ISSN 0869-5938, Stratigraphy and Geological Correlation, 2007, Vol. 15, No. 1, pp. 12–29. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.C. Kah, D.C. Crawford, J.K. Bartley, V.I. Kozlov, N.D. Sergeeva, V.N. Puchkov, 2007, published in Stratigrafiya. Geologicheskaya Korrelyatsiya, 2007, Vol. 15, No. 1, pp. 15–34.

C- and Sr-isotope Chemostratigraphy as a Tool for Verifying Age of Riphean Deposits in the Kama–Belaya Aulacogen, the East European Platform

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Received February 25, 2005

Abstract—The Kyrpy Group of the East European platform is regarded by tradition as correlative with the Lower Riphean Burzyan Group of the Bashkirian meganticlinorium in the southern Urals. Age and correlation of the Kyrpy Group remain problematic, however, because of a limited geochronological information and controversial interpretation of paleontological materials. Data of C- and Sr-isotope chemostratigraphy contribute much to the problem solution. In the Kyrpy Group of the Kama–Belaya aulacogen, the Kaltasy Formation carbonates 1300 to 2400 m thick (boreholes 133 and 203 of the Azino-Pal'nikovo and Bedryazh areas) show $^{87}Sr/^{86}Sr$ ratios ranging around 0.7040 and narrow diapasons of $\delta^{13}C$ values: about 0.5‰ (V-PDB) in shallow-water facies and –2.0‰ (V-PDB) in sediments of deeper origin. Despite the facies dependence of carbon isotope composition, $\delta^{13}C$ variations not greater than ±1.0‰ are depicted in chemostratigraphic profiles of carbonate rocks characterizing separate stratigraphic intervals up to 800 m thick in the above borehole sections. Low $^{87}Sr/^{86}Sr$ ratios and almost invariant $\delta^{13}C$ values in carbonates of the Kaltasy Formation are obviously contrasting with these parameters in the Middle and Upper Riphean deposits, being comparable with isotopic characteristics of the Lower Riphean sediments (Mesoproterozoic deposits older than 1300 Ma). Consequently, the results obtained evidence in favor of the Early Riphean age of the Kaltasy Formation and the Kyrpy Group as a whole.

DOI: 10.1134/S0869593807010029

Key words: aulacogens, Precambrian, Kaltasy Formation, carbon and strontium isotopes, chemostratigraphy, Lower Riphean.

INTRODUCTION

In the eastern margin of the East European platform and Volga–Ural region, many boreholes drilled in the Kama and Belaya river basins eastward of the Izhevsk meridian (Fig. 1) penetrated into the Meso- and Neoproterozoic (Riphean–Vendian) sedimentary successions concealed under Paleozoic deposits at the depth of 1500–2200 m. A regional unconformity divides the recovered successions into the lower carbonate-siliciclastic complex of the Riphean and upper siliciclastic complex of the Vendian. Despite a long-lasted investigation history, age constraints for the thick Riphean–Vendian complex widespread in a vast region are known inadequately. Available results of CDP seismic sounding, limited K–Ar isotopic geochronology and biostratigraphic investigation of stromatolites and microfossils are interpreted controversially, and age of Riphean deposits in the Volga–Ural region, the Kama–Belaya aulacogen included, remains problematic to some extent. As carbonate rocks, the most suitable objects for C- and Sr-isotope chemostratigraphy, are important components of the Kaltasy Formation that is a subdivision of the Kyrpy Group we studied isotopic and geochemical parameters of carbonate core samples from that formation in order to verify age of the Kyrpy Group (samples are from boreholes 133 and 203 drilled in Azino-Pal'nikovo and Bedryazh areas, respectively).

THE KYRPY GROUP STRUCTURE AND AGE CONSTRAINTS

During the last 40–50 years, the Upper Precambrian deposits have been recovered in the Volga–Ural region by more than 100 boreholes, 50 of which are parametric, and core samples from 40 drill sites are studied by several authors of this work. The stratigraphic chart of Riphean–Vendian deposits in the Volga–Ural region has been elaborated based on comprehensive analysis of all drilling results and associated geological and geophysical data. In the chart approved in 1999 by the All-Russia conference in Ufa (Aksenov and Kozlov, 2000),

