Sunspot cycles recorded in Mesoproterozoic carbonate biolaminites

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ABSTRACT

Well-preserved carbonate biolaminites from the early Mesoproterozoic Wumishan Formation (ca. 1.5–1.45 Ga) of North China show submillimeter-scale yearly couplets that consist of alternating dark and light laminae, and are texturally similar to those reported from Holocene tufas. Power spectrum and wavelet transform analyses of laminar couplet thickness variations and geochemical series (Ca, Fe, Co/Ti, Cr/Ti, and Br) reveal a prominent periodicity at 9.0–11.7 and a less prominent periodicity at 19.7–21.4 couplets. These coherent periodic modes match well with the 11-yr Schwabe sunspot cycle and 22-yr solar Hale cycle. The observed layering pattern is thus interpreted as recording solar induced climate changes that may have modulated microbial growth rate and biomass production in restricted subtidal environments on a broad epicontinental platform. The documented example represents the first reported solar signature in Mesoproterozoic marine carbonates and implies the sensitivity of microbial life to environmental changes prior to metazoan evolution.

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1. Introduction

The Sun is the most important driver of the Earth’s climate system (Beer et al., 2000) and periodic changes in solar radiation exert fundamental control on Earth’s climate cycles (Foukal and Lean, 1988; Gray et al., 2010; Reid, 2000). Sunspot cycles are short-term solar cycles that modulate solar wind and irradiance, and hence decadal to millennial climate changes (Foukal et al., 2006; Ineson et al., 2011; Reid, 2000). Their geological record, however, is rare and limited by conditions suitable for the preservation of solar climatic signature (Andrews et al., 2010; Foukal et al., 2006).

Examples of solar cyclicity in the rock record (Table S1) are mostly reported from glacially influenced lacustrine (e.g., Anderson, 1992, 1993; Hughes et al., 2003) and marine (e.g., Ernesto and Paccia, 1981; Milana and Lopez, 1998; Williams and Sonett, 1985) siliciclastic successions. Periodicity of laminar couplets in these examples is commonly expressed by compositional and/or grain-size changes of siliciclastic sediments that have been interpreted as recording solar-induced freeze-thaw glacial cycles, and relating to the changes of climate and weathering intensity. Only a few examples of solar cyclicity were documented from non-glacially influenced, argillaceous lacustrine laminites (e.g., Andrews et al., 2010; Bradley, 1929; Kokfelt and Muscheler, 2013; Ripepe et al., 1991; Zolitschka, 1992). Cyclic thickness variations of laminar couplets in these laminites were interpreted as recording sunspot periodicities that may have controlled rainfall and surface runoff, and therefore the terrestrial sediment influx to lacustrine basins.

Despite the abundance of microbial mats and their sensitivity to environmental changes, sunspot climate cycles have been rarely documented from marine carbonate successions (Table S1). The only carbonate example that recorded 11-yr Schwabe sunspot cycles was reported from the Holocene biogenic carbonate varves in Swiss lake (Livingstone and Hajdas, 2001), where periodic thickness variations of carbonate varves were ascribed to solar-induced variations in primary production and carbonate precipitation. The general lack of identifiable solar cyclicity in carbonate successions has limited our knowledge on whether and at what manner the carbonate depositional systems could potentially record solar activities (Jackson, 1985).

From the previous studies (Table S1), it can be seen that no matter what the lithologies are, persistent existence of yearly laminar couplets in the laminites and their thickness variations with regular cyclicity are commonly taken as prerequisites for the evaluation of potential solar cycles recorded in them. Study also shows...
that it is often difficult to distinguish solar-induced from tidal-induced cycles merely through field observations, especially in marine or glacio-marine environments (Williams and Sonett, 1985; Williams, 1990). Therefore, samples from marine setting should be more carefully treated with multiple approaches when used for solar cycle evaluation. In this paper, we report high-frequency cycles in the early Mesoproterozoic carbonate laminites from the North China platform. These laminites are composed of numerous vertically accreted fine laminae, and contain no current- or wave-influenced sedimentary structures, likely formed in a restricted subtidal environment below the fair-weather wave-base. The studied samples have negligible siliciclastic contents but abundant microbial remains as major constituents in their laminae, suggestive of biogenic origin. Thus the laminites have provided a valuable opportunity to explore the sensitivity of microbial community to solar-induced environmental changes in a low-latitude, Mesoproterozoic epicontinental platform. For this purpose, thickness variations of laminar couplets in the laminites were analyzed in combination with measurements of biological and environmental sensitive element contents.

2. Geological setting

The North China platform is a large (1.2 × 10^6 km^2), triangular-shaped continental block (Fig. 1, Wang, 1985) that contains Archean to early Paleoproterozoic basement (Zhao et al., 2001). Rifted margins occurred during the late Paleoproterozoic, particularly at the northern side of the craton, after the continental block was cratonized (Hou et al., 2006; Lu et al., 2002, 2008). The North China platform commonly refers to the stabilized interior of the craton. In the platform, Late Paleoproterozoic to Neoproterozoic strata are well preserved and they recorded the tectonic history from the breaking-up of supercontinent Columbia (Zhao et al., 2003, 2004, 2011) to the assembly of Rodinia (Li et al., 2008). The stratigraphic successions are only metamorphosed slightly and commonly subdivided into three groups (Fig. 2A), i.e., the Changcheng Group (1800–1600 Ma, Pt1), Jixian Group (1600–1400 Ma, Pt2), and the Qingbaikou Group (1000–800 Ma, Pt3). A significant hiatus of 400 Ma occurs between the Jixian and Qingbaikou groups (Gao et al., 2009).

The Wumishan Formation of the Jixian Group is one of the most widespread Mesoproterozoic lithostratigraphic units in the North China platform and was deposited in a post-rift epicontinental platform. According to the available age data (Gao et al., 2007, 2008a, 2008b; Li et al., 2010; Su et al., 2008, 2010), the time of Wumishan Formation was constrained as early Mesoproterozoic (the Ca--Ar period) between ca. 1.50 and ca. 1.45 Ga (Fig. 2A; Gao et al., 2009; Tang et al., 2013a, 2013b). On the basis of recent paleomagnetic study, the North China platform was most likely located between 10°N and 25°N latitude during 1.50–1.45 Ga (Zhang et al., 2012), where arid to semi-arid climate might have dominated.

