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Hirnantian Isotope Carbon Excursion in Gorny Altai, southwestern Siberia

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Abstract. The Hirnantian Isotope Carbon Excursion (HICE), a glaciation-induced positive $\delta^{13}C$ shift in the end-Ordovician successions, has been widely used in chemostratigraphic correlation of the Ordovician–Silurian boundary beds in many areas of the world. However, large regions with Ordovician sediments in Siberia are almost unstudied for stable isotope chemostratigraphy. The Burovlyanka section in the Altai area is one of the rare Hirnantian–Rhuddanian sections with both carbonates and graptolitiferous shales occurring in the succession. Here we report the discovery of the HICE in the uppermost beds of the Tekhten′ Formation, the *Dalmanitina* Beds in the Burovlyanka section. The *Dalmanitina* limestone Member between the graptolitiferous shales may correspond to the mid-Hirnantian glacial episode, which led to a global sea level drop and major extinction of marine fauna.

Key words: Russia, Gorny Altai, carbon isotope stratigraphy, Ordovician, Hirnantian, HICE.

INTRODUCTION

The stratigraphy of the Upper Ordovician Hirnantian interval has been intensively studied in different parts of the world. This is due to the increasing success in deciphering the palaeoenvironmental signal indicative of cooling and glaciation from this stratigraphic interval and accumulating new data on related biotic changes. The environmental and oceanographic changes related to the Hirnantian glacial event are expressed in the marine sediments as changes in stable carbon isotope composition. Both the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values of sediments show a positive excursion (the Hirnantian Isotope Carbon Excursion, HICE), starting in the earliest Hirnantian, rising to a peak of up to 7‰ and falling back to original values in the mid- or late Hirnantian (e.g., Underwood et al. 1997; Kump et al. 1999; Brenchley 2004; LaPorte et al. 2009).

The HICE has been widely used in chemostratigraphic correlation of the global Hirnantian Stage in different continents and basins (see Bergström et al. 2014). Still, there is a large geographical ‘hole’ comprising the Siberian area. The only Hirnantian carbon isotope curve reported from this huge area comes from the Mirny Creek section, representing the Kolyma Region in NE Siberia (Kaljo & Martma 2011; Kaljo et al. 2012). The uppermost Ordovician sediments on the Siberian Craton are widely eroded away, or may have never been deposited and the Hirnantian sections are found only in a few remote areas (Kanygin et al. 2010). The Late Ordovician lithofacies and fauna of the Altai-Sayan Folded Area, SW Siberia, are described in several publications (see Sennikov et al. 2008, 2014). One of the most important latest Ordovician sections with a diagnostic graptolite and trilobite fauna is the Burovlyanka section (Sennikov et al. 2014). Here we present the carbon and oxygen isotope data from the Burovlyanka section, which is the first study of the Hirnantian stable isotope stratigraphy in the Altai area and in entire central and western Siberia.

GEOLOGICAL SETTING

The Gorny Altai highland lies in the western Altai-Sayan Folded Area (ASFA), a collage of terrains within the Central Asian orogenic belt. The Altai-Sayan Area comprises several large geologic structures composed of Palaeozoic formations of different origin. Gorny Altai is one of these structures in between the Rudny Altai and Salair. The present tectonic framework of the ASFA has resulted from successive accretion of terranes at different times to the Siberian Craton (Dobretsov 2003; Sennikov et al. 2008). Ordovician–Silurian strata in Gorny Altai are represented mainly by shelf successions, with some deposits of oceanic setting known from the Lower Ordovician. The Ordovician and Silurian sedimentary successions of Gorny Altai consist mainly of the rhythmic alteration of siliciclastic and carbonate rocks with rare volcanic intercalations (Sennikov et al. 2008, 2011, 2014).