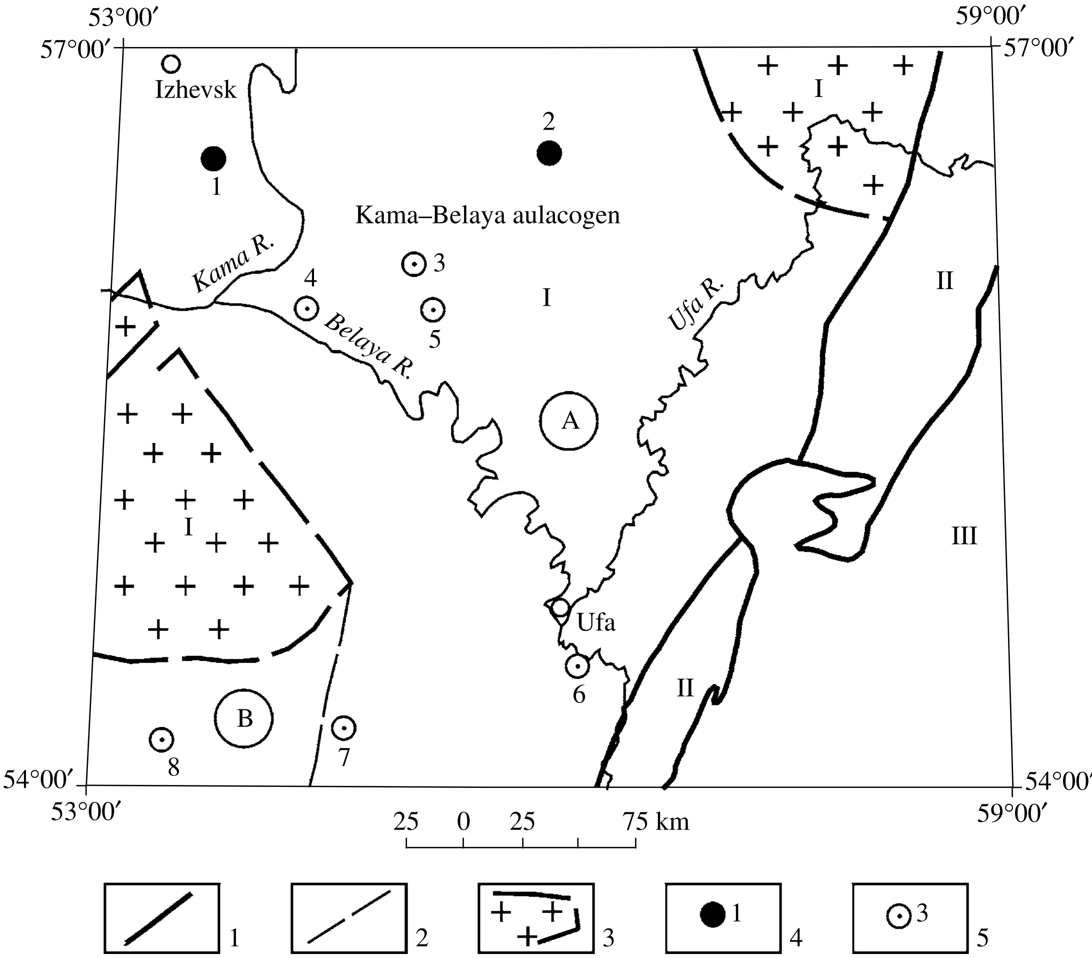


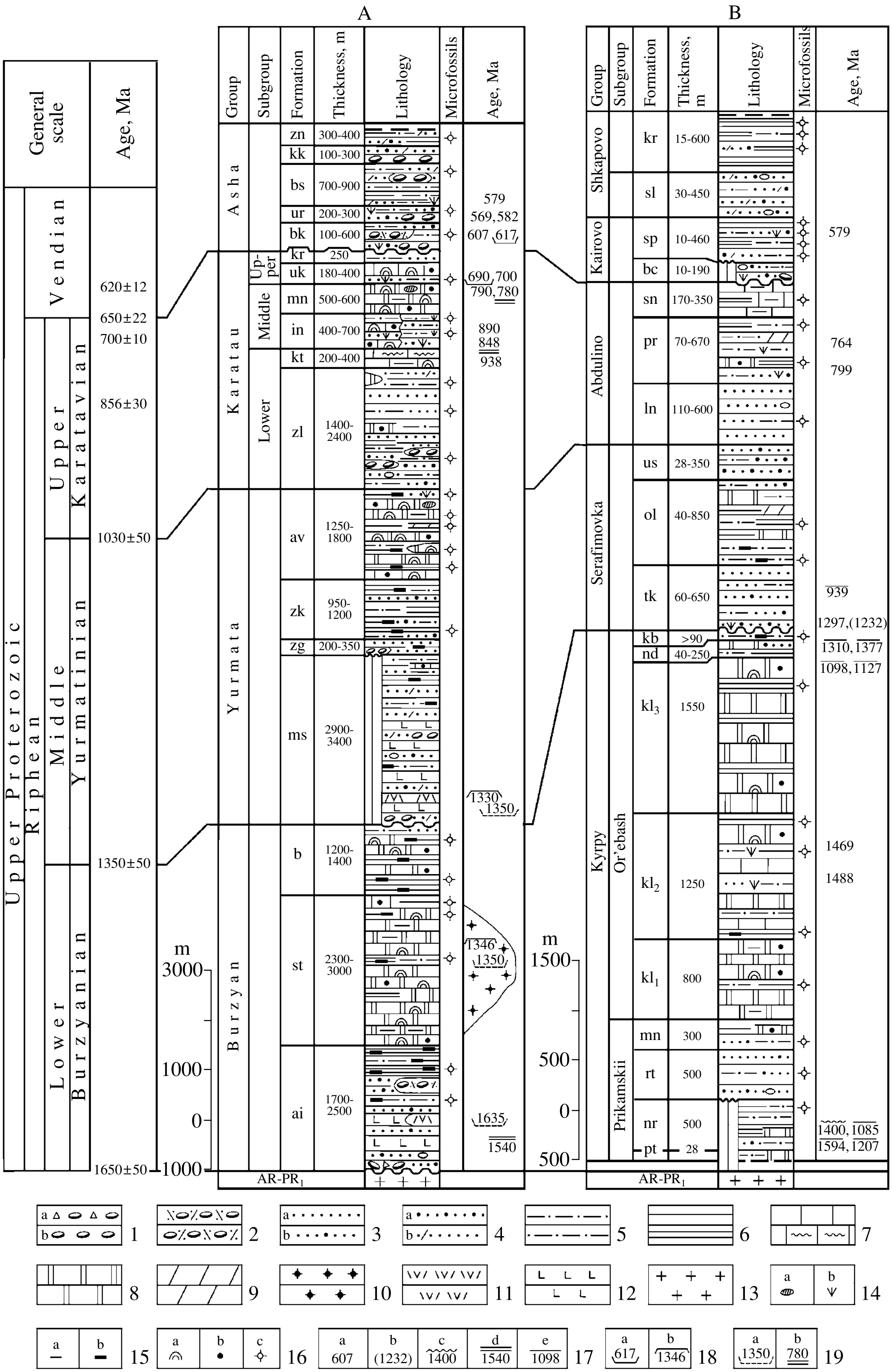
Fig. 1. Principal structures of the study region and borehole localities: (1) first- and (2) second-order structural boundaries; (3) outcrops of crystalline basement; (4) boreholes 133, Azino-Pal'nikovo (1), and 203, Bedryazh (2), studied in this work; (5) boreholes used to describe regional stratigraphy: (3) 83, Kaltasy, (4) 7000, Arlan, (5) 27, Nadezhdino, (6) 62, Kabakovo, (7) 4, Aslykul, (8) 20007, Sulino. Structural-tectonic zones: (I) eastern margin of the East-European platform with Kama–Belaya (A) and Sernovodsk–Abdulino aulacogens (B), (II) Uralian foredeep; (III) Uralian foldbelt.