The Wumishan Formation is dominated by peritidal carbonates and consists of hundreds of shallowing-upward parasequences (e.g., Mei et al., 2010; Tang et al., 2011, 2013a, 2013b, 2013c), in each of which several meter-scaled subordinate cycles can be further recognized. The studied laminites commonly occur as the lower units of the meter-scaled cycles (Fig. 2B), and form 0.4- to 1.8-m-thick layers that are interbedded with light-color dolostone beds (Fig. 3A). The light-color beds often contain some carbonate intraclasts (Fig. 3B), flat pebble conglomerates (Fig. 3C), and ooids (Fig. 3D), indicative of shallow subtidal to lower intertidal environments above fair-weather wave base (Tang et al., 2013c). Dark laminites, however, are typically composed of finely parallel-laminated micritic and some microsparitic dolostones, with authigenic carbonate fibers, but no wave- or current-influenced depositional structures, likely indicative of quiet environments below fair-weather wave base. In the upper part of the studied successions, a few of thin microdigitate stromatolite interbeds, which were found abundantly in other intervals of the Wumishan Formation and commonly interpreted as having
formed in subtidal environments (Tang et al., 2013a), are occasionally recognized in dark laminites. In the lower part of the studied successions, thin oolitic grainstone lens are occasionally observed in association with dark laminites (Fig. 3E), which were most likely transported by storms from oolitic shoals. Although adjacent to shallow water deposits in vertical succession, dark laminate layers themselves have no any disturbance structures. Collectively, these suggest that the dark laminites were likely deposited in a restricted subtidal lagoon environment behind oolitic shoals, where wave and tidal influences were very weak or imperceptible due to the barrier protection (Fig. 4). This depositional model is consistent with other sedimentary facies adjacent to the laminites (Fig. 4; Tang et al., 2013c), and also gains support from the study of tabular thrombolites in this succession (Tang et al., 2013a, 2013c), which are interpreted to have primarily developed in the lower subtidal setting. Oolitic grainstone with cross bedding in the succession were deposited in the upper subtidal to lower intertidal settings, while micritic dolostone with mat shrinkages and halite
Fig. 3. Dark laminites and their associated depositional facies. (A) Outcrop of dark laminite layers (arrows) in PS-4 of Fig. 2B, showing sharp contrast with overlying and underlying strata; (B) laminated dolostone with thin chert bands and an intraclastic bed; (C) flat pebble conglomerate in shallow subtidal dolostone; (D) oolitic dolostone with herringbone cross-bedding; (E) thin oolite lens embedded within dark laminate beds.

Fig. 4. A facies model suggested for the dark laminites in restricted subtidal lagoon environment of an epicontinental platform. Modified from Tang et al. (2013c).
pseudomorphs are interpreted to have been formed in the upper intertidal to supratidal environments.

3. Materials and study methods

Samples were mainly collected from the Fangshan area, suburb of Beijing and Yesano area, Hebei Province, with some additional samples from Huailai, Hebei. Field observation and thin section examination of these samples show that dark laminites in these localities have similar textures and facies associations. A 72-m-thick succession that contains 8 separate dark laminitite layers at Yesano was carefully investigated in field (Fig. 2B) and sampled systematically. Altogether, 45 samples collected from the dark laminitite layers were studied with thin sections and polished slabs under microscope and SEM. Samples from the third dark laminitite layer (bottom upwards, Fig. 2B) are best preserved, without obvious metamorphism and recrystallization (Fig. 5A and B). Therefore, a 129.12-mm-thick and a 116.80-mm-thick polished slabs were further made from this layer for measurements of laminites' thickness and element concentration. The thickest single layer of dark laminites is 1.8 m in this succession (lower part of PS-5, Fig. 2B), in which ~3780 couplets were counted in field with aid of magnifier. As dark laminites layers contain stylolites at roughly 10 cm interval for each, to ensure the samples used for spectral analysis with consecutive laminites sequence, most samples collected from these layers, except the two for series analysis, are less than 10 cm-thick.

Macroscopic features of the laminites were observed in outcrops and on polished slabs. Microfabrics were examined on thin sections using a Zeiss Axio Scope A1 microscope. Thin sections used for the measurements of laminal thickness variations were prepared carefully with stratigraphic overlap to ensure a continuous record, and the thickness of laminae was measured from a series of high-resolution digital photomicrographs using CorelDraw X4. The ultrafabrics were analyzed using a Zeiss SUPPA 55 field emission scanning electron microscope (FESEM) and micro-zone elemental contents were analyzed by Oxford energy disperse spectrometer (EDS) at the China University of Geosciences (Beijing). The software PAST (version 2.17) was used for the time series analysis (Hammer et al., 2001).

In order to ascertain the properties of organic remains in the dark laminites, some purported organic relics observed in the thin sections were examined by a LabRAM HR800 Raman spectrometer. The Raman microscope operating confocally at laser wavelength of 532 nm with a spectral footprint of 1 μm using a 100× lens objective gave a spectral resolution better than 1.5 cm⁻¹. Each spectrum required about 1 min total scan time.

To determine carbon and oxygen isotope variations between dark and light laminae, sample powders were drilled from a polished slab using a micro-drill of 0.4 mm diameter. About 100 μg of sample powders were drilled from each of the 11 separated laminae. Carbon and Oxygen isotopes were determined using a Finnigan MAT 253 mass spectrometer equipped with a Kiel IV carbonate preparation device at the Chinese Academy of Sciences, and are reported in parts per thousand (‰) relative to VPDB (Vienna PeeDee Belemnite). Precision monitored by NBS19 is better than 0.10‰ for δ¹³C and 0.15‰ for δ¹⁸O. It should be noted that, however, as the diameter of the drill bit (0.4 mm) used for sampling is larger than the thickness of most laminae, the isotopic differences between light and dark laminae could be reduced due to partially mixed signatures.

A 116.80-mm-thick polished slab was selected for line scanning analysis to obtain the variations of X-ray intensities for elements Al, Si, Ca, Mn, Fe, Co, Cr, Ti and Br, using an Itrax micro-XRF core scanner at the China University of Geosciences (Beijing). The acceleration voltage was 60 kV; probe current was 50 mA; and scanning steps were 200 μm.

