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Molar tooth structures in calcareous nodules, early Neoproterozoic Burovaya Formation, Turukhansk region, Siberia

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Abstract

Molar tooth structures are abundant in large (1–2 m diameter) carbonate nodules within fine-grained, subtidal carbonates of the early Neoproterozoic (lower Upper Riphean) Burovaya Formation along the Sukhaya Tunguska River, Turukhansk Uplift, northwestern Siberia. Although molar tooth structures are regionally abundant in this unit, here they occur only within the nodules. Stable isotopic compositions of molar-tooth-filling dolomicrospar cements and of thinly bedded dolomicrite within and surrounding the nodules are indistinguishable from one another. The carbon isotopic compositions (mean $\delta^{13}C = +2.8‰_{PDB} \pm 0.4$) reflect mean average oceanic surface water composition during their formation; the light oxygen isotopic compositions (mean $\delta^{18}O = -6.4‰_{PDB} \pm 2.2$) are generally similar to those of other little-altered Meso- to Neoproterozoic limestones and dolostones. These molar tooth structures have no features that would support a tectonic origin; they more likely formed through bacterial processes. Carbonate cement filling of these voids occurred soon after their formation, but the mechanism responsible for this carbonate precipitation is currently uncertain. Local restriction of molar tooth structures to early diagenetic nodules suggests that penecontemporaneous lithification was required for the formation, or at least preservation, of these widespread Mesoproterozoic to Neoproterozoic features.

Keywords: Molar tooth structures; Neoproterozoic; Carbonate; Stable isotopes

1. Introduction

Molar tooth structures are common features in fine-grained subtidal carbonates of Upper Mesoproterozoic to Lower Neoproterozoic age (James et al., 1998). Despite their abundance, the mechanism(s) by which these enigmatic structures developed is much debated. Recent interpretations invoke seismic shaking (Pratt, 1992, 1998, 1999; Fairchild et al., 1997) or bacterially produced gas voids (Furniss et al., 1994, 1998; Winston et al., 1999). Regardless of generating mechanism, most authors attribute molar tooth preservation to early lithification (Fairchild et al., 1997; Frank et al., 1997; Frank and Lyons, 1998, 2000; Furniss et al., 1998; James et al., 1998; Pratt, 1998).

Early diagenetic carbonate nodules are relatively common features of Proterozoic platform carbonates,

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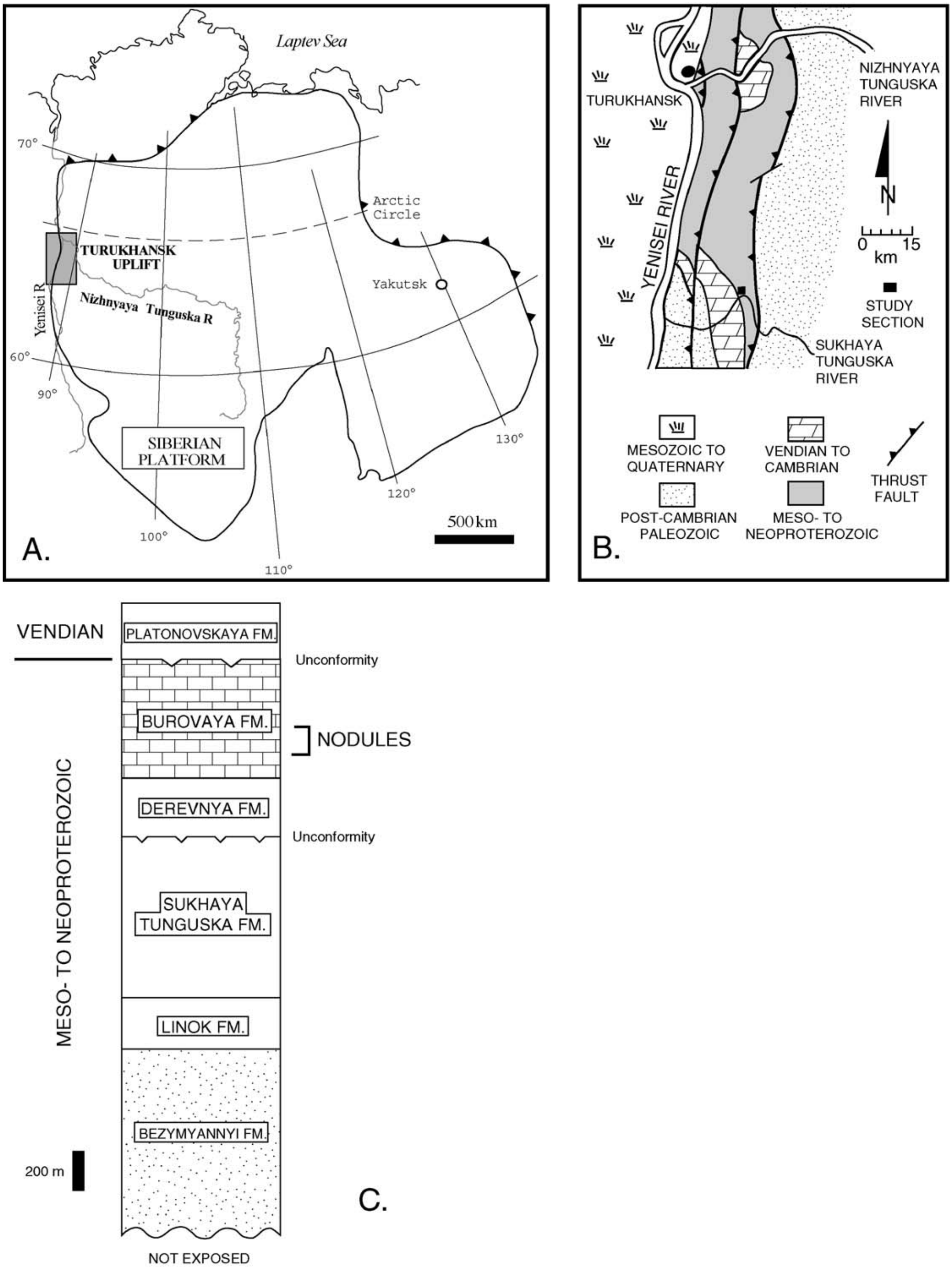
Laptev Sea
70°
Arctic Circle
TURUKHANSK UPLIFT
Yenisei R
Nizhnyaya Tunguska R
Yakutsk
60°
90°
SIBERIAN PLATFORM
130°
120°
100°
110°
500 km
A.
TURUKHANSK
NIZHNYAYA TUNGUSKA RIVER
YENISEI RIVER
N
0 15
km
STUDY SECTION
SUKHAYA TUNGUSKA RIVER
MESOZOIC TO QUATERNARY
VENDIAN TO CAMBRIAN
THRUST FAULT
POST-CAMBRIAN PALEOZOIC
MESO- TO NEOPROTEROZOIC
B.
VENDIAN
PLATONOVSKAYA FM.
Unconformity
BUROVAYA FM.
NODULES
DEREVNYA FM.
Unconformity
SUKHAYA TUNGUSKA FM.
LINOK FM.
MESO- TO NEOPROTEROZOIC
BEZYMYANNYI FM.
200 m
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where they are often highlighted by compaction and dolomitization of the surrounding matrix (e.g., Knoll and Swett, 1990). An unusual example of large, dolomitic nodules occurs in the early Neoproterozoic (lower Upper Riphean) Burovaya Formation of the Turukhansk Uplift, Siberia. These nodules are similar in size, shape and external morphology to calcareous concretionary nodules in Phanerozoic deeper water facies; here, however, they formed in mid-ramp carbonates. Further, these nodules contain abundant cement-filled molar tooth structures not found in surrounding thinly bedded dolomicrites. Preservation of molar tooth structures within these nodules indicates that molar tooth structures formed early in these carbonates and were cemented prior to sediment lithification and compaction. In this paper, we describe the physical and chemical characteristics of the Burovaya nodules and associated molar tooth structures and discuss implications for molar tooth genesis and preservation.