the Upper Precambrian of the region is divided into the Lower, Middle, Upper Riphean and Vendian (Fig. 2). In this work, characterization of pre-Devonian sedimentary complexes is given in accord with this chart. Information about Riphean–Vendian deposits of the Volga–Ural region that is presented below includes abridged data on composition of the Prikamskii Subgroup of the Kyrpy Group and on the Middle–Upper Riphean and Vendian formations. Composition and structure of the Kaltasy, Nadezhdino and Kabakovo formations, which belong to the Or'ebash Subgroup of the Kyrpy Group, are described with necessary details, because the Kaltasy Formation is the main object of our C- and Sr-chemostratigraphic research.

Lower Riphean. This division includes deposits of the Kyrpy Group, the basal one in the pre-Devonian sedimentary succession recovered in the Volga–Ural region. In the aforementioned chart, the group is correlated to the Lower Riphean stratotype of the southern Urals (Kozlov et al., 2000), but this is not a universal opinion. The group is subdivided into the Prikamskii and Or'ebash subgroups (Fig. 2), and its base has not been penetrated by drilling.

In the stratotype section, Borehole 7000 of the Arlan site (depth range 4516–3509 m), the Prikamskii Subgroup is composed of predominantly feldspar-quartz sandstones and siltstones with interlayers and members of shales and dolostones; it is subdivided into the Petnur, Norkino, Rotkovo and Minaevka formations (Fig. 3). In the stratotype, the formations are 1013 m thick in total, being of variable thickness from 870 to 3370 m in different areas of the Kama–Belaya aulacogen.

The Or'ebash Subgroup includes the Kaltasy, Nadezhdino and Kabakovo formations (Fig. 2) over 4000 m thick in total. The Kaltasy Formation is principal marker unit among the Upper Precambrian sedimentary complexes of the Volga–Ural region, as its top and base correspond to distinct reflectors in the CDP seismic profiles (Lozin, 1994; Kozlov et al., 2002). In


A
B
General scale
Age, Ma
Group
Subgroup
Formation
Thickness, m
Lithology
Microfossils
Upper Proterozoic
Riphean
Vendian
Upper
Karatavian
Middle
Yurmatinian
Lower
Burzyanian
620±12
650±22
700±10
856±30
1030±50
1350±50
1650±50
Asha
Karatau
Yurmata
Burzyan
Up-per
Middle
Lower
zn 300-400
kk 100-300
bs 700-900
ur 200-300
bk 100-600
kr 250
uk 180-400
mn 500-600
in 400-700
kt 200-400
zl 1400-2400
av 1250-1800
zk 950-1200
zg 200-350
ms 2900-3400
b 1200-1400
st 2300-3000
ai 1700-2500
AR-PR1
579
569,582
607 617
690,700
790,780
890
848
938
1330
1350
1346
1350
1635
1540
m
3000
1000
0
1000
Shkapovo
Kairovo
Abdulino
Serafimovka
Kyrpy
Or'ebash
Prikamskii
kr 15-600
sl 30-450
sp 10-460
bc 10-190
sn 170-350
pr 70-670
ln 110-600
us 28-350
ol 40-850
tk 60-650
kb >90
nd 40-250
kl3 1550
kl2 1250
kl1 800
mn 300
rt 500
nr 500
pt 28
579
764
799
939
1297,(1232)
1310, 1377
1098, 1127
1469
1488
1400, 1085
1594, 1207
m
1500
500
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607
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1400
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1350
780

type sections (Borehole 83 of the Kaltasy site and Borehole 7000 of the Arlan site), the formation is composed of dolostones, sometimes containing stromatolites and microphytoliths; dolostones enclose interlayers and members of shales with microfossils, intercalations of dolomitic marls and rare feldspar-quartz siltstones and sandstones. Transition to underlying Minaevka Formation is gradual. The Kaltasy Formation is subdivided into conformable (Ozhiganova, 1983; Kozlov et al., 1997) Sauzovo, Arlan and Ashit subformations (Fig. 3), which are traceable over the entire distribution area of the Kaltasy rocks. The Sauzovo Subformation (105 to 816 m thick) of dolostones locally containing stromatolites includes interlayers of dark gray (to black) shales and less frequent feldspar-quartz siltstones near its base. The Arlan Subformation (535 to 1216 m thick) is represented by feldspar-quartz to arkosic siltstones, shales frequently bearing microfossils, dolostones, limestones and dolomitic marls. The Ashit Subformation (230 to 1550 m thick) is composed of dolostones with stromatolite horizons. The Kaltasy Formation thickness ranges from 1230 to 3600 m.

The Nadezhdino Formation (60 to 367 m thick) with stratotype established in Borehole 27 (depth range 2463–2240 m) of the eponymous area includes alternating beds of shales, feldspar-quartz siltstones, sandstones and dolostones along with isolated thin lava flows of basic composition. Boundaries of this unit with underlying and overlying deposits have been observed nowhere.

The Kabakovo Formation (over 90 m thick), stratotype in Borehole 62 (depth range 5521–5431 m) of the eponymous area, is composed of dark gray to black micaceous shales and dark gray feldspar-quartz siltstones with sandstone interlayers of the same composition. The subformation base has not been recovered. This unit crowns the Lower Riphean succession that is over 5300 m thick in western Bashkortostan and 9200 m thick in the composite section of the Kama–Belaya aulacogen (Kozlov et al., 2002).