4. Characteristics of laminites

Macroscopically, the laminites appear as densely packed lamellar couples that consist of alternating dark and light laminae (Fig. 5A). Statistic analysis of the laminae indicates that there are about 19 couplets per centimeter on average; each of the couplets comprises a granular light lamina and a fibrous dark lamina (Fig. 5B).

In general, the dark laminae are thicker (mean ≈ 405 μm) than the light laminae (mean ≈ 123 μm). Dark laminae are characterized by vertically aligned fibers that contain abundant filaments (or bundles) showing orange-red autofluorescence under UV excitation, and their molds (Figs. 5B–E and 6). Whereas light laminae are primarily composed of micrite and microspar, with fewer filaments and filament molds (Fig. 7A–F). The boundaries between dark and light laminae are well defined, commonly sharper at the base of a dark lamina than at that of a light lamina (Fig. 5B). Mineralogically, the laminites are dominated by dolomite, with no detectable siliciclastic contents in both dark and light laminae.

Vertically aligned filament bundles and less abundant, variably aligned filaments are observed in dark laminae (Fig. 5C and D). In vertical section, filament bundles are preferentially concentrated along the centers of individual fibers and tend to form the axes of fibers (Figs. 5C and 6A). In cross section, these fibers commonly show as micropeloids, each of which comprises a core composed of sub-micron sized particles (Fig. 5E) and an enclosing micropar rim. Under FESEM, many of the filaments are seen to be preserved as molds (Fig. 6B). In the cases when filaments are preserved as body fossils, they were partially degraded to form organomineralized nanoglobules or their aggregates (Fig. 6C and D).

In light laminae, filaments are less well preserved, with lower abundance, shorter length, and more random orientation (Fig. 7A–F). Only in a few cases are vertically aligned filament bundles observed from the light laminae (Fig. 7C and D). In planar cross section, these filaments, as in dark laminae, also show as sub-micron sized particles concentrated at the centers of micropeloids (Fig. 7B), and are encased by organic-poor rims (Fig. 7B and C). FESEM observation confirms that, similar to those in dark laminae, the filamentary structures in the light laminae were preserved as molds (Fig. 7F).

Pyrite (pseudomorph) particles are common in light laminae, but rare in dark laminae. They are 5–30 μm in diameter and appear as quadrangular euhedral to subrounded anhedral crystals (Fig. 7G and H). EDX analysis reveals that they have high Fe, O contents and a minor amount of C, Ca, Si, Mg, Al, S (Fig. 7I), suggesting that most pyrites have been oxidized.

To better define the morphology of filaments in the laminites, four morphological parameters suggested by Hofmann et al. (2008) (including filament/ fiber widths, bending, tortuosity, and number of direction changes per unit length) were measured under the microscope. These morphometric data were summarized in Table S2, in comparison with those of known microbial filaments and natural abiogenic fibers. In general, filaments from the Wumihan laminites have apparently smaller variability in width, larger bending, more frequent directional changes, and larger variability of tortuosity. These features are similar to those of known microbial filaments, but distinct from abiogenic filaments described by Hofmann et al. (2008).

Some potential organic relics in dark (Fig. S1A) and light (Fig. S1B) laminae were analyzed using Raman spectrometry. Filaments examined in the dark lamina (Fig. S1A) show Raman bands at 173, 297, 724, 1097, 1348, 1585, ~2700 cm⁻¹ (Fig. S1C), and at 175, 297,
Fig. 5. Macro- and microscopic features of laminites from the Wumishan Formation. (A) Outcrop photo showing sub-millimeter laminar couplets in a laminitic layer; (B) photomicrograph showing clear vertical alternations of dark fibrous laminae (DL) and light granular laminae (LL) (cross-polarized light); (C) photomicrograph showing crystal fibers (between dash lines) in a dark lamina; vertically aligned filament bundles (yellow arrows) and a few horizontally aligned filaments (white arrows) visible in the fibers (plan-polarized light); (D) fluorescence photomicrograph of the same view as in (C), showing orange-red autofluorescence stimulated from purported bacterial relics (arrows); (E) cross section of crystal fibers in a dark lamina. Individual fibers appear as microspheres in transverse section, each of which has a microparticle-rich center (circles) and a microparticle-poor outer rim, and is walled by a very thin film on surface (arrows) (plan-polarized light photomicrograph). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

724, 1097, 1349, 1588, ∼2700 cm⁻¹ (Fig. S1D), respectively. Purported organic relics in the light lamina (Fig. S1B) show Raman bands at 173, 297, 725, 1097, 1351, 1590 and ∼2700 cm⁻¹ (Fig. S1E), while the adjacent micropor only shows Raman bands at 175, 297, 722 and 1097 cm⁻¹ (Fig. S1F). These data provided strong supports that the filament relics in laminae and the micron-sized particles in the centers of micropeloids are indeed of biotic origin.

The carbon and oxygen isotope ratios from dark and light laminae are shown in Fig. S2 and Table S3. Both carbon (δ¹³C) and oxygen (δ¹⁸O) isotope values of the dark laminae are higher than those from the light laminae (Fig. S2). The mean values of δ¹³C and δ¹⁸O in dark laminae are +0.67‰ (range: +0.56 to +0.78‰) and −4.35‰ (range: −4.56 to −3.97‰), respectively. Those in light laminae are +0.55‰ (range: +0.49 to +0.61‰) and −4.64‰ (range: −5.08 to −4.31‰), respectively.

Cycles of laminar couplets are identifiable under microscope (Fig. 8A–D). Each cycle includes 8–13 couplets and separated by a relatively thicker couplet (Fig. 8D). In each of the cycles, couplets at the lower and upper parts are comparatively thicker, and become thinner in the middle parts (Fig. 8A and D). Thickness variations
of dark laminae show a similar pattern with that of the couplets (Fig. 8B), but light laminae do not show persistent trend (Fig. 8C). This likely implies that the development of dark laminae has played a more important role than light laminae for the thickness variation of laminar couplets in each cycle.

5. Time-series analysis

The thickness of individual laminar couplets (Fig. 8A) varies from 169 to 1465 μm (mean ≈ 528 μm). Each of the 22 couplet cycles identified from thickness variations contains 8–13 couplets. Time-series analysis of thickness variations of 250 consecutive laminar couplets (Table S4) using software PAST (Hammer et al., 2001) produced first order peaks at 10.7 and 2.9 couplets (confidence level, CL >99%), and second order peaks at 21.455, 5.0 and 2.0 couplets (CL >95%; Fig. 8E and Table 1).