The late Katian–early Hirnantian sediments in the western and central parts of the Gorny Altai basin belong to the Tekhten′ Formation. This is a complex unit, 150–700 m thick, of predominantly carbonate composition where reef facies, siliciclastic–carbonate interreef facies and siliciclastic back-reef basin facies are represented in different parts of the basin (Sennikov et al. 2008, 2011). The reef facies with massive algal bioherms might have formed in an up to 700 km long and 3–5 km wide distinctive facies belt on the shelf edge (Sennikov et al. 2008). In some sections of western Gorny Altai a distinctive thin unit of *Dalmanitina* limestone is described in the topmost part of the Tekhten′ Formation. A transgression in the late Hirnantian terminated the carbonate deposition and black shales or argillaceous mudstones–siltstones of the Vtorye Utyosy Formation cover the carbonates. This formation is 40–200 m thick and is considered to be latest Hirnantian to Aeronian in age (Sennikov et al. 2008). Recently Sennikov et al. (2014) introduced an updated regional stratigraphic scheme of the ASFA with subdivision of the succession into horizons (regional stages). According to this chart, the Tekhten′ Formation is correlated with the Tekhten′ Horizon, except for its topmost member of the *Dalmanitina* limestone. The latter is attributed to the Listvyanka Horizon, together with the lowermost part of the Vtorye Utyosy Formation containing the Ordovician fauna. The main part of the Vtorye Utyosy Formation with the Silurian fauna comprises the Vtorye Utyosy Horizon (Sennikov et al. 2014).

MATERIAL AND METHODS

The Burovlyanka section, an outcrop of the Upper Ordovician and lower Silurian strata on the left bank of the Inya River (51°20′30″N, 83°01′30″E), was studied (Fig. 1). The rocks cropping out on the Inya River represent the Charysh–Inya structural-facies zone with the carbonate-siliciclastic Tekhten′ Formation and the fine-grained siliciclastic Vtorye Utyosy Formation (Sennikov et al. 2008, 2014). The whole section is tectonized and fragmented, with outcropping blocks of sedimentary rocks dipping at a high angle in various directions (Sennikov et al. 2008). Two parts of the nearly continuous interval of the Tekhten′ Formation in section S-833 (Sennikov et al. 2008) were sampled. The lower sampled interval represents the uppermost 8 m of the massive crystalline limestone, Member 1 (Sennikov et al. 2014) and the upper interval represents the uppermost carbonate unit in the formation, the 2.9 m thick *Dalmanitina* limestone bed (Member 5, Sennikov et al. 2014; Fig. 2). These intervals are separated by silty and shaly siliciclastic-dominated beds with a thickness of 50–200 m.

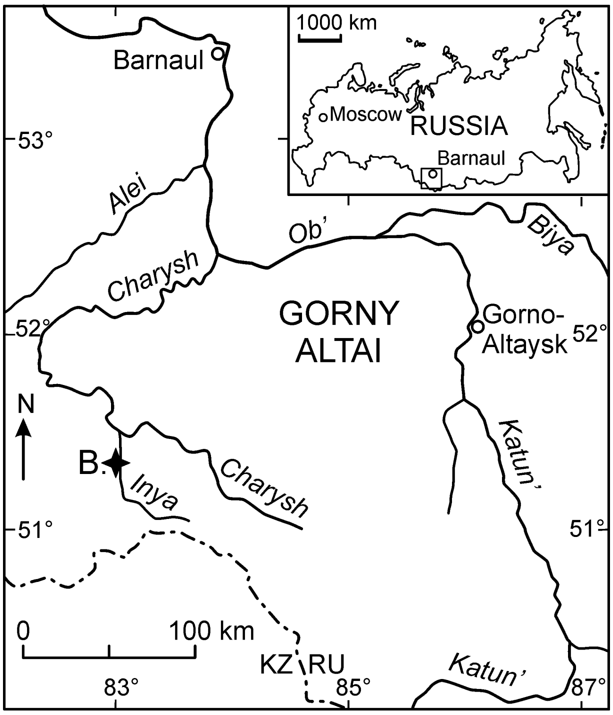

Fig. 1. Location of the Burovlyanka section (B.) in the Gorny Altai region. KZ, Kazakhstan; RU, Russia.