Middle Riphean. In the Volga–Ural region, this stratigraphic interval corresponds to the Serafimovka Group that includes the Tukaevo, Ol'khovka and Usa formations (Fig. 2) conformably grading one into another. Deposits of the group rest on the eroded surface of underlying sediments (*Working Scheme…*, 1981; Kozlov et al., 1995, 2002). Rocks prevailing in the group are quartz to feldspar-quartz sandstones and siltstones; subarkosic and arkosic varieties are less frequent and contain intercalations of dolostones, shales and dolomitic marls. The group is up to 1880 m thick.

Upper Riphean. This erathem includes deposits of the Abdulino Group divided into the Leonidovka, Priyutovo and Shikhan formations (Fig. 2), which are in conformable relations (*Working Scheme…*, 1981; Kozlov et al., 1995). The above formations are composed of variegated sandstones and siltstones of quartz and, less frequently, of feldspar-quartz composition, which are intercalated with shales and limestones. The Abdulino Group is in debatable relations with underlying deposits. Some geologists believe that the Leonidovka Formation, the basal one in the group, overlies the Serafimovka Group with erosion (*Working Scheme…*, 1981; Ivanova et al., 1990), while the other opinion is that both groups are interrelated via gradual transition (Timergazin, 1959; Solontsov et al., 1966; *Stratotype of the Riphean…*, 1983; Kozlov et al., 1995). The last opinion is consistent with data obtained by resent drilling in the Podgornaya (Borehole 20006), Aslykul (Borehole 4) and North Kushkul (Borehole 1) areas. The Abdulino Group is from 400 to 2600 m thick, and total thickness of the Riphean is estimated to be about 10 000–13 000 m in the composite section of the Kama–Belaya aulacogen (Kozlov et al., 1997, 2000).

Vendian. In the Vendian interval, deposits of the Volga–Ural region are attributed to the Kairovo (Baikibashevo and Staro-Petrovo formations) and Shkapovo (Salikhovo and Karly formations) groups (Fig. 2), which are composed exclusively of siliciclastic rocks (inequigranular polymictic, feldspar-quartz, subarkosic, arkosic and quartz sandstones and siltstones, shales with interlayers of gravelstones and small-pebbled conglomerates). Vendian deposits rest on eroded surface of underlying Riphean and Archean–Early Proterozoic rocks (*Working Scheme…*, 1981; Kozlov et al., 1995, 1997). In the Volga–Ural region, total thickness of Vendian deposits is from 150 to 1700 m.

Age interpretation of sedimentary successions considered above is controversial. The pre-Upper and

Fig. 2. Correlation scheme of Riphean–Vendian deposits in the Bashkirian meganticlinorium (axial zone and western limb, left column) and Volga–Ural region (right column): (1) conglomeratic breccia (a) and conglomerate (b); (2) tilloid conglomerate; (3) quartz (a) and feldspar-quartz (b) sandstone; (4) arkosic to subarkosic (a) and polymictic sandstone (b); (5) siltstone; (6) shale; (7) limestone (a), low-hummocky limestones (b); (8) dolostone; (9) marl; (10) granite; (11) rhyodacite; (12) metabasalt; (13) rocks of crystalline basement; (14) chert (a) or glauconite (b); (15) clayey (a) and carbonaceous (b) rocks; (16) stromatolite (a), microphytolith (b), microfossils (c); (17) K–Ar age, Ma, of glauconite (a), sericite (b), illite (c), whole rock (d), gabbro-dolerite dike (e); (18) Rb–Sr age of glauconite (a) and whole rock (b); (19) U–Pb zircon age (a) and Pb–Pb age of carbonates (b). Upper Precambrian formations of southern Urals and Volga–Ural region: (ai) Ai; (st) Satka; (b) Bakal; (ms) Mashak; (zg) Zigal'ga; (zk) Zigazy-Komarovo; (av) Avzyan; (zl) Zilmerdak; (kt) Katav; (in) Inzer; (mn) Min'yar; (uk) Uk; (kr) Krivaya Luka; (bk) Bakeevo; (ur) Uryuk; (bs) Basa; (kk) Kuk-Karauk; (zn) Zigan; (pt) Petnur; (nr) Norkino; (rt) Rotkovo; (mn) Minaevo; (kl) Kaltasy with Sauzovo (kl_1), Arlan (kl_2) and Ashit (kl_3) subformations; (nd) Nadezhdino; (kb) Kabakovo; (tk) Tukaevo; (ol) Ol'khovka; (us) Usa; (ln) Leonidovo; (pr) Priyutovo; (sn) Shikhan; (bc) Baikibashevo; (sp) Staro-Petrovo; (sl) Salikhovo; (kr) Karly. Numbers on the columns: 1, 2—Subgroups: 1—Middle Karatavian, Upper Karatavian; 3—Sampling sites of microfossils.