To investigate variations in the spectral profile over time, a wavelet transform analysis was computed using the software PAST. The result (Fig. 8F) shows that two peaks (10.7 and 21.4 couplets) appear as coherent modes throughout the dataset. Other spectral peaks have limited persistency and may not be used as coherent frequency.

X-ray fluorescence analysis (XRF) data of the laminites were shown in Table S5. These include elements Al, Si, Ca, Mn, Fe, Co, Cr, Ti and Br, but only certain environment sensitive elements (Ca, Fe and Cr), and those indicative of microbial activity (Co and Br) were selected for further spectral analyses. Power spectral analyses were performed for variations of Ca, Fe, Br contents, and Co/Ti, Cr/Ti ratios on a 116.80-mm-thick polished slab with 200-μm data resolution (Fig. 9). In order to eliminate the potential influence from terrigenous siliciclastics, Co/Ti and Cr/Ti ratios rather than Co and Cr concentrations were used for the power spectral analyses. Major peaks in Ca, Fe, Br contents and Co/Ti, Cr/Ti ratios are shown in Table 1, and their spectral patterns are shown in Fig. 10. As listed in Table 1, the common peaks occur at 9.0–11.7, 6.4–7.2 and 3.5–5.1 couplets, and several other peaks also occur at 89, 53, 29.5, 19.7, 13.8 and 2.3 couplets. It is important to note that the periodicities revealed from element contents or their ratios were originally expressed as stratigraphic thickness, and then converted...
to counts of laminar couplet, through dividing periods (expressed as stratigraphic thickness) by the average thickness of laminar couplets (0.528 mm, n = 250). It is true that the calculated periodicity of couplets from cyclicity of stratigraphic thickness may cause some errors. However, the scanning step (0.2 mm) is much smaller than the average thickness of laminar couplets (0.528 mm), any potential solar-induced cycles recorded by element concentrations in the laminites should be properly revealed. In addition, similar methods have been proved feasible and successfully applied to spectral analyses (e.g., Han et al., 2003).

In order to assess the potential correlation among XRF data of the Wumishan laminites, correlation coefficients were calculated and shown in Table S6. As shown in this table, there exist an obvious negative correlation between Ca and Si ($r^2 = 0.92$), a weak negative correlation between Ca and Cr/Ti ($r^2 = 0.52$), and a weak positive correlation between Cr/Ti and Si ($r^2 = 0.64$). Other correlations are much lower ($r^2 < 0.25$) and can be neglected.

Wavelet transform analyses were computed for the geochemical series using the software PAST (Fig. 10F–J; Hammer et al., 2001). The results reveal that the periodicity at 9.0–11.7 couplets exhibits coherent modes consistently almost throughout the dataset (Fig. 10F–J), and the periodicity at 19.7 couplets appears as coherent modes throughout Ca series. Other spectral peaks also exist in the profile, but none of them show persistent patterns and likely resulted from noises.

6. Discussions

6.1. Biogenic origin of the laminites

Morphological information is very important in interpretation of biogenic features (Guidry and Chafetz, 2003), and fossilized microbes can be readily distinguished from abiogenic features by their distinctive fabrics (Hofmann et al., 2008). Filaments in the
Fig. 8. Thickness variations of laminar couplets, and light and dark laminae. (A–C) thickness distribution of 250 laminar couplets, and their constituent dark and light laminae in a measured laminite slab; a total of 22 integral cycles of couplet/lamina thickness are observed, with each cycle comprising ∼11 couplets; (D) thin section photomicrograph showing thickness variations of laminar couplets in three successive cycles (cycles 1–3 in (A)), with arrows indicating the boundary of each couplet; (E) power spectral analysis of 250 couplet thickness; (F) wavelet scalogram of the couplet thickness showing spectral power over time; two spectral peaks stand out over the time span of the measured column, with clear periodicities of 11.7 and 21.4 couplets, respectively.

Wumishan laminites (Fig. 5C and D), similar to those identified in modern calcified microbial mats (e.g., Pacton et al., 2010) or tufas (e.g., Perri et al., 2012), have apparently smaller variability in width, larger bending, more frequent directional changes, and larger variability of tortuosity than those of abiogenic fibers (Table S2, Hofmann et al., 2008). Thus, these filaments should be recognized as biogenic origin in terms of morphology.

In addition, relatively well preserved filaments in the laminites show clear orange-red autofluorescence under UV excitation (Fig. 5D), which is generally thought to be caused by kerogen remains and has been widely used as an important criteria in identification of biogenic components in carbonates (e.g., Bezouska et al., 1998; Neuweiler et al., 2003; Tang et al., 2013a).

Besides, Raman spectroscopy study reveals that the filaments show both a first-order disordered (D) Raman band at ∼1350 cm⁻¹ and a graphitic (G) band at ∼1590 cm⁻¹, and a second order, lower and broader band around ∼2700 cm⁻¹ (Fig. S1C and D). These are commonly taken as the characteristics typical of biogenic kerogen (Kudryavtsev et al., 2001; Schopf et al., 2002, 2007; Villar and Edwards, 2006). In contrast, the microspar in the laminite (Fig.
S1B) does not show any signature of kerogen (Fig. S1F), probably indicative of inorganic origin. All the analyzed spots show vibration bands at $\sim 177$, $\sim 300$, $\sim 725$ and $\sim 1098$ cm$^{-1}$, which are generally regarded as corroborative bands of dolomite (Kudryavtsev et al., 2001; Villar and Edwards, 2006), suggesting that the laminites have been extensively dolomitized.

Based on their morphological, fluorescent and Raman spectral characteristics, we think that most of the laminites, if not all, in the laminites are of biogenic origin and may represent the relics of bacterial filaments.

It is worth noting that the diameter of filaments in the laminites is about 0.6 μm in average ($n = 100$), which is obviously smaller than those identified in modern calcified microbial mats (e.g., Pacton et al., 2010) or tufas (e.g., Perri et al., 2012), but quite close to those in the coeval stromatolites and thrombolites (Tang et al., 2013a, 2013b). This can be ascribed to the destruction and degradation of organic components during long-lasting complex diagenesis and metamorphism (Altermann, 2008; de Wet and Davis, 2010), and more importantly the absence of calcified sheaths in Neoproterozoic microbes, which is thought to be caused by a high atmosphere-ocean CO$_2$ concentration of that time (Arp et al., 2001a; Kah and Riding, 2007; Riding, 2006), and therefore unfavorable for the preservation of microbial remains (Bartley et al., 2000). Thus, we believe that fast calcification is critical for the preservation of microbial fabrics in the ancient laminites.

