simonson 2003).

Morphology of observed spherules agrees with all these criteria (Figure 10, 12, 13, 14). Also, some of the spherules in Zaonega Formation contain recrystallized remains of dendritic textures that indicate rapid quenching of melted droplets (Figure 19) that, in addition, suggest that some of these spherules could be considered as microkrystites. Nevertheless most spherules show devitrification textures of fibrous inward radiating crystals and also randomly oriented fibrous crystals which are thought to form when glass spheres are reheated after setting down (Lofgren 1971). Spherules often have vesicles inside which do not necessarily locate in the middle at all and can have an isopachous outline like gas bubble or scalloped outline (Simonson 2003).

A mentioned before impact spherules are divided into two groups by crystallization features as microtektites and microkrystites (Smit 1999). These are both formed of melted-evaporated terrestrial material (Glass and Burns 1988), though microkrystites are described as the vapour condensate which is ejected more than 4000 km away from impact site (Smit 1999).

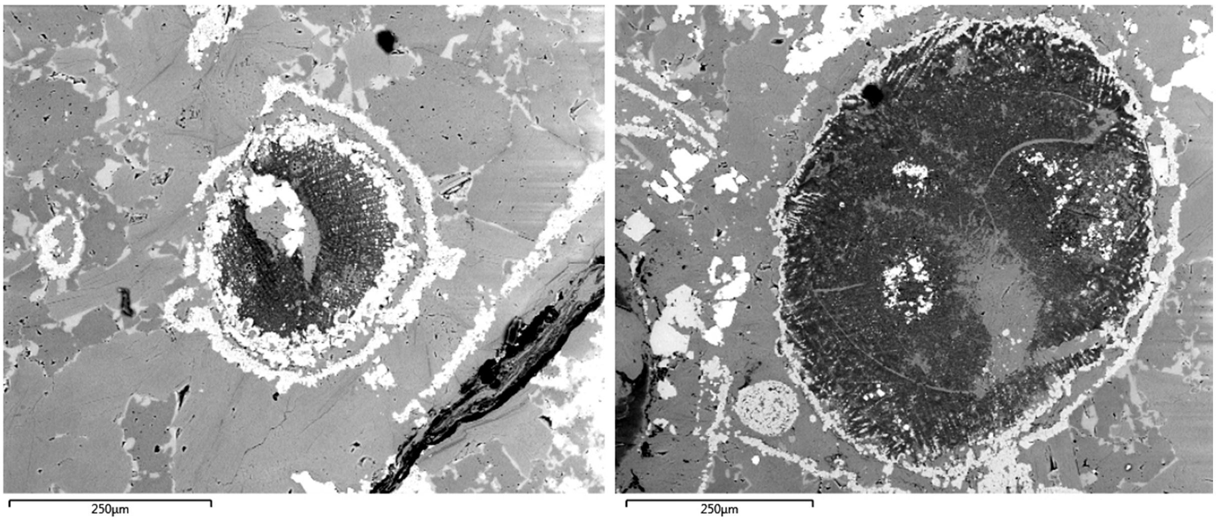

Figure 19. Quenching textures in spherules from Zaonega spherule layer

Additionally microkrystites are thought to have elevated amounts of extraterrestrial components like Ir and other PGE abundances and contain crystals which are formed during atmospheric transport while microtektites are exclusively composed of amorphous glass (Glass and Burns 1988).

If these spherules are microkrystites then these should locate more than 4000 km away from crater though Huber (2014) has suggested the distance to be less than 2500 km, the range of microtektites. Also, if these are microtektites there is a low probability for elevated Ir or PGE abundances to confirm the meteoritic origin.

Different of other Precambrian spherules that are typically replaced with K-feldspar (Simonson 2003) the spherules in Zaonega Formation are mainly replaced by mica/clay (phlogopite) and calcite, and in some cases phosphate, pyrite or quartz (Table 1). Spherules with calcified insides occur in 13A lower interval whereas upper interval of 13A and OnZap-1 have spherules mainly of phlogopite fillings and sometimes Ca-phosphate is mixed in which does not occur in 13A lower interval, which is probably due to different diagenetic environment and fluidal/hydrothermal reworking of the Zaonega section. During the devitrification of volcanic glasses the zeolite/feldspar association forms typically in a geochemically closed system whereas the clay mineral assemblage is characteristic to the (more) open system alteration of metastable glasses (Kastner and Siever 1979).