2. Stratigraphic and structural setting

Mesoproterozoic to Neoproterozoic (upper Middle to lower Upper Riphean) sediments of the Turukhansk Uplift of the western Siberian Platform (Fig. 1) comprise ~ 4 km of marine siliciclastics and carbonates deposited in a ramp to shelf setting (Petrov, 1993). The Burovaya Formation (Fig. 1) is the uppermost Riphean unit exposed along the lower reaches of the Sukhaya Tunguska River. Molar tooth structures are abundant in Burovaya exposures in the Turukhansk region (Kirichenko, 1940; Kozlov et al., 1988; Petrov and Semikhatov, 1998). At the study site, molar-tooth-bearing Burovaya Formation nodules are well exposed (Fig. 1) in the core of a gentle anticline immediately below the unconformity at the base of the Vendian to Cambrian Platonovskaya and Kostino Formations (Dragunov, 1963; Petrakov, 1964; Bartley et al., 1998). Drilling at this site (Dragunov, 1960) and regional lithostratigraphic correlations indicate that these nodules occur in subtidal facies approximately 250 m above the base of the Burovaya Formation (Fig. 1).

Pb–Pb dates on underlying Sukhaya Tunguska carbonates suggest that the Burovaya Formation is younger than 1035 ± 60 Ma (Ovchinnikova et al., 1995), whereas (reset) K–Ar dates on glauconite suggest it is older than 800–850 Ma (Gorokhov et al., 1995 and references therein). Similarly, C-isotopic profiles suggest that the entire Riphean succession of the Turukhansk Uplift is older than ca. 850 Ma but younger than 1300 Ma (Knoll et al., 1995; Bartley et al., 2001). Burovaya deposition also postdates the first appearance of typically Neoproterozoic (Upper Riphean) acanthomorphic acritarchs in the subjacent Derevnya Formation (Petrov and Veis, 1995). Thus, the Burovaya Formation was probably deposited during Early Neoproterozoic (early Late Riphean) time (Semikhatov and Serebryakov, 1983).

3. Field description

Exposures of the Burovaya Formation at the study site (~ 6 m) consist of dark grey-laminated dolomicrite containing abundant spheroidal nodules, each 1–2 m in diameter (Figs. 2 and 3A,B). Many nodules have saucer-shaped tops (Fig. 2). Both the nodules and surrounding carbonates are thinly bedded and finely laminated dolomicrite. Individual laminae can be traced from surrounding host rock into and through the nodules (Figs. 2 and 3B,C). The beds (2–8 cm thick) and laminae within nodules are about three times as thick as contiguous beds (1–3 cm thick) and laminae in the surrounding dolomite. Laminated beds within the nodules contain abundant molar tooth structures (Figs. 2, 3C and 4). Additionally, larger scale cracks that widen upward occur in the nodules; these are differentiated from molar tooth structures on the basis of size and stratigraphic relationships. Molar

Fig. 1. (A) Location map showing Siberian craton (adapted from Pelechaty et al., 1996). The box with dark grey shading shows the Turukhansk region and is shown in greater detail in B. (B) Inset map showing location of the Burovaya nodules along the Sukhaya Tunguska River approximately 30 km from its junction with the Yenisei River. (C) Generalized representation of Meso- to Neoproterozoic (Middle to early Late Riphean) stratigraphy along the Sukhaya Tunguska River. All units above the Bezymyannyi are predominantly carbonate. Burovaya nodules occur immediately below the Riphean–Vendian unconformity: however, regional correlations suggest they occur in the lower part of the formation.