Microscopic observation reveals that filaments account for a substantial volume in the Wumishan laminites (Fig. 5C and D), implying that they have played a substantial role in the formation of the laminites. Furthermore, as the major components of laminites, fibers commonly have filaments (or bundles) concentrated in their center, forming the axes (Fig. 5E). These likely indicate that fibers were formed through mineralization of filaments or carbonate encrustation around the filaments, during which filaments served as preferential templates or sites for carbonate nucleation and precipitation. Micropeloids are abundant in light laminae, and commonly composed of relatively organic-rich nuclei and organic-poor encasing rims. Similar features have been well documented from both contemporary stromatolites (e.g., Tang et al., 2013b) and modern calcified microbial mats (e.g., Spadafora et al., 2010), and are interpreted as resulting from the mineralization of degraded organic remains. Thus, microbes must have played constructive roles in the formation of laminae, and the Wumishan dark laminites should be recognized as biolaminites, a kind of microbialites.

6.2. Origin of laminar alternation

The duration of each laminar couplet is critical for interpreting the periodicities recorded in laminites. For instance, it was once argued that Neoproterozoic varve-like laminates had recorded the signal of sunspot cycles (Williams and Sonett, 1985), but
later reevaluation indicated that those laminates actually recorded tidal cycles (Williams, 1990). In the studied sections, the thickest laminite layer is 1.8 m (Fig. 2B) and contains about 3780 laminar couplets. Such couplets could potentially record tidal, diurnal or annual cycles (e.g., Kano et al., 2003; Okumura et al., 2011; Williams, 1990).

Directly determining the duration of Mesoproterozoic laminar couplets is extremely difficult, and we can only provide a first order estimation based on the available zircon U–Pb ages of the Wumishan Formation. The duration of the Wumishan Formation is about 50 Ma (Gao et al., 2009) and its thickness is about 3000 m. It gives an average depositional rate of ~60 µm/yr. Given the potential variations in depositional rate and possible unconformities/hiatus existing during its deposition, this depositional rate is in first-order agreement with the average thickness of laminar couplets (~528 µm). In contrast, if the couplets were of tidal or diurnal origin, it requires that during deposition of the biolaminites, the depositional rate (~180 mm/yr) was three orders higher than the average rate of the Wumishan Formation, which seems unlikely.

Thus, an annual origin for the laminar couplets seems more reasonable.

Tidal influence is widespread in coastal marine environments, particularly in the areas where high tides predominate (Davis, 2012). Due to the active swashing of tidal currents and waves, however, only in a few specific environments can tidal rhythmites be deposited and preserved as rock records (Kvale et al., 1995; Mazumder and Arima, 2005), such as in upper intertidal flat, estuary and delta, as well as the channels and inlets included there (Davis, 2012).

Tidal rhythmites have been documented from both modern sediments (e.g., Kvale et al., 1995) and ancient rocks (e.g., Eriksson and Simpson, 2000), but much more common in siliciclastics (Mazumder and Arima, 2005; Davis, 2012). As sediment in tidal rhythmites was mainly laid down with rapid depositional rate by flood- and ebb-tides twice a day, substantial fine-grained terrigenous influx and high concentrations of suspended sediment produced by offshore wave dynamics are among the basic requirements (Williams, 1998; Mazumder and Arima, 2005). Structurally

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Fig. 10. Power spectral patterns and wavelet scalograms for Ca, Fe, Co/Ti, Cr/Ti and Br series in the Wumishan laminite slab from 0.05 mm to 116.85 mm (scanning step = 200 µm). (A–E) Power spectral patterns. The periods (wavelength) are expressed in numbers of laminar couplets, which are calculated through dividing periods (expressed as stratigraphic thickness in mm) by 0.528 mm (average thickness of the studied laminar couplets); (F–J) wavelet scalograms showing variation in spectral composition over time. Clear cyclicity of ~11 couplets appear in all Ca, Fe, Co/Ti, Cr/Ti and Br series and cyclicity of ~22 couplets appear as coherent modes consistently throughout the Ca series.
tide-tilted laminae commonly show both vertically accreted flat laminae to thinly bedded medium- to fine-grained sandstone, silstone and rhyolite (e.g., Williams, 1998) or as laterally accreted bundles of sandstone foresets separated by mudstone drapes (e.g., Eriksson and Simpson, 2000), in which successive laminae or beds exhibit progressive thickening and thinning (Kválek et al., 1995). In carbonate systems, tidalite is commonly known from upper intertidal flat and channels cut into the flat, commonly associated with wave- or tide-influenced sedimentary structures (such as flaser bedding) and exposure makers (e.g., mud cracks and bird-eyes) (Lasemi et al., 2012).

In our case, the Wumishan biolaminites are devoid of silicilastic contents, consisting almost completely of authigenic carbonate minerals, except for numerous microbial remains (Figs. 6 and 7). In these biolaminite layers, neither current- and wave-influenced sedimentary structures (such as flaser to lenticular bedding, wave ripples and climbing ripples) nor evidence of subaerial exposures (such as mud-cracks, bird-eyes, and raindrop impressions) have been identified. In addition, the lithology and thickness of the layers are very stable and can be traced over more than 10 km without observable variations (Fig. 1). These characteristics, along with the analyses of facies associations and facies sequences in the studied successions, suggest that the dark biolaminates were not likely deposited in unstable tide-dominated environments, such as tidal channels; instead they were most likely formed in quiet back-barrier subtidal lagoon environment (Fig. 4). Due to the protection of barrier in the environment, current- and wave-influences were greatly reduced, and terrigenous influx was negligible, thus not suitable for the development of tidal laminites.

Texturally, the biolaminites consist of alternating light and dark laminae, with clear laminar couplets (Fig. 5A and B). The light laminae are dominated by micrite with subordinate microparticle (Fig. 7A–F) and pyrite (Fig. 7C–I). These features were possibly derived from in situ carbonate precipitation induced by organic matter (e.g., filamentous microbes) degradation through sulfate reduction. Dark laminae are dominated by fibers devoid of pyrites (Fig. 5B–E), which could be formed through fast mineralization of vertically aligned microbial filaments or their bundles during active photosynthesis. These features are similar to those seen in Holocene tufas (e.g., Kano et al., 2003; Merz-Preiß and Riding, 1999) and in Mesoproterozoic microdigitate stromatolites (Tang et al., 2013b).