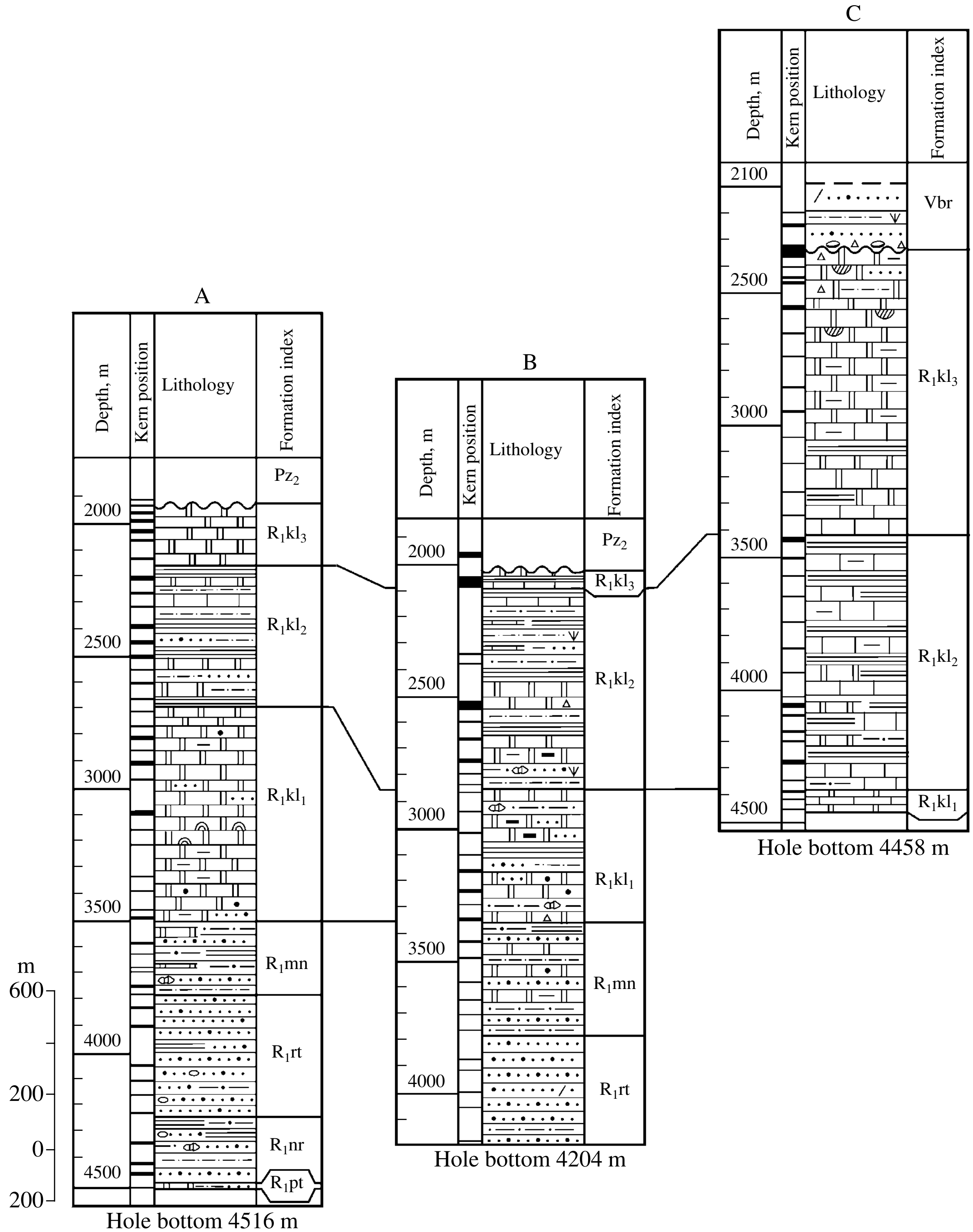

Fig. 3. Lithology of the Kaltasy Formation recovered by boreholes 7000 Arlan (A), 133 Azino-Pal'nikovo (B) and 203 Bedryazh (C) (symbols as in Fig. 2). (V br) Borodulino Group; (Pz_2) undivided Middle Paleozoic.

probably pre-Middle Riphean stratigraphic position of the Kyrpy Group is confirmed by results of CDP seismic sounding. The base and top of the Kaltasy Formation, the marker unit of predominantly carbonate composition, are well recognizable in all seismic profiles, which show general eastward dip of Riphean strata. The Early Riphean age of the Kyrpy Group is substantiated by particular stromatolite assemblage occurring in the Kaltasy Formation (member I of the Lower Riphean) and by K–Ar dates obtained for illite, authigenic glauconite and gabbroid bodies crosscutting deposits of the group.

Stromatolites *Stratifera omachtella* Kom., a species occurring in the Early Riphean of the Uchur–Maya region in Siberia, and *Gongulina differenciata* Kom. known from the Satka Formation of the Burzyanian type section, the Bakal–Satka area of the southern Urals, are identified by N.P. Panova and M.A. Semikhatov in dolostones of the Kaltasy Formation, which have been recovered by drilling from the depth 2966 m, Borehole 20007, Sulino area (Kozlov et al., 1995). In dolostones of the same formation penetrated by Borehole 4, the Aslykul area, V.A. Komar determined stromatolite taxa *Kussiella kussiensis* Kryl., *Gongylina differenciata* Kom. (depth range 4965.3–4959.4 m) and *Nucliella cortinata* Kom. (depth range 4944.3–4940.7 m), which are characteristic of the Lower Riphean type sections in southern Urals. A series of K–Ar dates obtained for glauconite from the Arlan Subformation penetrated at several sites is as follows: 1510, 1520 and 1425 Ma, Borehole 3, Buranovo area; 1488 and 1469 Ma, Borehole 36, Arlan area; 1358 and 1334 Ma, Borehole 191, Urustamak area (*Stratotype of the Riphean…*, 1983). Illite from aleuropelite of the Norkino Formation penetrated by Borehole 20005, Karachevo area, is dated at 1400 Ma by K–Ar method (Gorozhanin, 1995). The K–Ar dates of 1368, 1377 and 1310 Ma are obtained for whole-rock samples of gabbroids that intruded the Nadezhdino Formation according to drilling results in the eponymous area, Borehole 27 (*Stratotype of the Riphean…*, 1983). These dates are comparable with age value exceeding 1350 Ma that was obtained for diabases (Rb–Sr method, whole rock sample, Kheraskova et al., 2002), which occur in similar situation in the Krestets aulacogen, the central East European platform. All stromatolite taxa and isotopic-geochronological dates listed above approve the Early Riphean age of the Kyrpy Group.