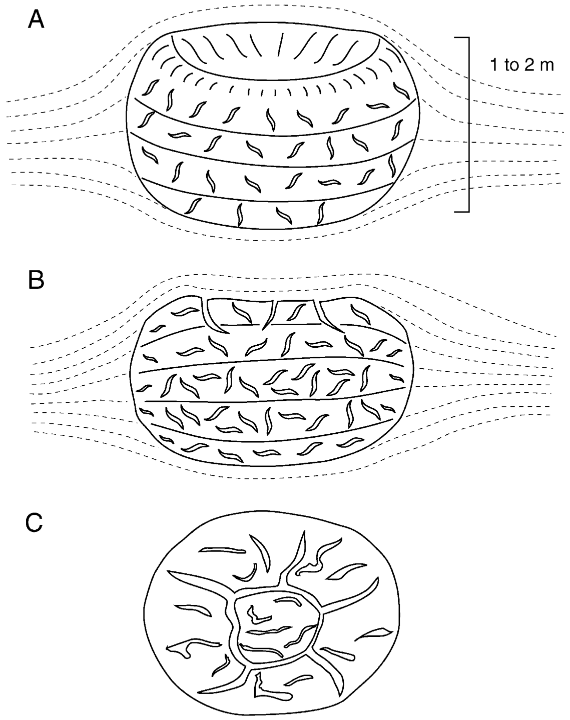


Fig. 2. (A) Idealized three-dimensional representation of a Burovaya nodule approximately 1–2 m in diameter with slightly ellipsoidal shape. Many nodules have "collapsed" tops similar to the nodule portrayed here. Contiguous external laminae are dashed. (B) Idealized cross-sectional view of Burovaya nodule with a collapsed top. Note the two different types of cement-filled features: molar tooth structures and upward-widening cracks. Molar tooth structures are confined to individual thin beds, whereas larger scale cracks crosscut bedding and molar tooth structures in the upper part of the nodules. (C) Plane view of Burovaya nodule. Large-scale cracks are confined to the apex (center) of the nodule top surrounded by smaller molar tooth structures.

tooth structures and larger scale cracks are absent in the surrounding carbonates.

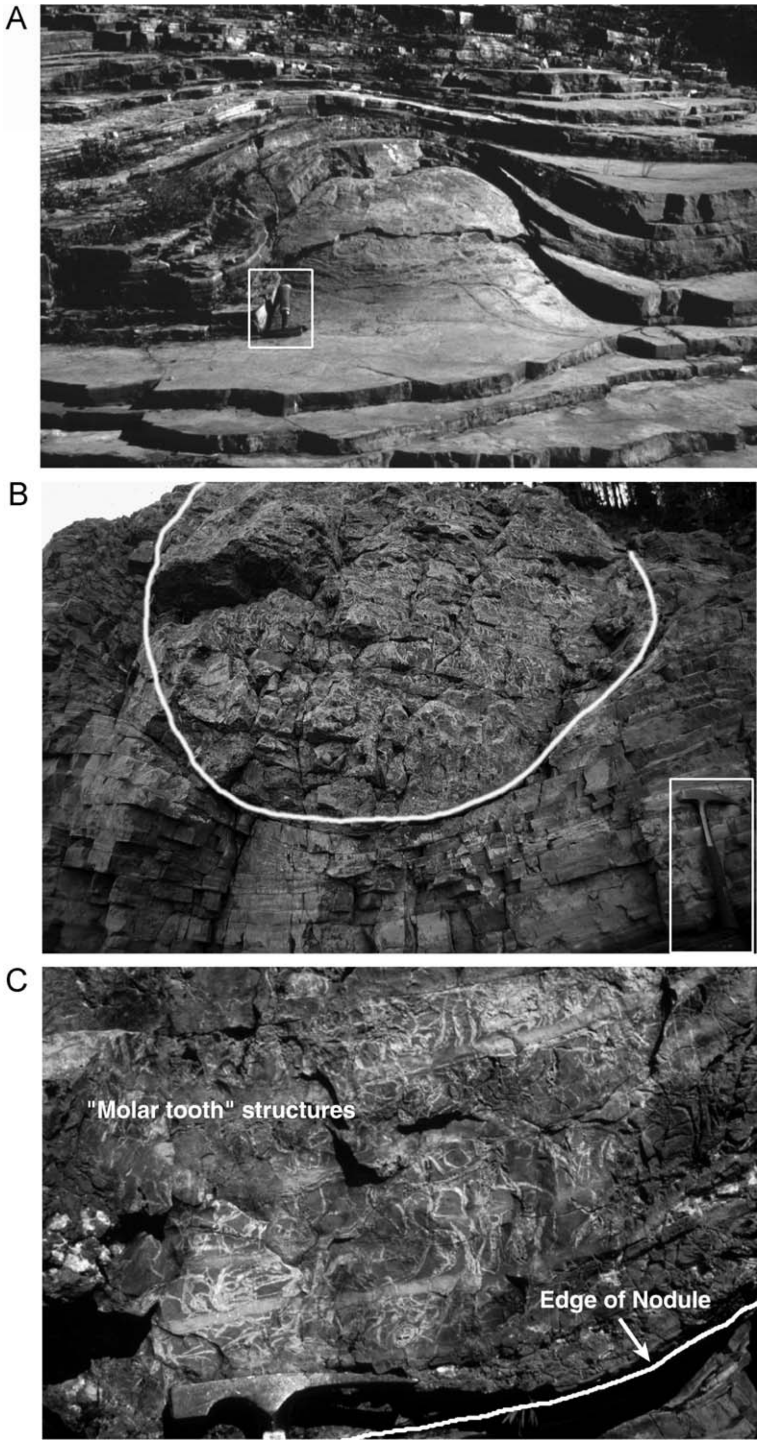
Molar tooth structures occur throughout the nodules as light grey, irregularly shaped, subhorizontal to subvertical sheets encased within the darker grey-laminated dolomicrite (Figs. 2, 3B,C and 4). Mean size of the molar tooth structures decreases toward the edges of the nodules. In cross section, most molar tooth structures are irregularly lensoidal—generally widest at their centers (up to 1 cm wide though commonly < 0.5 cm wide) and tapering toward both ends. Microspar cement fills the molar tooth structures. Laminae surrounding the molar tooth structures commonly diverge around the structures. In plane view, molar tooth structures define curvilinear fields (Fig. 4B) or are linear. Locally, molar-tooth-filling cements are preferentially dissolved beneath the Riphean–Vendian unconformity, producing vugs that are commonly filled with bitumen (Kirichenko, 1940; Dragunov, 1960). The molar tooth structures in these nodules are morphologically similar to molar tooth structures elsewhere in the Burovaya Formation (Dragunov, 1963; Petrov and Semikhatov, 1998) and to those described from Meso- to Neoproterozoic carbonate successions elsewhere (James et al., 1998).