Table 1. At the header of the table is given the name of the dill core and interval which is represented with thinsection. In the brackets are number of spherules measured in thinsections. Note that not all measured spherules could be entered in the table. Some types seem to be clearly distinguishable but there are also a lot of spherules that only occur once or twice. The composition of spherules does not show their original matter but rather the difference of alterations inside the layer. Illustrations of spherules are shown in appendix.

Drillcore	13A					OZ1		
Interval, m (spherules observed)	26.51 (8)	26.70 (6)	26.73 (17)	66.83 (10)	67.21 (20)	42.77 (8)	42.87 (8)	43.46 (5)
1.Calcite - Phlogopite		1		1	7			
1.1.Calc.-Phlo.+ Pyrite					9			
1.2.Calc.-Phlo.+ Organics					2			
1.3.Calc.+org. - Phlo				7	1			
2. Phlogopite - Calcite						2	6	1
2.1.Phlo. – Ca-phosphate			7					
2.1.1.Phlo.- Ca-phosp.+Pyrite			3					
2.1.2.Phlo.- Calc.+Ca-phosp.						5		
2.2.Phlo.- Pyrite			2					
2.3.Phlo.- org.+Pyrite	1	2		1		1	1	
3.Pyrite		1			1			
4.Quartz(+Phlo.)-Phlo(C, Ca-P)	5							3
5.Phlogopite		1	1					

Most of the spherules investigated have radial sheaf-shaped fibrous rim composed of phlogopite (Figure 12c) whereas randomly oriented lath-shaped crystals are described in vesicles in spherules as well (Figure 12b). This suggest that most of the spherules are microtektites because devitrification in these forms are characteristic to originally glass spheres which have been reheated after solidifying (Lofgren 1971).

The 13A core contains two major intervals with spherule beds – at depth of 27 m and 67 m, ca. 40 m apart from each other. In nearby core OnZap1 there is only one layer of spherules like in 12A that is located 25 km away. This would suggest two distinct events recorded in 13A core sequence. However, the morphology of spherules in these beds are similar though the (recrystallized) composition is somewhat different, which might reflect not the different origin, but different environment of digenetic recrystallization.

Moreover, the sequence of sedimentary beds in drill core 13A seems to be repeated. There is a brecciated zone below the uppermost spherule bed interval that might indicate a fault crosscutting the core. In cores 12A and OnZap1 there are characteristic chert layers under the spherule layer as it is in 13A upper interval as well as it appears under the lower interval, though the last is brecciated. The fault plane in 13A core could be placed under calcareous mudstone layer in depth ca. 45 m where heavily brecciated dolostone starts.

This might also mean that spherules found in 12A are not correlative to the lower bed in 13A core as suggested before (Črne et al. 2013a; Huber et al. 2014), but correspond to the upper bed in 13A and the bed in OnZap1 core (Figure 20). Difference between chemical composition of altered spherules in two intervals in core 13A but similarity between spherule composition in OnZap1 core and the upper interval in core 13A could suggest that hydrothermal alteration took place after faulting.

It is particularly interesting that though cores OnZap1 and OnZap2 are located close to each other (only 50 m apart), no spherules were found in OnZap2 core suggesting that spherules occur in lenses not in a continuous layer. Moreover, it is not that surprising to not find spherule layer in all drillcores from Onega basin though found samples of layer is quite thick. Precambrian spherule layers are not easily traced over large areas, because of higher degree of tectonic deformation (Simonson and Harnik 2000).

Similar Paleoproterozoic impact spherule layer where reworked spherules containing carbon material as well as phosphate (Lai and Davatzes 2014) is described in a dolomite-chert succession of the Ketilidian orogen, South Greenland and tentatively dated as 2130-1848 Ma (Chadwick et al. 2001). The spherules and sediment succession there is very similar to Zaonega spherule interval. The age of Greenland spherule layer is within the range of Zaonega formation that is dated younger than ca. 2060 Ma (Hannah et al. 2008; Ovchinnikova et al. 2007) but older than 1969 ± 18 Ma (Puchtel et al. 1999). Therefore it could be that these impact spherule layers are formed by the same event.

Huber et al. (2014) has suggested Zaonega spherules could be related to Vredefort impact structure in South Africa which is dated as ca. 2025 Ma (Grieve 1998). The age of the Vederfort is close to the older limit of the Zaonega Formation, but this connection is still possible. It is important that Vredefort impact structure is large enough to form global impact ejecta blankets (Grieve 1998) and can be the source for both Zaonega and Ketilidian spherule layers.