Situation with microfossils is not so clear. As is stated in explanatory notes to the stratigraphic chart of Riphean–Vendian deposits in the Volga–Ural region (Aksenov and Kozlov, 2000), there are two assemblages of characteristic organic-walled microfossils known from the Kyrpy Group besides the transit taxa of no stratigraphic value. One of the assemblages is microbiota of the Kabakovo Formation that includes several morphotypes, which are typical of the Bakal Formation, the upper unit of the Lower Riphean stratotype. The other assemblage is represented by microfossils from the upper part of the Prikamskii Subgroup (Kozlova, 1990) and by the Pal'nikovo microbiota of very high diversity (Kozlov et al., 1998; Veis et al., 2000). The last microbiota is confined to shales of the Kaltasy Formation recovered by Borehole 133 in the Azino-Pal'nikovo area. Many representatives of both microbiotas have been known in the Urals until recent time only from the Upper Riphean deposits (*Stratotype of the Riphean…,* 1983; Kozlova, 1990). In Siberia, analogues of the Pal'nikovo microbiota are known in the Anabar massif, Uchur–Maya and Turukhansk regions, where they include certain morphotypes of relatively large size and complex structure, which have been regarded by Veis and some other experts in microfossils as indicative of the Late Riphean age. However, two independent lines of arguments disprove this viewpoint. First, nearly all morphotypes characteristic of the Pal'nikovo microbiota are described from those deposits of the Anabar massif, which certainly antedate the Upper Riphean according to C-isotope chemostratigraphic indicators and apparently belong to the Lower Riphean, as is inferred from biostratigraphic (stromatolites) and geochronological (K–Ar and Rb–Sr ages of glauconite and authigenic illite) data (Semikhatov, 1995; Gorokhov et al., 1995). In addition, some acanthomorphic and ornamented acritarchs, the form genus *Valeria* included, are reported to occur in the Ruyang Group of China that is 1600 Ma old (Xiao et al., 1997). Second, Veis et al. (2000) discovered analogues of Pal'nikovo microbiota below basal Zilmerdak Formation of the Upper Riphean stratotype in the so-called Kuzha deposits corresponding to upper horizons of the Yurmata Group, the Middle Riphean stratotype of the Bashkirian meganticlinorium. The quoted evidences eliminate contradictions in viewpoints on the Kyrpy Group age in the Volga–Ural region, which are grounded by stromatolites, isotopic-geochronological and geological data, on the one hand, and by microfossils, on the other.

In lithology and stratigraphic succession, formations of the Kyrpy Group are well correlative with formations of the Burzyan Group recorded in the Riphean type sections of the southern Urals (Fig. 2), where that group represents stratotype of the Early Riphean. The principal marker horizon enabling interregional correlation is the Kaltasy Formation representing in the study region a geological body of complex structure that is composed predominantly of carbonate rocks. Considering stratigraphic position in regional sedimentary successions and available biostratigraphic and isotopic-geochronological data (see above), we regard this formation as equivalent of the Satka Formation in the Lower Riphean type sections of the Bashkirian meganticlinorium. Consequently, predominantly siliciclastic deposits of the Prikamskii Subgroup, which underlie the Kaltasy carbonates, appear to be correlative with the Ai Formation, while the Nadezhdino and Kabakovo formations above the latter can be correlated, though with some reservations, with the Bakal Formation of the Burzyan Group in the Bashkirian meganticlinorium (Kozlov et al., 1999).

Deposits of the Serafimovka and Abdulino groups are attributed to the Middle and Upper Riphean, respectively, based on K–Ar dates known for authigenic glauconite and gabbroids that intrude them (*Stratotype of the Riphean…*, 1983). The Late Riphean age of the Abdulino Group is also inferable from composition of microfossils discovered in the Priyutovo Formation (Aksenov and Kozlov, 2000). The upper siliciclastic complex is of the Vendian age according to date of 579 Ma obtained for glauconite from Borehole 23, Menzelino-Akantysh area, and to typical Vendian assemblages of microfossils identified by N.G. Pykhova, I.K. Chepikova, T.V. Yankauskas and E.V. Kozlova in core samples of many boreholes drilled in the Volga–Ural region (Aksenov and Kozlov, 2000; and references therein).

As we expect, the Kyrpy Group age can be additionally substantiated by data of C- and Sr-isotope chemostratigraphy after investigation of carbonate rocks in the Kaltasy Formation.

CHARACTERIZATION OF STUDIED OBJECTS

To clarify age of the Kaltasy Formation, we studied core samples from boreholes 133 (Azino-Pal'nikovo area) and 203 (Bedryazh area), which are drilled in the north of the Kama–Belaya aulacogen (Fig. 1), and analyzed associated geological and geophysical materials.

Lithologic description. Deposits recovered by mentioned boreholes can be discriminated in four lithologic-facies associations. Clastic association (1) includes the following rock types: parallel- to cross-bedded fine-grained sandstones containing carbonate clasts with shear fabrics and casts of evaporite crystals (Figs. 4A, 4B); layered dolomitic microbreccias with clasts 3 to 10 mm across and rounded quartz grains (Fig. 4C); and irregularly bedded dolomicrites often containing ooliths. These peculiarities suggest deposition of sediments in peritidal settings. Micrites and microsparites of association (2) are composed of laminated dolomitic microcalcite (indicator of microbial sedimentation in shallow-sea settings) and of thin (5 to 30 mm) laminae of homogeneous micrite evidencing in favor of low-energy deeper environments. Micrite beds of association (3) are intercalated either with thin laminae of quartz sand and silt, or with thin interbeds enriched in organic matter, characteristic of which is molar tooth structure (Fig. 4D) that originates by sediment degassing in the course of early diagenetic decomposition of organic matter (Frank and Lyons, 1998), being typical of shallow subtidal facies (James et al., 1998). In micritic varieties of carbonates, micrite and silty micrite laminae 5 to 30 mm thick, enriched in organic matter (Fig. 4E), alternate frequently with graded laminae 3 to 10 mm thick, which are composed of silty to pelitic fraction rich in organic substance and of shaly material; these patterns suggest turbidity origin of sediments. Aleuropelites and silty micrites enriched in organic matter and often displaying synsedimentary slump folds (Fig. 4F) belong to association (4).