Larger scale cracks that widen toward the exterior of the nodules (up to 3 cm wide on their exterior surface) and locally extend >20 cm into the nodules (Figs. 2 and 5) are restricted to the upper parts of nodules. These cracks crosscut thin beds and the molar tooth structures within them. The cracks define irregular polygonal patterns in plane view with radiating cracks propagating away from corners of the polygons (Figs. 2 and 5). These cracks are filled with light-grey dolomicrospar.

4. Petrography

The laminated carbonate within the nodules is similar to surrounding rocks, consisting of thin beds of finely laminated dolomicrite containing up to 15% muddy carbonate intraclasts (≤ 2 mm diameter). Rare opaque grains and silt-sized quartz grains are also present. Molar tooth structures and larger scale cracks are filled by uniform crystals of equant dolomicrospar (commonly less than 10 μm, with rare crystals to 15 μm). Faint zonation within molar tooth cement

Fig. 3. Photos of Burovaya Formation nodules containing molar tooth structures. (A) Cross-sectional view of the upper part of a large nodule along the Sukhaya Tunguska River. Hammer for scale (30 cm) is located to left of right-hand nodule. (B) Cross-sectional view of a portion of a Burovaya nodule. The nodule consists of abundant white-weathered dolomitic molar tooth structures which are absent from the surrounding laminated dolomicrite. Hammer top for scale is approximately 15 cm. (C) Molar tooth structures within a Burovaya nodule. The molar tooth structures consist of irregularly shaped, light-grey dolomicrospar in a laminated darker grey dolomite.


A
B
C
"Molar tooth" structures
Edge of Nodule

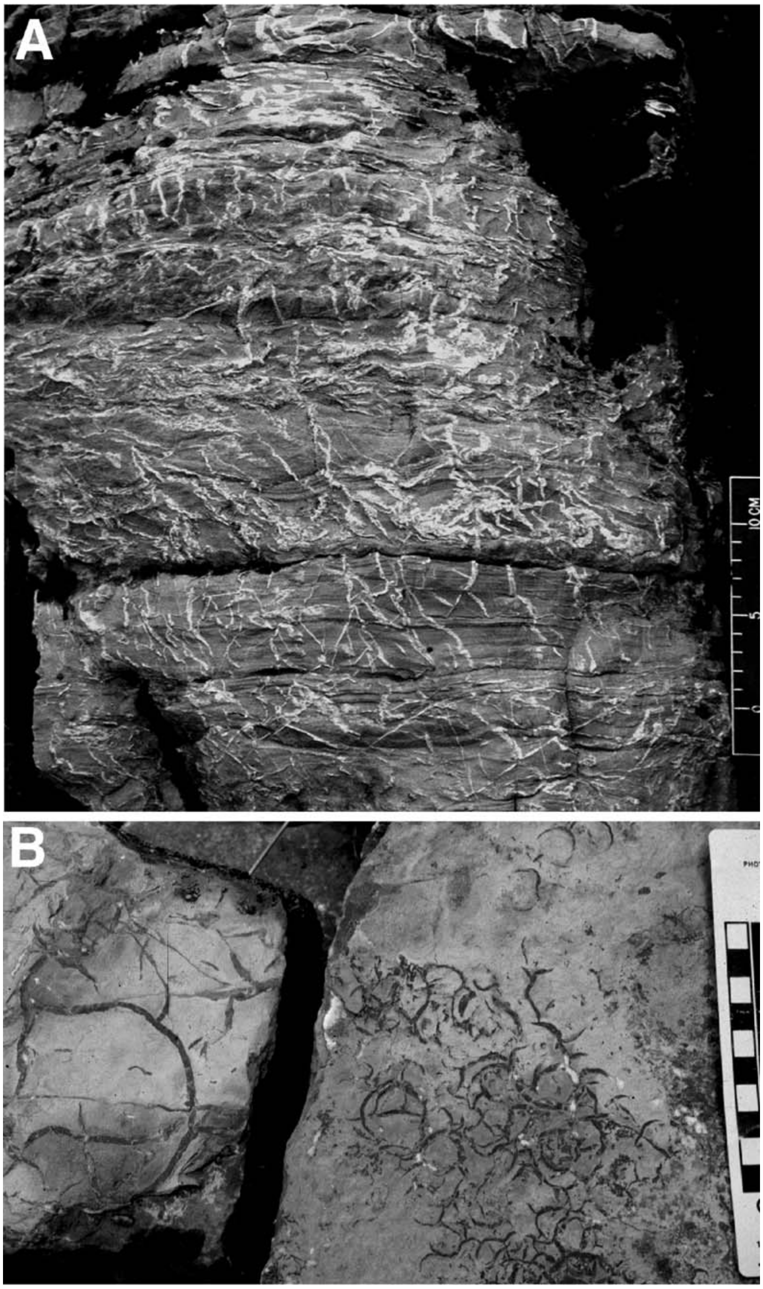


Fig. 4. Photos of molar tooth structures in Burovaya nodules. (A) Cross-sectional view of molar tooth structures within a Burovaya nodule. (B) Bedding plane view of molar tooth structures showing irregular, ellipsoidal shapes. Scale bar is in centimeters.

reflects subtle variations in crystal size. Late stage fractures that crosscut all earlier structures are filled with coarse, blocky, euhedral dolospar and brown organic residue.