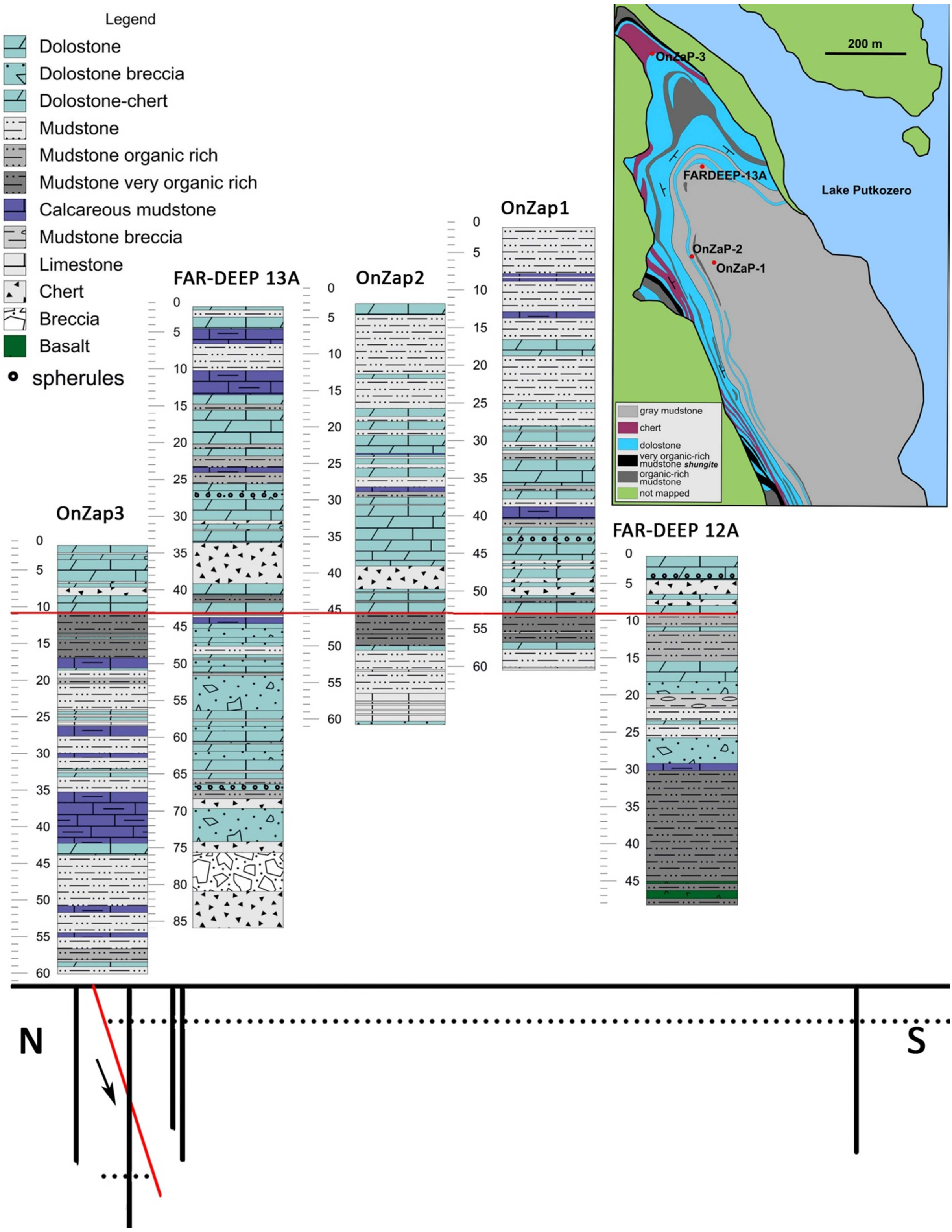

Figure 20. Lithological columns of drillcores and location on S-N line. The simplified scheme of drillcores and possible fault to illustrate if the layer of spherules is doubled in core 13A then it should be correlated with upper interval. Map after A.Lepland (2013), lithology and correlation made by T. Kreitsmann.

7. Conclusions

Despite the weak chemical signals that are not sufficient to confirm the impact origin of Paleoproterozoic Zaonega Formation spherule layer/lenses, the morphology of spherules found in Zaonega sediments strongly suggest these to be impact spherules. Spherules are altered and recrystallized though morphology is well preserved. Both ballistic shapes of molten silica droplets and devitrification textures have been found.