Some scholars suggest that the precipitation of laminated tufa is primarily induced by the increase of carbonate saturation in ambient water, largely controlled by temperature-dependent physicochemical processes (Kano et al., 2003; Kawai et al., 2009; Merz-Preiß and Riding, 1999), even though microbial mats or biofilms may have provided preferential sites for carbonate nucleation (Grądziński, 2010; Merz-Preiß and Riding, 1999). Others insist that the driving mechanism for carbonate precipitation in stromatolitic tufa is biofilm photosynthesis (Arp et al., 2010; Shiraishi et al., 2008). No matter what roles microbes may have played in tufa formation, it is widely accepted that alternations of dark and light laminae in modern and recent laminated tufas have recorded seasonal variations (Andrews and Brasier, 2005; Arp et al., 2010; Grądziński, 2010; Kano et al., 2003; Kawai et al., 2009). Some of them have been confirmed by δ18O variations between laminae (Kano et al., 2003; Shiraishi et al., 2008) and preferential existence of plant pollens (Freytet and Plet, 1996; Janssen et al., 1999) or larvae tubes (Brasier et al., 2010; Janssen et al., 1999) in the summer (commonly dark) laminae. Laminitar alternations in Holocene tufas can result from changes in microbial groups (Freytet and Plet, 1996; Freydet and Verrecchia, 1998; Janssen et al., 1999), their growth patterns (Arp et al., 2001b; Janssen et al., 1999) and/or calcification patterns (Kano et al., 2003) in response to seasonal changes in temperature, light intensity, carbonate saturation and precipitation rate (Andrews and Brasier, 2005; Kawai et al., 2009).

In the Wumishan biolaminites, putative microbial filaments are present in both light and dark laminae, but much more abundant and better preserved in dark laminae. Most of the filaments in light laminae appear as randomly dispersed relics, but some of them are seen to retain their vertically aligned orientation (Fig. 7C and D), similar to those in the dark laminae. This likely implies that filament orientation or microbial groups may not be the major cause for alternating dark and light laminae in the laminites. Thus, we interpret that laminar couplets of the Wumishan biolaminites were formed by seasonal temperature changes that may have controlled microbial growth rate, biomass production and carbonate precipitation. The light laminae may have formed in late autumn to early spring seasons when lower temperature led to slower microbial growth and higher water-column oxygen concentration. Mineralization of microbial mats may have occurred mainly in sediment due to the lack of carbonate encrustation in their shales and low carbonate saturation in ambient seawater (Merz-Preiß and Riding, 1999). Degradation of microbial mats through sulfate reduction would produce HCO3− and release bivalent cations (e.g., Ca2+, Mg2+) previously absorbed by EPS (Dupraz et al., 2004, 2009), providing preferential sites for carbonate nucleation (Spadafora et al., 2010). The presence of pyrites in light laminae is consistent with sulfate reduction during organomineralization (Dupraz et al., 2009). The dark laminae were likely formed in late spring to early autumn seasons, during which increasing temperature would facilitate microbial growth and rapid EPS secretion, forming densely packed bacterial filaments (Fig. 5C–E). Active photosynthesis would lead to quick consumption of CO2 in microenvironments, resulting in high pH and alkalinity, and consequently fast carbonate precipitation (Arp et al., 2010; Dupraz et al., 2009). In such environments, bacterial filaments could be rapidly calcified even when they were still alive or immediately after their death (Freytet and Plet, 1996; Janssen et al., 1999), promoting microbial filament preservation in their primary growth orientation.

The seasonal origin of laminar couplets is consistent with the supposed climate for the Mesoproterozoic North China platform and the depositional environment of the Wumishan biolaminites. Recent paleomagnetic data (Zhang et al., 2012) suggested that the North China platform was located between 10° N and 25° N during the Mesoproterozoic and was likely predominated by an arid to semi-arid climate, under which seasonal changes would be able to generate palpable influences on microbial activities and sedimentation (Janssen et al., 1999; Andrews et al., 2010). Facies analysis suggests that the biolaminites were likely deposited in a restricted subtidal lagoon environment on a broad epicontinental platform (Fig. 4). In these circumstances, summer–autumn seasons would have strong evaporation and elevated carbonate saturation, promoting calcification of bacterial filaments, as seen in the dark laminae (Fig. 5C and D). Active photosynthesis and high biomass production could result in relatively higher δ13C values in dark laminae (Fig. 52). High evaporation in a restricted lagoon could also lead to higher δ18O values (e.g., Kah, 2000), although high temperature in summer–autumn seasons would partially counteract the increase of δ18O (Hays and Grossman, 1991). This is consistent with generally higher δ13C and δ18O values in dark laminae (summer–autumn seasons) than in light laminae (winter–spring seasons).

### 6.3. Periodicities recorded in biolaminites

Power spectrum and wavelet transform analyses of laminar couplet thicknesses and geochemical series reveal coherent modes at 9.0–11.7 and 19.7–21.4 couplets. Although high-frequency (2.0–2.9 couplets, possible period of Quasi-Biennial Oscillation (QBO, Baldwin et al., 2001); and 3.5–7.2, possible period of El Niño
Southern Oscillation (ENSO; Trenberth, 1997) and low-frequency (89, 53, 29.5 and 13.8 couplets) periods also exist, none of these is as stable and persistent as the two periods. If our annual interpretation for laminar couplets is correct, the periods of 9.0–11.7 and 19.7–21.4 couplets (Table 1) are most likely to have recorded ~11 yr and ~22 yr climate cycles. These periods match well with the 11–yr Schwabe sunspot cycles (range of 8–17 yr) and 22-yr solar Hale cycles, respectively (Weedon, 2003). The periodic signals of thickness variations within ranges of 10–14 yr and of 20–26 yr have been reported from glacial or non-glacial marine and lacustrine varves of Holocene to Mesoproterozoic ages (Table S1), and were commonly interpreted as recording Schwabe sunspot cycles and solar Hale cycles, respectively. The similarity of periodicities between the Wumishan biolaminates and those reported from younger sedimentary varves (Table S1) suggests the stability of solar processes since 1.45 Ga.