Altogether 21 samples were collected from the Burovlyanka section and analysed for carbon and oxygen stable isotope composition in bulk carbonate. For the stable carbon and oxygen isotopic analysis, ca 2 g of each rock sample were selected avoiding secondary veins and large crystals, and powdered. Samples of powdered material were analysed on the mass spectrometer Delta V Advantage and (for preparation of gases) GasBench II by Thermo Scientific, using the international standards NBS 18, NBS 19 and LSVEC. The analytical work was conducted in the mass spectrometry laboratory in the Department of Geology, the University of Tartu, Estonia. Preliminary results of the isotope composition of the uppermost Ordovician beds in the Burovlyanka section were presented by Sennikov & Ainsaar (2012), and for this study an additional sampling of the section was performed.

A

B

Fig. 2. **A**, the 3 m thick *Dalmanitina* Limestone Member in the Burovlyanka outcrop with the light grey lower unit and the dark grey (beige) upper unit. The ruler is 2.8 m long. **B**, upper part of the *Dalmanitina* Member with fine-bedded argillaceous limestone. The hammer is 30 cm long. Photos by N. Sennikov.

STABLE ISOTOPE RESULTS AND BIOSTRATIGRAPHY

The studied section in Burovlyanka starts with massive light grey recrystallized limestone of the Tekhten′ Formation (Member 1), which does not contain fossils, except for some unidentified crinoid and conodont fragments (Sennikov et al. 2008, 2014).The uppermost 8 m of this member are characterized by $\delta^{13}C_{carb}$ values from 0.5‰ to 1.5‰ (Fig. 3) and $\delta^{18}O$ values from –7‰ to –15‰ (Table 1). The highly variable and depleted $\delta^{18}O$ values support the lithological observations about bad preservation (secondary alteration) of the limestone, however, the good concentration of $\delta^{13}C$ values within the range of normal marine carbonate composition of the Palaeozoic rocks suggests that these values are useful for chemostratigraphy.

The following interval of shales and siltstones in the upper part of the Tekhten′ Formation (members 2–4) was not suitable for $\delta^{13}C_{carb}$ study. Member 4 with a thickness of 50–190 m contains the important zonal graptolites *Appendispinograptus supernus* (Elles & Wood), *Dicellograptus ornatus ornatus* (Elles & Wood) and *Metabolograptus ojsuensis* (formerly *Normalograptus ojsuensis*, Koren & Mikhaylova), positioning this unit within the regional *A. supernus* and *M. ojsuensis* graptolite