Detailed description of drillcores suggests that 1) spherule layer occurs as lenses rather than a continuous layer, 2) spherule layer is possibly doubled in core 13A due to faulting, 3) hydrothermal alteration has modified the composition of spherules after faulting.

The spherule layer described in Zaonega formation, Karelia could be a record of the same event as spherule layer in South Greenland. According to datings available today the source crater could be Vredefort but due to uncertainties in dates it could also be ejecta layer from still unknown impact site.

8. Acknowledgements

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10. Paleoproterosoilised sfäruliitsed kihid Zaonega läbilõikes, Karjalas, Loode-Venemaal

Kokkuvõte

Sfäruliitseid kihid koosnevad erineva suurusega sfäärilistest osakestet, mis võivad olla erinevat päritolu ja erineva tekkega. Selliseid setteosakesi võivad moodustada varajased mikrofossiilid (Javaux and Benzerara 2009; Sergeev 2009), settesisesed protsessid, nagu näiteks ooiidide kujunemine (Sommers et al. 2000; Schröder et al. 2006)ja kivimlõhedesse migreerunud nafta-bituumeni tilgakesed (Mancuso et al. 1993). Sfäärilisi osakesi tekkib ka vulkaanipursetel (Brown et al. 2012, Brown et al. 2010), meteoriidi impaktil (Glass 2002; Cannon et al. 2010; Johnson ja Melosh 2012; French ja Koeberl 2010) või isegi atmosfääri läbiva meteoroidi lagunemisel (Harvey et al. 1998; van Ginneken et al. 2010). Seega võimaldab sfäruliitsete settekivimite uurimine koguda informatsiooni settebasseini tekkekeskkonna, diageneesi protsesside ja üksikute vulkaanipursete ning meteoriidiplahvatuste kohta.

Käesolevas töös uuriti ligikaudu 2 Ga vanust sfäruliitset kihti Onega Basseini Zaonega kihistu orgaanikarikastes hüdrotermaalselt mõjutatud settekivimites Venemaal Karjalas. Seda kihti on kirjeldatud kolme puursüdamiku põhjal, mis sisaldasid kuni paarimillimeetrise läbimõõdga sfäärilisi objekte, mis asusid peamiselt bretšastunud dolomiidi tükkide-kildudevahel koos kaltsiitse mudaga ning mis olid kohati fosfatiseerunud või ränistunud.

Teema muudab aktuaalseks see, et hiljuti arvati ned kihid impakt sfääruliteks kuigi iseloomulikud keemilised signaalid (Ir ja üldisemalt plaatina grupi elementide sisaldus) ei ole veenvad (Huber et al. 2014), ja kõrge orgaanilise ainese sisalduse tõttu on neid peetud ka bakterite fossiilideks (Medvedev et al. 2009). Nüüdseks on kahele varem uuritud puursüdamikule (13A ja 12A aastast 2007) lisandunud veel kolm puursüdamiku (OnZap 1, 2 ja 3, aastast 2012), millest kaks läbivad ka sfäruliitset kihti, kuid sfäärilised objektid leiti vaid ühest (OnZap1).