Cathodoluminescence of the laminated dolomicrite within and surrounding the nodules, as well as the molar tooth and crack-filling dolomicrospar cement, shows uniform dull luminescence. Late stage

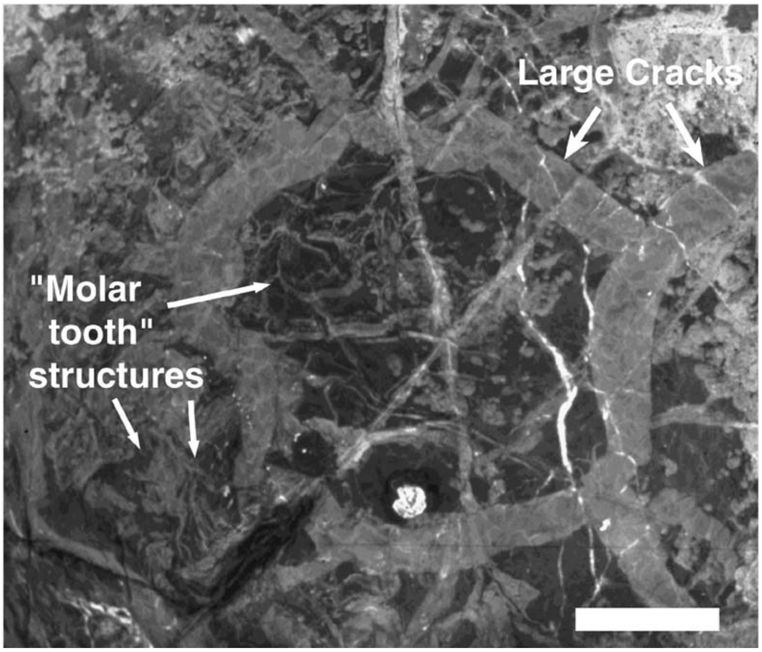


Fig. 5. Irregular, polygonal-shaped cracks at the top of a Burovaya nodule. Large-scale cracks radiate outward from the apices of the polygon. Molar tooth structures are smaller and crosscut by the larger cracks. White, light-coloured cracks which crosscut the radial cracks and molar tooth structures are tension gashes filled with late stage dolomite. Scale bar is approximately 5 cm.

fractures display uniform bright yellow cathodoluminescence.

5. Geochemical analysis

5.1. Sample preparation

Paired thin (30 μm) sections and polished thick sections were prepared from eight samples within and surrounding the nodules. These were examined petrographically in plane polarized light and by cathodoluminescence, and microsamples of molar tooth cement and the dark-laminated dolomicrite within and surrounding the nodules were drilled from paired chips using 1-mm diamond drill bits (Kaufman and Knoll, 1995). Because of the relative homogeneity of carbonate phases within molar tooth structures and in surrounding carbonate, these subsamples represent single carbonate phases.

Microdrilled samples were analysed for carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) isotopic compositions using methods outlined in Kaufman and Knoll (1995). The analytical uncertainty for these measurements was ± 0.2 ‰ for carbon and ± 0.4 ‰ for oxygen. Fractionation factors used for the calculation of ^{18}O abundances of carbonates based on analyses of CO_2 prepared at 90 °C were 1.00798 for calcite and 1.00895 for dolomite (Rosenbaum and Sheppard, 1986).

5.2. Results

The results of the isotopic analyses are presented in Table 1 and Fig. 6. The $\delta^{13}C$ compositions for all samples (including laminated dolomicrite within the nodules, molar-tooth-filling dolomicrospar, and laminated dolomicrite surrounding the nodules) lie between $+2.6‰_{PDB}$ and $+3.2‰_{PDB}$, with a mean of $+2.9‰_{PDB}$. $\delta^{18}O$ compositions are less tightly clustered, ranging from $-5.5‰_{PDB}$ to $-11.3‰_{PDB}$; most compositions, however, lie between $-5.5‰_{PDB}$ and $-6.9‰_{PDB}$, with a mean of $-6.4‰_{PDB}$. $\delta^{13}C_{org}$ compositions of the laminated dolomicrite within and

Table 1
Isotopic composition of Burovaya carbonates

Sample	$\delta^{13}C_{carb}$ (‰)	$\delta^{18}O_{PDB}$ (‰)	$\delta^{13}C_{org}$ (‰)	Location
SR-29	2.9	−6.0		Dolomicrite outside nodule
SR-30	2.6	−8.9	−29.0 −28.9 −28.9	Dolomicrite outside nodule
K95-111	3.2	−6.8	−28.3	Dolomicrite outside nodule
SR-31s	2.6	−6.9	[a]	Molar tooth dolomicrospar
SR-31s	3.0	−11.3	[a]	Molar tooth dolomicrospar
K95-112s	3.0	−5.5	[a]	Molar tooth dolomicrospar
K95-112g	2.6	−6.3		Dolomicrite inside nodule
SR-31g	2.7	−6.6	−27.5	Dolomicrite inside nodule

[a] Organic carbon isotopes for the molar tooth fill was not determined because the TOC contents were too low.

surrounding the nodules are also uniform ranging from −27‰$_{PDB}$ to −29‰$_{PDB}$. The organic content of the molar-tooth-filling cement was too low to determine its isotopic composition.

5.3. Evaluation of diagenesis

Proterozoic carbonates commonly have $\delta^{18}O_{PDB}$ compositions near −5‰ (e.g., Veizer et al., 1992; Kaufman and Knoll, 1995; Kah, 2000), and because meteoric or hydrothermal diagenesis tends to decrease $\delta^{18}O$, samples with compositions less than −8‰ are considered altered during subsequent diagenesis. Where the volume of diagenetic fluid is great enough to also alter carbon isotopic compositions, a $\delta^{13}C$ vs. $\delta^{18}O$ cross plot reveals correlation with a line of positive slope (Hudson, 1977; see Fig. 6).