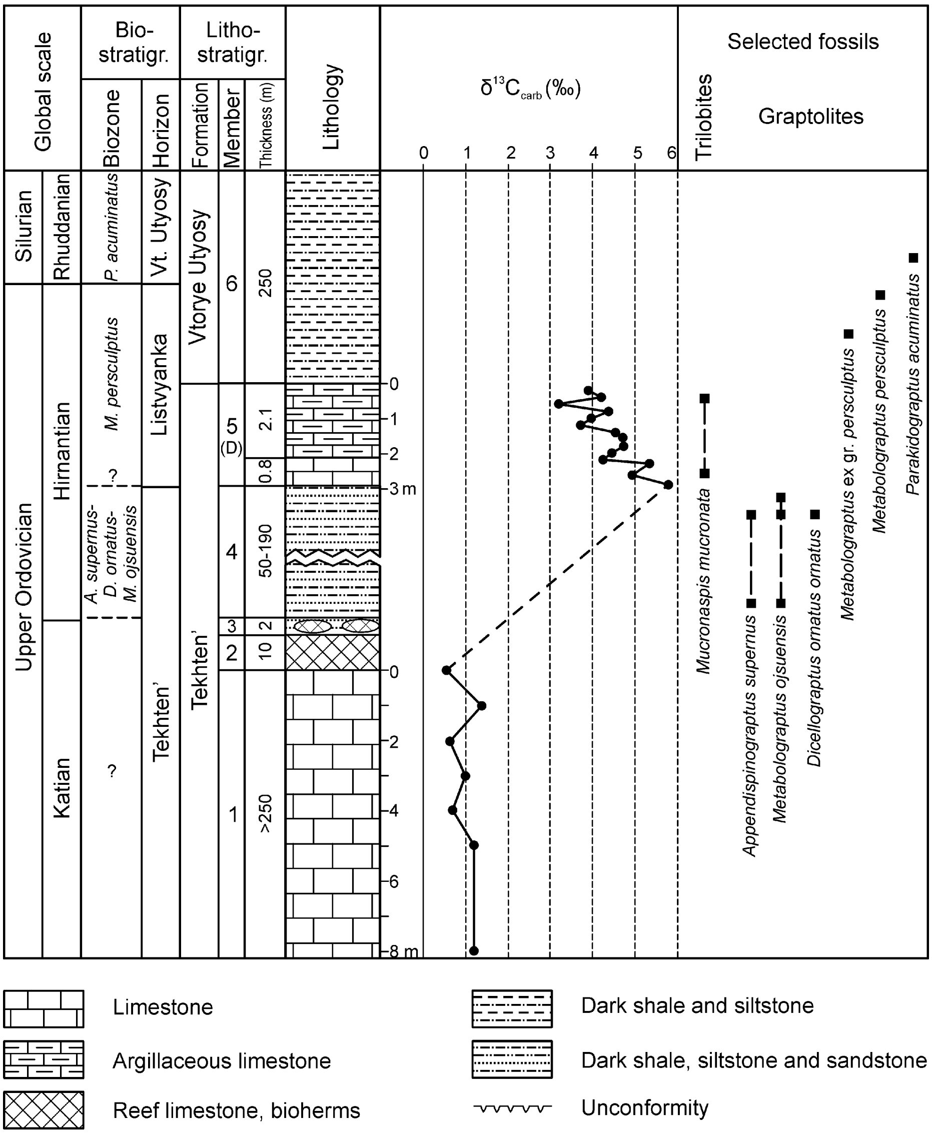

Fig. 3. Stratigraphy, selected fossils (after Sennikov et al. 2014) and carbon isotope data of the Burovlyanka section. Note that thicknesses of the stratigraphic units are not to scale, except for the sampled intervals (members 1 and 5). D, *Dalmanitina* Member (Member 5).

Table 1. Carbon and oxygen stable isotope composition of the samples from the Tekhten′ Formation, Burovlyanka section. The position of the samples is measured from the top of Member 5 and Member 1, respectively

Sample No.	Member	Position (m)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
B-101	Member 5	0.1	3.90	–9.08
B-102	Member 5	0.3	4.19	–8.95
B-103	Member 5	0.5	3.20	–9.06
B-104	Member 5	0.7	4.39	–8.71
B-105	Member 5	0.9	3.99	–9.24
B-106	Member 5	1.1	3.73	–9.25
B-107	Member 5	1.3	4.55	–9.27
B-108	Member 5	1.5	4.70	–9.13
B-109	Member 5	1.7	4.74	–8.91
B-110	Member 5	1.9	4.48	–9.13
B-111	Member 5	2.1	4.26	–9.05
B-112	Member 5	2.2	5.37	–8.91
B-113	Member 5	2.5	4.94	–8.48
B-114	Member 5	2.8	5.81	–8.31
B-7	Member 1	0.1	0.56	–12.53
B-8	Member 1	1.0	1.39	–12.83
B-9	Member 1	2.0	0.62	–15.25
B-10	Member 1	3.0	1.00	–15.00
B-11	Member 1	4.0	0.70	–14.80
B-12	Member 1	5.0	1.19	–7.32
B-13	Member 1	8.0	1.20	–10.71

biozones (Sennikov et al. 2014; Fig. 3). The *M. ojsuensis* Zone has been correlated with the global *Metabolograptus extraordinarius* Biozone (Sennikov et al. 2014) as these key graptolites co-occur in the Wangjiawan section, the stratotype section of the Hirnantian Stage. However, the FAD of *M. ojsuensis* in the Wangjiawan section is slightly lower than that of *M. extraordinarius* (Chen et al. 2006) and in the Mirny Creek section, Kolyma, the range of *M. ojsuensis* is clearly below the range of *M. extraordinarius* (Koren′ & Sobolevskaya 2008). This means that the shale Member 4 in the Burovlyanka section is probably of latest Katian and/or early Hirnantian age.