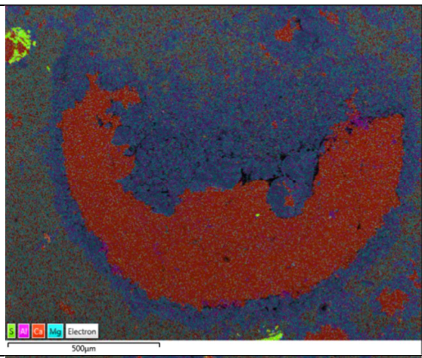
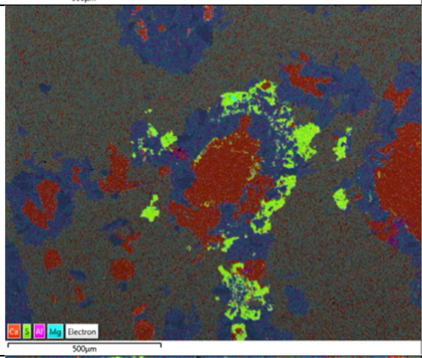
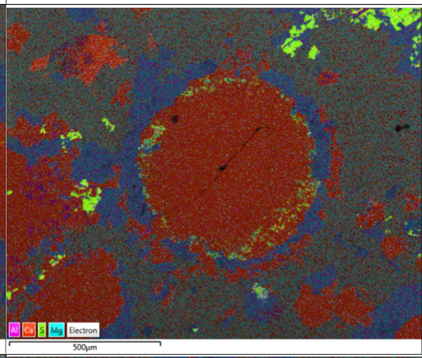
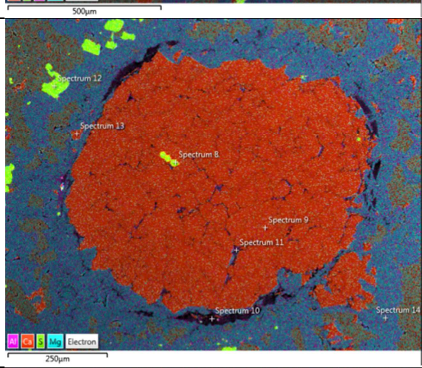
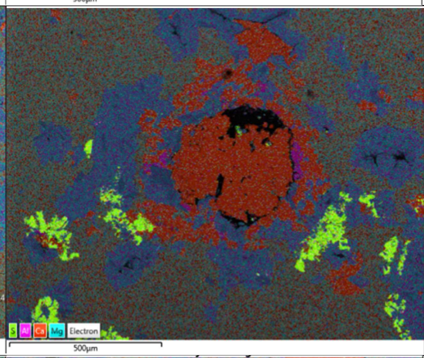
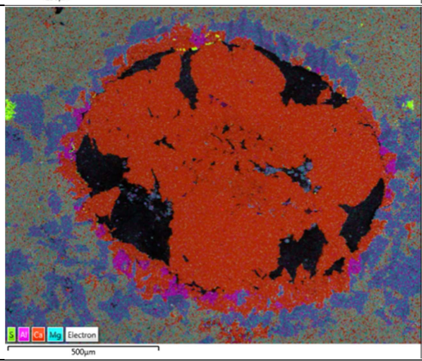
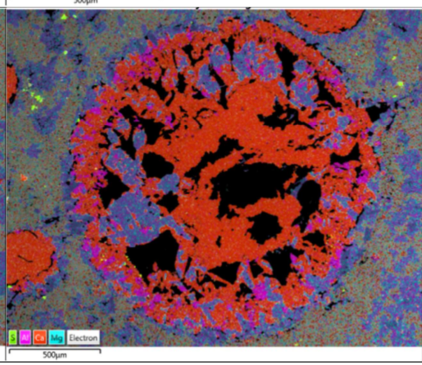
Nii varasemate kui ka uute puursüdamike materjalis võrreldi sfäärilisi osakesierinevate eelpool mainitud setetes esinevate sfääriliste moodustistega ning hoolimata nõrgast Ir signaalist (Huber et al. 2014) kinnitavad sfäärulite morfoloogia ja ümberkristalliseerumise struktuurid nende impakti tekkelist päritolu ning neid võiks nimetada impaktsfääruliteks.