According to known chemostratigraphic generalizations, $\delta^{13}C$ values in marine carbonates of the Lower Riphean are relatively constant, corresponding to $0.0 \pm 1.5‰$ in average (Abell et al, 1989; Buick et al., 1995; Knoll et al., 1995b; Frank et al., 1997; Xiao et al., 1997; Lindsay and Brasier, 2000). In carbonates younger than 1300 Ma, they moderately range around basic values of $0.0 \pm 1.5‰$ up to +2…+3.5‰ with episodic excursions to –1 and –2‰ (Knoll et al., 1995b; Kah et al., 1999; Bartley et al., 2001; Frank et al., 2003). Small positive $\delta^{13}C$ values are recorded until commencement of the Upper Riphean, being grown afterward up to +6‰ with brief excursions down to –2‰ (Kaufman and Knoll, 1995, and references therein). As to worldwide characteristics of the Rb–Sr systematics, very low $^{87}Sr/^{86}Sr$ initial ratios of about 0.7040–0.7050 are characteristic of the Lower Riphean carbonate beds all over the globe (Gorokhov et al., 1995; Hall and Veizer, 1996; Kuznetsov et al., 2003).

Sedimentation. Boreholes 133, Azino-Pal'nikovo area, and 203, Bedryazh area, penetrated through thick (40 to 100 m) coarse-bedded cycles composed of silty–shaly sediments in their lower intervals and of carbonates in the upper ones (Fig. 3). Cycles form thicker strata reflecting relative sea-level changes. A greater proportion of granular dolostones and fine-grained sandy material in thinner cycles recovered by Borehole 133 in Azino-Pal'nikovo area is indicative of shallow-water high-energy platform environments near western limit of the Kama–Belaya aulacogen (Fig. 1). Cycles with less abundant sandy fraction are penetrated here at the depth of about 3000 m; thick member composed predominantly of shale at the depth of about 2550 m. These changes suggest a considerable sea-level rise and related limitation of siliciclastic influx into the basin (an exception is a short-term event responsible for sudden appearance of sandy material at the depth of 2375 m). A long-term sea-level drop and intensified influx of sandy material is recorded at the depth of about 2000 m.

In thicker cycles recovered by Borehole 203 in the Bedryazh area, siliciclastic material is of lesser grain size, and proportion of deep-water sediments (micrites enriched in organic matter, silty limestones and aleuropelitic turbidites) is higher. Consequently, sedimentation settings were deeper in the relevant part of the Kama–Belaya aulacogen (Fig. 1). In the lower 1400 m of the succession (depth range 3100–4500 m), transitions from deep- to shallow-water carbonate facies crowning the cycles and indicating relatively narrow sea-level fluctuations are recorded within intervals of several hundreds meters. A considerable sea-level rise is detected here at the depth of 3000 m, where shaly–silty interlayers are more frequent, and next less significant appearance of sandy material is established at the depth of 2850 m. A decline of sea level in the basin is recorded at the depth of about 2700 m marking a higher abundance of aleuropsammitic material and presence of dolostones.

The observable changes in lithology controlled most likely by long-term sea-level fluctuations present an opportunity to correlate particular intervals of sections recovered by boreholes 133 (Azino-Pal'nikovo area) and 203 (Bedryazh area). As is noted above, abundance of coarse-grained siliciclastic components is considerably reduced at the depth 2550 m in Borehole 133 and 3000 m in Borehole 203. A sudden short-term appearance of coarse clastic sediments is established at the depth 2350 m in the first case and 2850 m in the second one,