The uppermost limestone unit of the Tekhten′ Formation, Member 5 (*Dalmanitina* Member; Sennikov et al. 2014) in the Burovlyanka section, can be subdivided into two parts. The lower part comprises light-coloured massive limestone of a thickness of 0.8 m and the upper part is represented by a dark grey (on weathered surfaces – beige) unit of argillaceous bedded limestone of a thickness of 2.1 m (Fig. 2). In the lower 0.8 m member, bedding is weakly expressed, the thickness of individual beds being about 15–20 cm. Within the upper 2.1 m member, the thickness of individual distinct beds varies between 0.3 and 1.5 m and weathered surfaces look finely ribbed because of the protruding thin argillaceous laminae. The highest content of argillaceous matter is confined to the top of the member and the lowest concentration to the middle part of the upper 2.1 m unit.

Member 5 contains the graptolite *Glyptograptus* sp. and the trilobite *Mucronaspis mucronata* (Brongniart) (Sennikov et al. 2008, 2014). *Mucronaspis mucronata* represents the benthic Hirnantian fauna found in the Hirnantian Stage in Baltica and elsewhere, both in the *M. extraordinarius* and *M. persculptus* graptolite biozones (Budil 1996; Hints et al. 2012; Bergström et al. 2014). The $\delta^{13}C_{carb}$ values in the *Dalmanitina* Member are relatively high and demonstrate a clear decreasing trend from 6‰ at the base of the member to 3–4‰ at the top (Fig. 3, Table 1). At the same time, the $\delta^{18}O$ values of carbonates are all ordered in a narrow range between –8.3‰ and –9.3‰ (Table 1), suggesting a relatively low secondary alteration of the isotope composition in these beds.

The following unit, Member 6 at the base of the Vtorye Utyosy Formation, is represented by highly foliated dark shales and siltstones with a total thickness of about 250 m (Sennikov et al. 2008, 2014). Among the numerous graptolites present, *N.* ex. gr. *persculptus* (Salter) has been found at the level of 23 m, *M. persculptus* (Salter) at 36 m and *Parakidograptus acuminatus* (Nicholson) 57 m above the member base (Sennikov et al. 2008). These findings allow us to correlate the lower ~50 m of the Vtorye Utyosy Formation with the upper Hirnantian *M. persculptus* graptolite Biozone and the rest of the unit with the Rhuddanian Stage.

GLOBAL CORRELATION

Detailed Hirnantian–Rhuddanian $\delta^{13}C_{carb}$ curves for sedimentary successions containing carbonate sediments have been reported and chemostratigraphically correlated from several palaeocontinents such as Baltica (Kaljo et al. 2008; Bergström et al. 2012), North America (Finney et al. 1999; Bergström et al. 2006), South China (Fan et al. 2009) and elsewhere. However, many pelagic Katian–Hirnantian successions do not contain carbonates but are important for graptolite stratigraphy. Several of these have been studied for $\delta^{13}C_{org}$ composition, e.g. those in the British Isles (incl. the stratotype of the base of the Silurian at Dobs Linn; Underwood et al. 1997), South China (incl. the Wangjiawan section; Chen et al. 2006), North America (LaPorte et al. 2009), Baltica (Bergström et al. 2014) and elsewhere. The few sections studied for both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ (incl. the Wangjiawan section; Gorjan et al. 2012) show nearly synchronous isotope curves. The Burovlyanka section is important in the context of the stratigraphy of the Ordovician–Silurian boundary beds as it contains both fossiliferous carbonate beds and graptolitiferous shales.