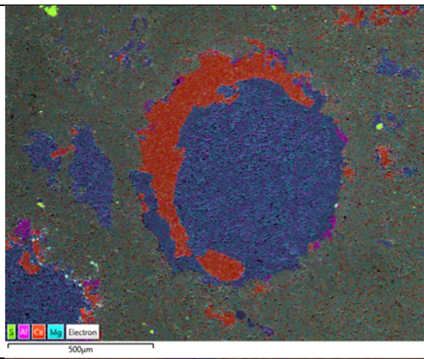
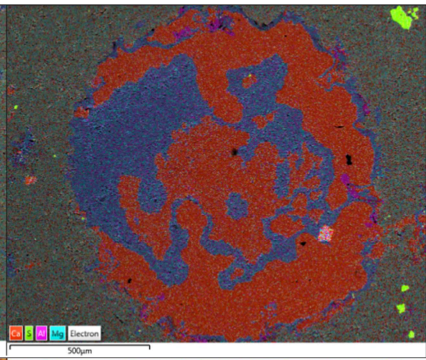
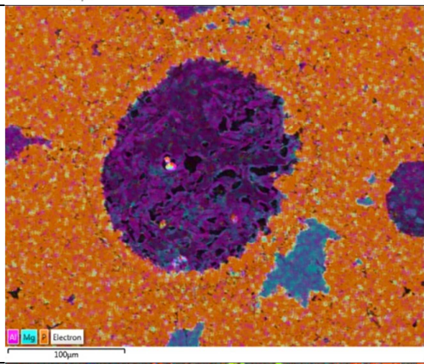
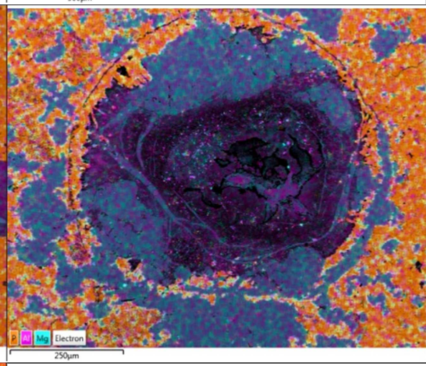
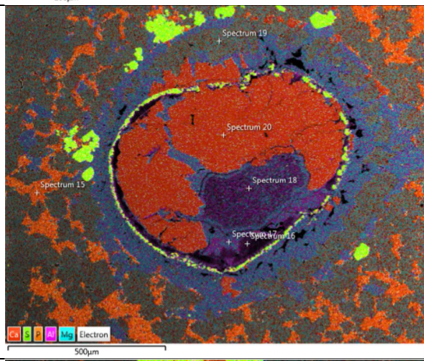
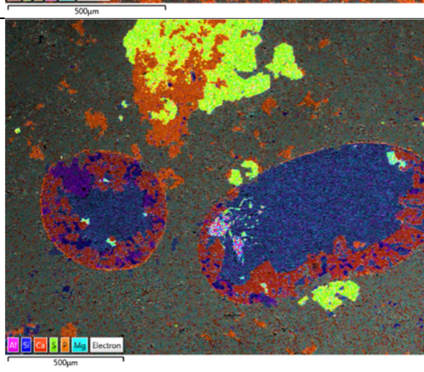
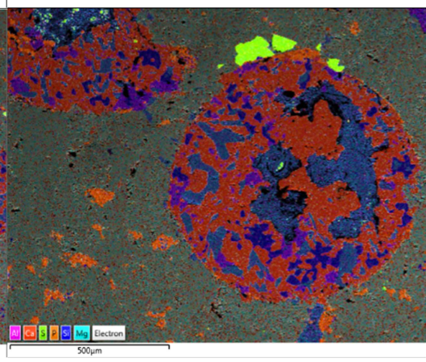
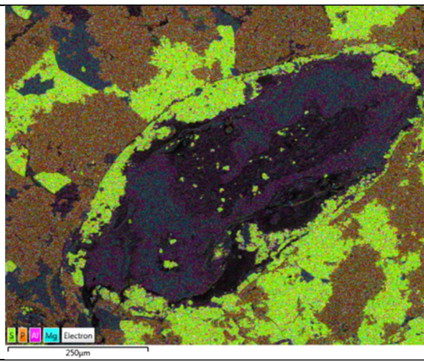
Uuritud sfäärulitele on iseloomulikud ballistilisele transpordile viitavad piklikud ja liivakella/hantli kujud ning struktuuris radiaalsed klaasi devitrifitseerumise kristallid, mis kasvavad väljast sisse. See annab kinnitust, et tegu on olnud mikrotektiitidega – algselt amorfsed klaasjad sulatilgad, mis langevad kuni 2500 km raadiusesse impakti paigast ning ei kanna endaga kõrgeid Ir teisete Plaatina grupi elementide sisaldusi (Glass ja Burns 1988, Smit 1999). Kuigi peab arvestama, et uuritud sfäärulite kihid on väga vanad ja mitmeid kordi ümber kristalliseerunud, algseid mineraale ega klaasi pole säilinud, seega ka mikrokristiite leidmisel, ei ole nende elementne koostis tavaliselt säilinud (Simonson ja Harnik 2000).