Diagenesis in carbonates can also be evaluated by examination of the relationship between $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$. Because the difference (ΔC) between these compositions is controlled primarily by biological carbon isotope fractionation, if biological fractionation is constant and samples are little altered, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ should track together with a constant ΔC. Although both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ may be altered during diagenesis, no process is known to alter both compositions simultaneously and in the same direction (Knoll et al., 1995).

Oxygen isotopic compositions (> −8‰) of sampled phases suggest minimal diagenetic alteration for most Burovaya carbonates. Two samples have isotopically light $\delta^{18}O$ values (Table 1), indicating more significant alteration during diagenesis. An oxygen–carbon cross plot shows no covariant decreasing trend (Fig. 6), suggesting that the carbon isotopic compositions of these carbonates are likely little altered by meteoric diagenesis. Uniform compositions of ΔC in these samples also support this interpretation, though the sample set is small.

6. Interpretation and discussion

Molar-tooth-bearing Burovaya Formation nodules are unique features in the lower Neoproterozoic stratigraphic succession of northwestern Siberia. The dark, fine-grained, finely laminated sediment surrounding and within the Burovaya nodules indicates they developed in a moderately deep, organic-rich subtidal setting. The absence of stromatolites or subaerial exposure surfaces, both of which are common in shallow water exposures of the Burovaya Formation, indicates these nodules formed in a mid to deep carbonate ramp setting. The uniformity of nodule size suggests that growth was limited by three-dimensional diffusive or physical barriers among widely dispersed nucleation sites.

Though their morphology, shape and size are similar to those of deepwater concretions in Phanerozoic sediments (e.g., Dix and Mullins, 1987; Mozley and Burns, 1993), the Burovaya nodules differ in sedimentary context. Most strikingly, the nodules contain early cemented molar tooth structures, features that are rare in the surrounding sediments but common elsewhere in the Burovaya Formation. Whereas carbonate nodules and molar tooth structures are individually common in Meso- to early Neoproterozoic carbonate platforms, their cooccurrence is rare. Broadly, similar (albeit much smaller) molar-tooth-bearing nodules occur in Neoproterozoic dolomites in Tasmania (Calver and Baillie, 1990) and in central Australia (lacustrine facies of the Bitter Springs Formation; AHK, personal observation).

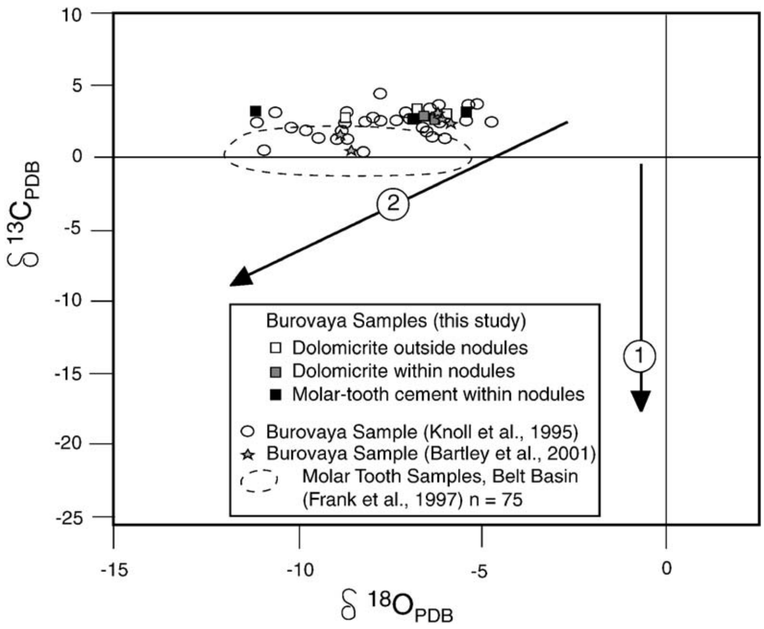


Fig. 6. Carbon–oxygen cross plot of Burovaya molar tooth structures and laminated dolomicrite within and surrounding the nodules (grey squares). Additional Burovaya isotopic data are whole rock and microdrilled analyses from Knoll et al. (1995) and Bartley et al. (2001). Carbon and oxygen data field from molar tooth structures in the Mesoproterozoic Belt Supergroup (Frank et al., 1997) are plotted for comparison. Trend lines show: (1) Palaeozoic carbonate concretions formed in shaly deepwater settings during methanogenesis (Dix and Mullins, 1987; Desrochers and Al-Aasm, 1993; Mozley and Burns, 1993); and (2) approximate decrease of carbon and oxygen compositions due to meteoric diagenesis during increasing burial depths and temperatures (Hudson, 1977).

6.1. Formation of molar tooth structures

Recent mechanisms postulated for the generation of molar tooth structures focus on tectonism (Pratt, 1992, 1998, 1999; Fairchild et al., 1997) and high gas pressures generated by bacterial metabolism (Furniss et al., 1994, 1998). Several observations suggest that molar tooth structures in the Burovaya nodules did not form by tectonic shaking. First, none of the laminated dolomicrite within and surrounding the nodules is brecciated or otherwise deformed (cf. Fairchild et al., 1997). Secondly, these molar tooth structures contain none of the dykelets, fractures or potential tsunami scour features expected from large earthquakes (cf. Pratt, 1998). Thirdly, the molar tooth structures show no obvious alignment vertically or horizontally.

On the other hand, in experiments involving a mixture of sugar and yeast stiffened by plaster, gas pressure of confined, metabolically produced gas generated features that morphologically resemble the molar tooth structures in Burovaya nodules (Furniss et al., 1998). The local restriction of molar tooth features to nodules indicates that early lithification was necessary for the formation—or at least preservation—of Burovaya molar tooth structures. Significantly, when Furniss et al. (1998) ran their experiment using unstiffened mud, gas bubbles percolated upward through the permeable matrix and escaped. In the Helena Formation of the Belt Supergroup, molar tooth structures are typically distinct in fine-grained lithologies and indistinct or absent in coarser-grained, higher porosity lithologies. Molar tooth morphology changes abruptly across boundaries between finer- and coarser-grained layers, suggesting that rheology of matrix carbonate is critical to the generation of molar tooth structures (Pollock et al., 2002). Thus, experimental and field data agree in suggesting that the rheology of matrix carbonate and rate of lithification are critical factors in both the generation and preservation of molar tooth structures.