The HICE with elevated $\delta^{13}C_{carb}$ values begins in the earliest Hirnantian, rising to peak values of up to 7‰, and falling back to original values in the mid- or late Hirnantian in many carbonate sections of the world (e.g., Marshall et al. 1997; Kump et al. 1999; Brenchley 2004). A similar trend is exhibited by the $\delta^{13}C_{org}$ values (Underwood et al. 1997; Fan et al. 2009; LaPorte et al. 2009). Analysing the carbon isotope curves of the HICE interval from deeper shelf graptolite-bearing environments (Finney et al. 1999; Kump et al. 1999; LaPorte et al. 2009; Bergström et al. 2014), we see the peak HICE in the *M. extraordinarius* Biozone and the end of the HICE at the base, or in the lowermost part, of the *M. persculptus* Biozone.

The high $\delta^{13}C_{carb}$ values (up to 6‰) in the *Dalmanitina* Member of the Burovlyanka section in the beds with the *Hirnantia* fauna (incl. *Mucronaspis mucronata*) definitely represent the HICE interval as there are no other isotope events in the Ordovician with such high $\delta^{13}C$ values and this correlation does also have good palaeontological control. The clearly decreasing trend of the $\delta^{13}C$ curve may represent the upper limb of the HICE (Fig. 4). This could place the *Dalmanitina* Member in the boundary interval between the *M. extraordinarius* and *M. persculptus* graptolite biozones, probably near the base of the *M. persculptus* Biozone. It is noteworthy that the *Dalmanitina* limestone Member between the shales has a very similar stratigraphic position as the Kuanyinchiao Bed in South China, which also represents a thin carbonate unit with the *Hirnantia* fauna between the shales at the boundary of two Hirnantian graptolite biozones (Fig. 4; Chen et al. 2006; Gorjan et al. 2012). The *Dalmanitina* Member may correspond to the second major glacial episode of the Hirnantian glaciations, which led to a sea level drop, widespread unconformities on the shallow shelf and major extinction of marine fauna in the middle Hirnantian (Bergström et al. 2014). The Dalmanitina Member is conformably bounded by overlying mudstones and siltstones of the Vtorye Utyosy Formation but the base of the member may be represented by unconformity. The lower limestone unit of the Tekhten′ Formation with low $\delta^{13}C_{carb}$ values obviously represents the pre-Hirnantian interval and the peak of the HICE is hidden in the upper part of the shale unit of the Tekhten′ Formation with the graptolite *M. ojsuensis*. Further studies on the C_{org} isotope composition of these shales and siltstones are needed to refine the Hirnantian chemostratigraphy in the Altai area.