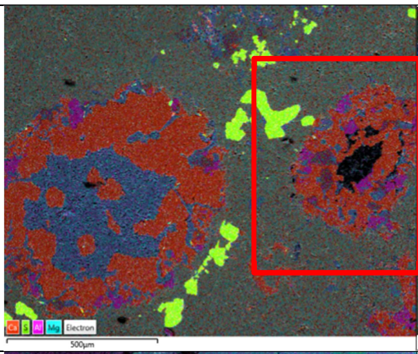
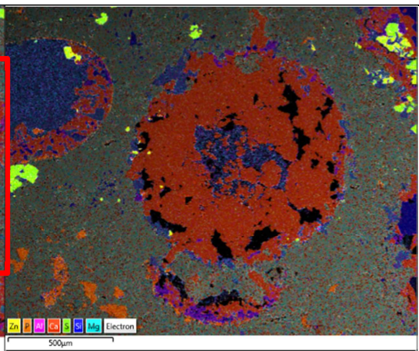
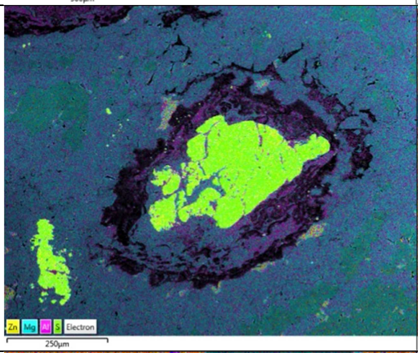
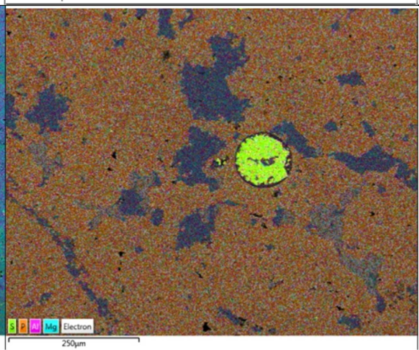
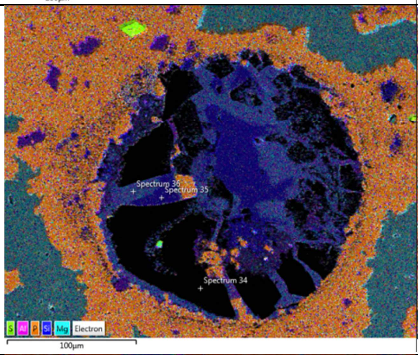
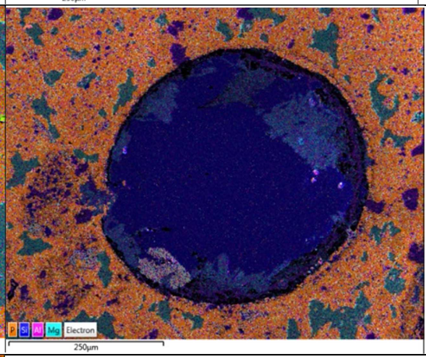
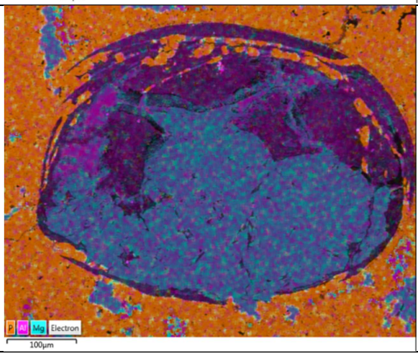
Lisaks sfääride impakti päritolu kinnitamisele leiti ka, et kui seni on puursüdamiku 13A alumist sfääre sisaldavt intervalli rööbistatud 12A puursüdamikus esineva intervalliga siis puursüdamiku 13A läbilõige on läbistatud nihkemurrangust ning on tegelikult korduses. Seega ei ole Xaonega läbilõikes mitte kaks vaid üks sfäärulite intervall.

11. Appendix

Table 1. Morphotypes of spherules

	Material in the middle	Material of the rim	Samples (EDS maps)	
1.	Blocky calcite	Phlogopite		
1.1	Blocky calcite	Phlogopite+ pyrite		
1.2	Blocky calcite	Phlogopite+ organic matter		
1.3	Blocky calcite + organic matter	Phlogopite (pyrite)		

2.	Phlogopite	Calcite	 
2.1	Phlogopite	Ca-phosphate	 
2.1.1	Phlogopite	Ca-phosphate + pyrite	
2.1.2	Phlogopite	Calcite + Ca-phosphate	 
2.2	Phlogopite	Pyrite	

2.3	Phlogopite (Organic matter)	Organic matter + Calcite	 
3.	Pyrite	Rim unclear	 
4.	Silica + Phlogopite	Phlogopite (Organic matter, Ca-phospate)	 
5.	Phlogopite	Rim of Phlogopite or no rim	

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