Precipitation of microspar cements in molar tooth structures and later cracks is thought to have occurred by diffusive void-filling precipitation (e.g., Lippman, 1955; Raiswell, 1971). The uniformity of $\delta^{13}C$ and petrography of the molar-tooth-filling microspar cement indicates that these formed from a marine fluid similar in composition to that which formed the matrix carbonate. Geochemical analysis of molar tooth structures and their surrounding sediments in the Mesoproterozoic Helena Formation of the Belt Supergroup in western MT (Frank et al., 1997; Frank and Lyons, 1998, 2000) show trends similar to those of the Burovaya samples (Fig. 6). In both cases, the molar-tooth-filling cements have a narrow range of $\delta^{13}C$ compositions and a wider range of $\delta^{18}O$ compositions, both reflecting the broader spectrum of compositions observed stratigraphically within their respective units.

6.2. Formation of nodules

Like many carbonate nodules in younger rocks, the Burovaya nodules are interpreted to be products of microbial activity, with anaerobic bacterial heterotrophs decomposing organic matter, thereby driving the oversaturation of pore waters to critical compositions (Canfield et al., 1991; Mozley and Burns, 1993). This suggests that the oxic–anoxic transition was close to the sediment–water interface, similar to the situation in some Phanerozoic deepwater shales (cf. Morad and Eshete, 1990) but unlike modern shelf carbonates, where diffusion and bioturbation push this interface many centimeters below the sediment surface.

Samples from the Burovaya nodules and surrounding matrix are isotopically indistinguishable from one another. Carbon isotopic data from complete sections of the Burovaya Formation elsewhere in the Turukhansk Uplift show a gradual overall decrease in $\delta^{13}C$ upsection (Knoll et al., 1995; Bartley et al., 2001). The moderately positive $\delta^{13}C$ values of these samples compare closely to values obtained from the lower part of the Burovaya Formation in agreement with lithostratigraphic correlations. The absence of a discernible microbial C-isotopic signature indicates that either early cements are a volumetrically small component of Burovaya nodules (unlikely in view of the three-fold compaction of encompassing sediments), or that seawater saturation levels with respect to $CaCO_3$ minerals were sufficiently high so that only limited bacterial activity was sufficient to drive precipitation without substantially altering C-isotopic composition.

Field and petrographic evidence indicate that nodules formed prior to compaction and were well cemented before burial diagenesis. The uniformity of carbon and oxygen isotopic compositions among molar-tooth-filling dolomicrospar cements, laminated dolomicrite within and surrounding the nodules, and whole rock and microdrilled Burovaya samples from other localities (Knoll et al., 1995; Bartley et al., 2001) precludes pervasive differential diagenetic alteration of the nodules or the surrounding rocks, suggesting that the nodules, molar tooth structure, and cement formed near the sediment–water interface in fluids isotopically similar to coeval seawater. The fine textural preservation of molar tooth cements and uniformly dull cathodoluminescence of dolomite within and surrounding the nodules also suggest a common early marine source and that carbonate precipitation during nodule growth occurred in fluids that were isotopically buffered by surrounding micritic sediments.

As bacterial processes are interpreted to have formed the nodules and molar tooth structures, they might also have induced void-filling cementation, possibly through increases in carbonate saturation levels associated with anaerobic bacterial metabolism, although no independent data lend support to this possibility. Such a model would suggest a common origin for molar tooth cement and nodule cement. On the other hand, since Proterozoic seawater was highly oversaturated with respect to calcium carbonate minerals, carbonate precipitation in these voids could have been associated with common environmental events such as temperature or salinity change (see discussion in Frank and Lyons, 1998). In any case, cementation of molar tooth structures must have occurred early prior to significant compaction of the nodules.

Thus, bacterial metabolism could have provided the proximal driver for both nodule growth and molar tooth development. Of course, bacterial decay must have proceeded throughout the beds in question not just at the precise locations of nodules. Nodules were likely initiated by (random?) nucleation at scattered sites within the sediments, following which continuing precipitation took place preferentially on early formed carbonate crystals.

As noted above, early diagenetic nodules are common in Meso- and Neoproterozoic carbonates ranging from peritidal calcisiltites (Knoll and Swett, 1990) through subtidal ribbon rocks (e.g., Buick et al., 1995; Knoll et al., 1995). Not surprisingly, they appear to be less well developed in Paleoproterozoic carbonates, which are characterized by widespread precipitation of macroscopic carbonate crystal fans at or just below the sediment–water interface (Grotzinger, 1989, 1993). We consider it likely that the widespread formation of early diagenetic nodules in later Proterozoic carbonates reflects the confluence of relatively high oversaturation of seawater with respect to calcium carbonate minerals (e.g., Grotzinger, 1989; Knoll and Swett, 1990) with a sharply declining oxygen gradient in organic-rich sediments, associated with the absence of bioturbation, and likely, with lower oxygen concentrations in contemporaneous seawater. Whereas aerobic respiration is generally associated with a decrease in saturation with respect to $CaCO_3$ minerals, anaerobic metabolisms such as dissimilatory sulfate reduction increase saturation levels (Canfield et al., 1991). Thus, the early establishment of anoxia would have increased the likelihood of early carbonate cementation in Proterozoic carbonate platform sediments. During the terminal Neoproterozoic Era, evolutionary radiation of macroscopic animals, declining $CaCO_3$ associated with skeleton formation (Knoll et al., 1993) and increasing sediment aeration associated with both increased pO_2 (Canfield and Teske, 1996) and bioturbation (Bottjer et al., 2000) progressively restricted nodule distribution to deeper water facies as observed in the Phanerozoic stratigraphic record.