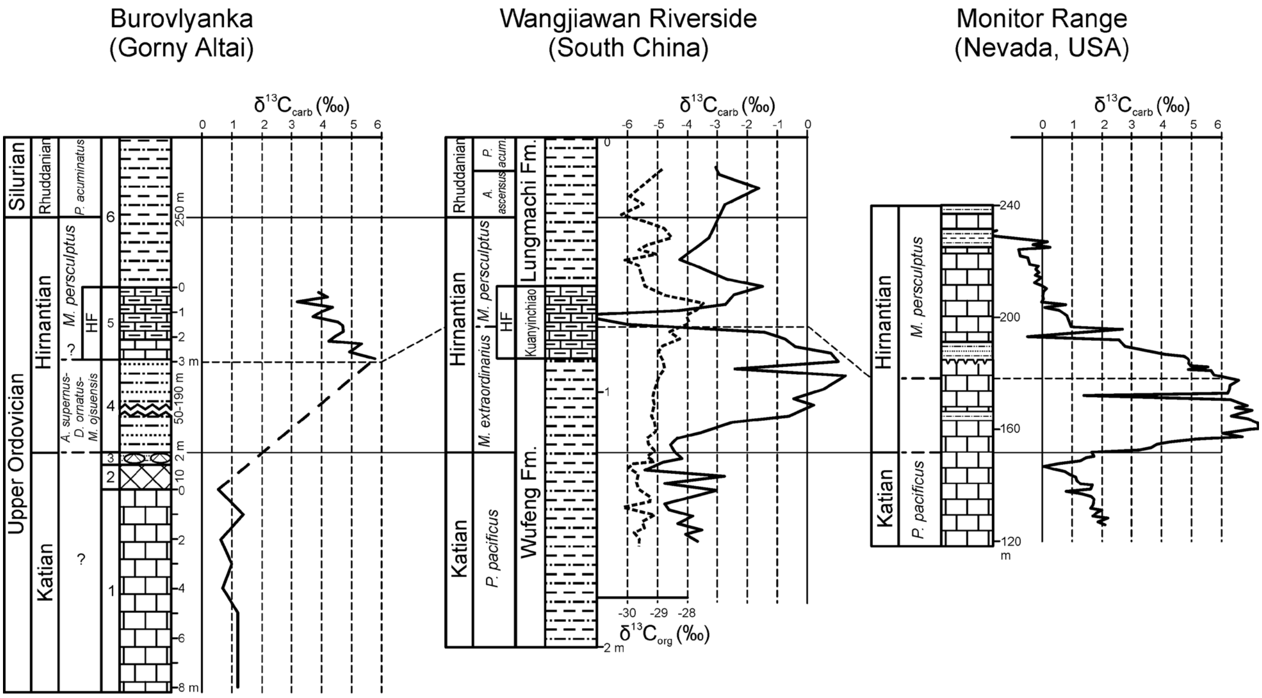

Fig. 4. Comparison of the $\delta^{13}C$ curves in the Burovlyanka section, the Wangjiawan Riverside section (Gorjan et al. 2012; $\delta^{13}C_{org}$ curve shown by a dashed line) and the Monitor Range section (LaPorte et al. 2009). The *Dalmanitina* Member (Bed 5) in the Burovlyanka section could be correlated with the lowermost part of the *M. persculptus* graptolite Biozone, situated on the upper falling limb of the HICE. HF, carbonate beds with the *Hirnantia* fauna (*sensu lato*); for lithology see Fig. 3.

CONCLUSIONS

1. The carbon isotope study of the Burovlyanka section has led to the recognition of the HICE with high and upward decreasing $\delta^{13}C$ values in the uppermost part of the Tekhten′ Formation, in the *Dalmanitina* limestone Member containing the Hirnantian trilobite fauna. This first discovery of the HICE in the Altai area suggests a stratigraphic position of the *Dalmanitina* Member in the boundary beds between the *M. persculptus* and *M. extraordinarius* graptolite biozones, probably at the base of the *M. persculptus* Zone.
2. The *Dalmanitina* Member, a limestone bed between the graptolitic shales, may correspond to the second major glacial episode of the Hirnantian glaciations, the mid-Hirnantian glacial episode, equivalent to the stratigraphic position of the Kuanyinchiao Bed in South China in the stratotype section of the Hirnantian Stage.
3. The Burovlyanka section deserves further detailed isotope study as it is one of the few Hirnantian–Rhuddanian sections in the world where both carbonate facies with Hirnantian-type benthic fauna and pelagic dark shales with biostratigraphically diagnostic zonal graptolites have been described.

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Hirnanti süsinikisotoopekskursioon Edela-Siberis Mägi-Altais

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Hirnanti süsinikisotoopsündmus (HICE), positiivne $\delta^{13}C$ hüpe Ordoviitsiumi ajastu lõpul, on maailmas laialt kasutatav Ordoviitsiumi–Siluri piirikihtide kemostratigraafilises korreleerimises. Siberi piirkonna suured Ordoviitsiumi settekivimite levilad on stabiilsete isotoopide kemostratigraafia osas siiski praktiliselt veel uurimata. Burovljanka karbonaatkivimite ja graptoliitkiltade läbilõige Altai piirkonnas on üks harvadest paljanduvatest Hirnanti ning Rhuddani lademe paljanditest Siberis. Käesolevas töös on kirjeldatud HICE sündmuse esinemist Tehteni kihistu ülemistes, *Dalmanitina* kihtides Burovljanka läbilõikes. Graptoliitkiltade vahel paiknevad *Dalmanitina* lubjakivi kihid võiksid stratigraafiliselt vastata Hirnanti ea keskel toimunud jäätumisepisoodile.