6.4. Possible mechanisms of biolaminate cyclicities in response to solar activity

The Sun is the ultimate driver of the Earth’s climate system (e.g., Beer et al., 2000), and the variability of sunspot-related solar output forces climate changes in various ways (Reid, 2000). It is commonly thought that during the periods of less sunspot activity, a relatively cold climate would be resulted in the Earth system. For instance, it has been argued that the coldest period of the “Little Ice Age” in the late 17th century was closely correlated to the Maunder sunspot minimum, during which almost no sunspot activity was detected for a period of about 45 yr (Haigh, 2003; Reid, 2000).

However, the mechanism, by which sunspot-related solar activity forces climate, has been controversial (e.g., Andrews et al., 2010; Gray et al., 2010; Reid, 2000). Three possible forcing mechanisms have been proposed (Reid, 2000; Gray et al., 2010). Mechanism-I invokes sunspot-related variance in solar irradiance. However, sunspot-related irradiance variation is only ~0.1% of the total irradiance (Beer et al., 2000; Haigh, 2003), and can only cause less than 0.1 °C change in surface temperature of the Earth (Fröhlich and Lean, 1998; Gray et al., 2010) due to the thermal inertia of oceans (Carslaw et al., 2002; Gray et al., 2010; Reid, 2000). Mechanism-II emphasizes the importance of solar ultraviolet radiation (Haigh, 1996; Ineson et al., 2011). Ultraviolet wavelengths influence the production and loss of ozone in the stratosphere and they may be considerably larger than previously thought (Harder et al., 2009), but how changes in stratospheric chemistry and dynamics affect the Earth’s surface climate is still unclear (Gray et al., 2010; Reid, 2000). Mechanism-III invokes galactic cosmic rays (GCR) as the driver of climate changes (Carslaw et al., 2002; Kirby and Laaksonen, 2000; Ney, 1959). The GCR and related ion influx have been linked to the formation of cloud condensation nuclei (Kirby and Laaksonen, 2000). More GCR cause more low-altitude clouds and lower temperature. Sunspot activity controls the generation of solar wind, which deflects the influx of GCR (Carslaw et al., 2002; Reid, 2000). Therefore, during periods of low sunspot activity, the reduction in solar wind permits higher GCR incident on the Earth’s atmosphere, leading to increased cloud generation and cooler–wetter climate periods (Andrews et al., 2010). The observed variation of low-altitude clouds by about 1.7% corresponds to a change in Earth’s radiation budget of about 1 Wm⁻² between solar maximum and minimum (Carslaw et al., 2002). This change is significant when compared, for example, with the estimated radiative forcing of 1.4 Wm⁻² from anthropogenic CO₂ emissions (Carslaw et al., 2002). Thus, the third mechanism seems to be more plausible in terms of the energy budget and may help to explain why a relatively small change in solar output can have significant impact on Earth’s climate.

Study of ancient sediments with identifiable sunspot cycles shows that laminar couplets deposited during periods of lower sunspot activity have thicker and coarser siliclastic laminae (Andrews et al., 2010; Milana and Lopez, 1998), suggesting high surface runoff and low carbonate saturation during these periods. Microbes are sensitive to environmental changes, especially to illumination (Diehl, 2002; Diehl et al., 2002; Grima et al., 1999) and temperature (Roberts and Zohary, 1987). In an optimal system without other limiting factors, the light availability determines the rate of photosynthesis and productivity, but excessive light could be harmful and create photoinhibitory response (Alba, 1982; Bannister, 1979). Considering that solar luminosity was probably 90–94% of present level during Mesoproterozoic (Gough, 1981; Kasting and Howard, 2006), light intensity may not have exceeded the saturation level for cyanobacteria photosynthesis and increase of light intensity might be preferred for microbial growth. Thus, during periods of lower sunspot activity (weaker illumination), slower microbial growth might result in thinner laminar couplets, while during periods of higher sunspot activity (stronger illumination), faster microbial growth would produce thicker laminar couplets. Illumination-controlled productivity change has been detected by photosynthetic pigments (primary productivity indicator) in annually laminated sediments over the last four centuries (Romero-Viana et al., 2010), in which thinner laminae commonly have lower concentration of photosynthetic pigments, suggesting lower productivity. Sunspot activity might also influence atmospheric precipitation (Andrews et al., 2010; Fröhlich and Lean, 1998; Kirby and Laaksonen, 2000) and change the carbonate saturation in the restricted lagoon environment. During solar minimum, more GCR influx would cause higher precipitation and consequently, lower carbonate saturation in the depositional environment. Lower carbonate saturation might slow down calcification of microbial mats and deposit thinner laminar couplets.

Sunspot modulated temperature fluctuations would exert similar influences on laminar thickness by affecting the activity of microbes as the illumination does. But considering that temperature fluctuations caused by variation of sunspot-related solar irradiance is less than 0.1 °C (Fröhlich and Lean, 1998; Gray et al., 2010), and that the difference between optimal and severe temperatures for cyanobacterial photosynthesis is about 10 °C (Roberts and Zohary, 1987), temperature changes of low amplitude alone during a sunspot cycle may be less efficient in affecting primary production.

The interpretation of solar-induced biomass production and precipitation change is consistent with the periodicity shown in elemental concentrations of the Wumishan biolaminates (Fig. 10). As the sample used for XRF analyses has not suffered from obvious metamorphosis and no evidence of hydrothermal activity has been found in the studied succession, Si precipitation in the biolaminates is likely caused by early-diagenesis processes. Although the Si may not be primary (depositional), early diagenetic silification probably selectively tracks concentrations of original organic matter (e.g., Shi et al., 2008), and the clear negative correlation (r² = 0.92) between Si and Ca is possibly caused by the selective silification. Therefore, Ca and Si content series obtained from the samples are still able to record solar cycles. It is likely that during the period of high sunspot activity, stronger illumination and higher temperature would increase the biomass production, leading to more organic matter deposition and more intense silification.