6.3. Large-scale cracks, compaction and summary

The depressed tops of many of the nodules probably represent the collapse or dissolution of early formed internal cement during compaction. Restriction of large-scale cracks to the upper parts of nodules and their crosscutting relationships with small-scale molar tooth structures suggest that the larger structures formed later in response to compaction (Fig. 7) like septarian cracks in younger carbonate nodules (Desrochers and Al-Aasm, 1993; Sellés-Martínez, 1996). Burovaya cracks differ from the cracks in most Phanerozoic carbonate septarian

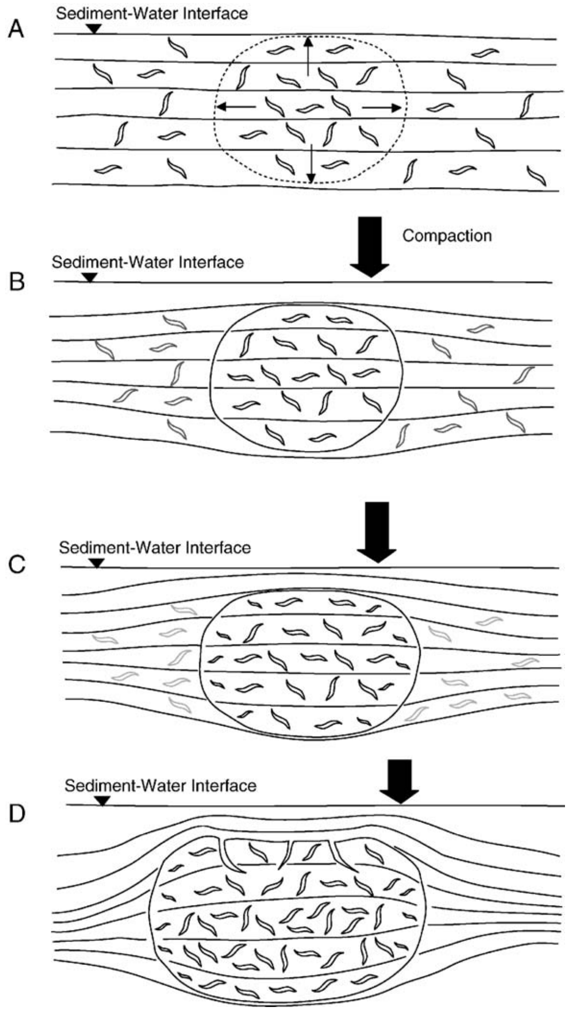


Fig. 7. Model for Burovaya nodule formation. (A) Nucleation of molar tooth features below the sediment–water interface. Molar tooth structures taper toward ends and are filled by dolomicrospar. Limit of nodule growth is marked by dashed line. (B) During initial compaction, the cemented area resists compaction while surrounding beds are compacted. Molar tooth structures that formed outside of the limit of nodules may have been destroyed by dissolution during this and subsequent compaction; however, this is not indicated on the outcrops or polished slabs. (C) With continued compaction, the surrounding sediments are compressed, molar tooth structures developed near the exterior of nodules are smaller, likely due to a diffusive cement gradient established within the nodule. (D) Dissolution of early cement leads to the "collapse" of the top of the nodule leading to mechanical cracking of the nodule and formation of the large-scale cracks, which are morphologically similar to cracks formed within septarian nodules.

nodules, however, because they formed only on the upper surface not throughout the nodule. Additionally, the dolomicrospar cement that fills the Burovaya cracks is morphologically quite distinct from the coarse fibrous or blocky calcite cements typically filling cracks in Phanerozoic septarian nodules (cf. Morad and Eshete, 1990; Desrochers and Al-Aasm, 1993).

Compaction of laminae around the nodules and continuity of laminae through nodules into surrounding sediment demonstrate that both laminae and cements within the nodules formed prior to the onset of burial compaction (Fig. 7). The 3:1 compaction ratio for muddy laminae surrounding the nodules versus those within the nodules supports the interpretation that these nodules formed early at shallow burial depths; it might indicate abundant pressure dissolution within the sediments surrounding the cemented nodules (Goldhammer, 1997). If so, the lack of molar tooth structures in the sediments surrounding the nodules may indicate that in the absence of cementation, any such early formed features were obliterated during compaction. However, the lack of such features on the outcrops and in polished hand samples likely precludes this possibility.

Based on field, petrographic, and geochemical data, we can propose a model for formation of Burovaya nodules containing molar tooth structures (Fig. 7): (1) laminated calcisiltite was deposited in a subtidal marine setting; (2) molar tooth structures developed by gas escape related to bacterial metabolism, either in sites of future nodules or throughout a semilithified calcisiltite matrix; (3) nodules formed by microbial activity, perhaps cementing both molar tooth cracks and the surrounding nodules; (4) compaction cracked the nodule tops and the cracks were filled by cement, perhaps also generated by bacterial metabolism as the surrounding sediment was compressed.

7. Conclusions

On the basis of field and petrographic evidence, we conclude that these Burovaya Formation nodules formed during early diagenesis in a mid-ramp setting prior to compaction and lithification of surrounding carbonate sediment. Molar tooth structures in these early-cemented nodules provide field observations in support of Furniss et al.'s (1998) recent hypothesis for the genesis of these distinctive Proterozoic features within the zone of anaerobic microbial activity. The restriction of molar tooth structures to nodules suggests that early carbonate cementation and a relatively rigid carbonate matrix are required for the generation and/or preservation of molar tooth structure. This unusual association between early cemented nodules and molar tooth structures also provides a possible explanation for the restriction of molar tooth structures to subtidal environments of the Mesoproterozoic and Neoproterozoic (James et al., 1998; Shields, 2002). Perhaps, the high carbonate saturation levels in muddy carbonate sediments combined with an anoxic–oxic boundary very near the sediment–water interface create the carbonate depositional environment necessary to produce and preserve molar tooth structures.

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