The negligible Fe–Ca correlation (r² = 0.18) could be caused by multi-source of Fe, such as diagenetic authigenic pyrite and tiny allochthonous siliciclastics. During solar maximum, higher microbial productivity would provide more organic matters for precipitation of pyrite during early diagenesis through bacterial sulfate reduction, but meanwhile reduced atmospheric precipitation would lead to less surface runoff and thus less siliciclastics.
input. Considering that pyrites are observable and probably the
dominated form of Fe in the biolaminites (Fig. 7G and H), while
silicilastic related elements (e.g., Al) are nearly undetectable and
silicilastics should be secondary form of Fe (Table S5), it is more
likely that sunspot activity has influenced the Fe concentration
(authigenic pyrite) in the biolaminites mainly through modulating
microbial productivity.

The periodic variations of Cr/Ti, Co/Ti, and Br contents may have
recorded the changes of redox conditions in seawater and biomass
production. During the Mesoproterozoic, anoxic environment was
pervasive in the oceans (Canfield, 1998; Reinhard et al., 2013), with
a shallow chemocline (redox interface) probably around the fair-
weather water base (Brooks et al., 2005; Tang et al., 2011). Within
the oxygen minimum zone around the chemocline, active bacterial
sulfate reduction would result in a sharp redox gradient (Poulton
et al., 2010; Planavsky et al., 2011), and therefore fluctuations of
redox sensitive element concentrations during solar cycles, which
could be sufficient large for detection. Inoxic environments, Cr
mainly exists as mobile Cr(III) anion ([HCrO₄⁻]), which is thermo-
dynamically stable (Frei et al., 2009). In anoxic environment, Cr(VI)
would be reduced to Cr(III) by aqueous Fe(II) or Fe(II)-bearing min-
erals (Ellis et al., 2002; Konhauser et al., 2011) and Cr(III) would be
subsequently incorporated (scavenged) into Fe(III)–Cr(III) oxy-
hydroxides (Fendorf, 1995; Konhauser et al., 2011). Although Cr(III)
could be rapidly reoxidized into Cr(VI) in a catalytic reaction with
MnO₂, the correlation between Cr and Mn is negligible (r² = 0.04) in
the Wumishan laminites. Thus, Cr variations in the laminites may
be related to the bottom-water redox conditions. During high solar
activity (solar maximum), stronger solar illumination led to fast
microbial growth, bottom-water anoxia, and high Cr/Ti ratio.

The similar mechanism may also apply to variations of Co/Ti ratio.
Co is thought to be one of the important bio-essential ele-
ments for cyanobacteria metabolism (e.g., Price and Morel, 1991;
Saito et al., 2002) and commonly enriched in cyanobacteria cells
and associated EPS (e.g., Huerta-Diaz et al., 2011, 2012). During
periods of high productivity, high Co/Ti ratios would be expected
in the carbonate records.

Bromine enrichment in particulate sediments is thought to be
entirely related to organic matter (Harvey, 1980). Its exclusive asso-
ociation with marine organic matter makes it a valuable proxy to
estimate primary production in marine environments (Malcolm
and Price, 1984; Mayer et al., 1981, 2007; Upstill-Goddard and
Elderfield, 1988; Ziegler et al., 2008), though the specific mecha-
nism is still not properly known. The 10.6 yr periodicity identified in
the bromine content series (Fig. 10E) possibly records fluctuations
in biomass production.

Alternatively, sunspot activity might have modulated the con-
centration of trace elements in the biolaminites by influencing
carbonate deposition rate, which might merely dilute or con-
centrate allochthonous contributions, or result in differences in
porosity permitting slightly different mobility of trace elements
during diagenesis. In addition, through modulating illumination
and temperature, sunspot activity could also influence biomass
production and therefore the trace element concentrations, as
the growth or decomposition of microbes (organic matter) might
concentrate trace elements directly (Tribovillard et al., 2006). How-
ever, obvious correlations only exist between Ca and Si (r² = 0.92),
while the correlations between other elements are weak or neg-
ligible (Table S6). Thus, the partition coefficients of precipitation
rate-dependence or other common fact-dependence are too incon-
spicuous to be taken as primary causes for the cyclicity of element
concentrations.

Collectively, sunspot activity could influence the element con-
centrations in the Wumishan biolaminites, through changing the
biomass production (by modulating illumination and tempera-
ture) and/or carbonate precipitation rate (by changing atmospheric
precipitation and microbial activity), during stages of primary
deposition and early diagenesis.

7. Conclusion

Dolomitic biolaminites deposited in restricted subtidal lagoon
environments are well preserved in the Mesoproterozoic Wumis-
shan Formation (ca. 1.50–1.45 Ga) in North China. They are
characterized by densely packed sub-millimeter couples com-
posed of alternating fibrous dark and micritic light laminae,
texturally similar to Holocene tufas. Laminar alternations are inter-
preted as recording annual seasonal changes, consistent with
carbon and oxygen isotope variations between dark and light
laminae. Dark laminae contain abundant microbial filaments and
vertically aligned fibers that were likely mineralized when fil-
amentous bacteria were still alive or shortly after death during
summer-autumn seasons. Light laminae are mainly composed of
micrite, with subordinate dolospars and pyrites; they were likely
formed by post-mortem microbial mat degradation during winter-
spring seasons.

Time series analyses of laminar couplet thickness, Ca, Fe, Br con-
tent series, and Co/Ti, Cr/Ti ratio series of biolaminites revealed a
prominent peak at 9.0–11.7 yr and a less prominent peak at
19.7–21.4 yr. Wavelet transform analyses of the same data series
also exhibited coherent modes at 9.0–11.7 yr and 19.7–21.4 yr.
These two major periodicities are interpreted as recording the 11-
yr Schwabe sunspot cycles and 22-yr solar Hale cycles, respectiv-
ely. Sunspot cycles may have influenced the laminar couplets by reg-
ulating microbial growth rate and biomass production through
illumination, precipitation, and temperature. Changes in micro-
bial growth rate and biomass production could have created redox
fluctuations in restricted lagoon environment, leading to direct or
indirect cyclic variations in element concentrations of Ca, Fe, Br
and ratios of Co/Ti and Cr/Ti during the stage of primary deposi-
tion or early diagenesis. The preservation of solar cyclicity in early
Mesoproterozoic carbonate biolaminites reflects the sensitivity of
microbial life to subtle solar-induced climate changes. Similarity of
solar periodicities between early Mesoproterozoic biolaminites
and younger examples implies the stability of sunspot cycles since
cia. 1.45 Ga.

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Appendix A. Supplementary data

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