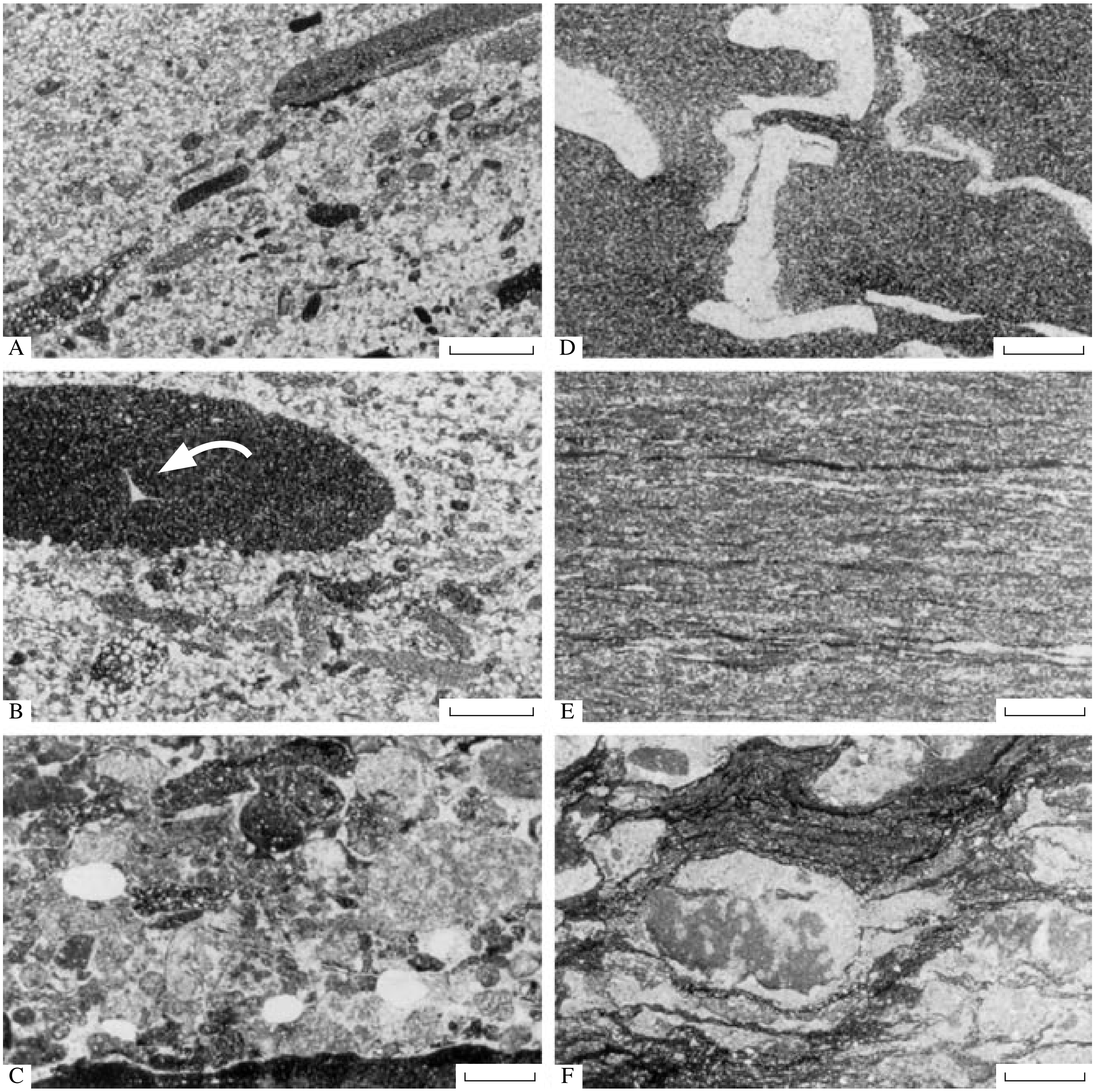

Fig. 4. Structure of carbonate rocks recovered by boreholes 133 Azino-Pal'nikovo and 203 Bedryazh: (A) cross-bedded fine-grained sandstone with dolomite intraclasts; (B) pseudomorph after evaporite crystal in dolomite interlayers; (C) dolomitic microbreccia with rare rounded quartz grains; (D) micritic limestone with molar tooth structure; (E) clayey carbonate with laminae enriched in organic matter; (F) laminae enriched in organic matter and deformed around limestone clasts (scale bar is 1 mm in all photographs).

while occurrence frequency of shallow-water lithofacies is gradually increasing above the depth levels of 2000 and 2700 m, respectively. These observations suggest certain difference between sedimentation settings in two areas under consideration (Fig. 3). Borehole 133 of the Azino-Pal'nikovo area that is drilled not far away from northwestern limit of the Kama–Belaya aulacogen (Fig. 1) recovered predominantly sediments of subtidal (clayey siltstones) and peritidal settings (dolosparites and fine-grained sandstones). Borehole 203 penetrated in the central Bedryazh area of aulacogen (Fig. 1) predominantly through the subtidal facies of clayey siltstones and fine-grained limestones.

ANALYTICAL PROCEDURE AND RESULTS

Analytical procedure. We analyzed carbonate material of 58 core samples selected from two boreholes under examination. With due regard for core recovery and cyclic character of stratigraphic succession (thick shale members crowned by thin carbonate sediments), we sampled the recovered core sections with interval of 50 m in average.

Standard petrographic examination of polished and thin sections was used to select samples most appropriate for geochemical analysis. Sedimentary and diagenetic carbonate phases were discriminated by means of cathodoluminescence microscopy. Carbonate material for isotopic analysis (2 to 15 mg) was bored out of polished samples by dental drilling machine, bits tip diameters from 250 to 1000 μm. To remove volatile contaminants, the material extracted to analyze C- and O-isotope composition (samples 5–8 mg in weight) was heated in vacuum during one hour under temperature 350°C. After dissolution of samples in anhydrous phosphoric acid under 25°C, the extracted CO_2 was purified by standard method of cryogenic distillation. Isotopic composition was analyzed on Finnigan MAT mass spectrometer with gas ion source and double puffing system at the University of Tennessee, the United States. The results are quoted in per mile (‰) relative to V-PDB (Vienna Pee Dee Belemnite) standard. Analytical accuracy checked daily on internal laboratory standard was better than ±0.2‰ for $\delta^{13}C$ and ±0.01‰ for $\delta^{18}O$.

Concentrations of major and trace elements (Ca, Mg, Sr, Mn, Fe) are measured after dissolution of carbonate samples (from 0.5 to 2 mg in weight) during 2 h in 5.0 ml of ultrapure 2N HNO_3 with subsequent separation of insoluble residue by centrifuging and decanting. Measurements are performed at the State University of West Georgia (USA) on Perkin-Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) equipped with microconcentric nebuliser and calibrated to a series of gravimetrically determined standards. Analytical accuracy determined through replicate analysis of sample and standard solutions is better than ±5% for Sr and Mn, and better than ±10% for Mg and Fe.

The Sr isotopic composition is very sensitive to diagenetic alterations (Brand and Veizer, 1980; Banner and Hanson, 1990), and researchers consider Mn/Sr, Fe/Sr and Rb/Sr ratios as indicators of diagenesis impact (Derry et al., 1992; Kaufman et al., 1995; Montanez et al., 1996; Kuznetsov et al., 1997; Podkovyrov et al., 1998). In every case, the assumed threshold ratios are empirical and arbitrary (Melezhik et al., 2001a, 2001b, 2002). Therefore, selection of least altered ("best") should be accepted with caution.

Carbonates with Mn/Sr <10 used to be commonly regarded as suitable for Sr-isotope systematics as they are shown to retain the $^{87}Sr/^{86}Sr$ initial ratios (Knoll et al., 1995a, 1995b). In this work, we analyzed samples with Mn/Sr <5. Selected carbonate sample splits (<5 mg) were treated first in ammonium acetate to remove Sr residing in exchangeable positions (Gorokhov et al., 1995; Montanez et al., 1996) and then dissolved in ultrapure 0.5 M acetic acid. The Sr aliquots (500–1000 ng) extracted from solution using ion-exchange Sr Spex resin were dissolved in H_3PO_4 and analyzed on Ta-filament multicollector mass spectrometer VG-Sector 54 TIMS at the University of Maryland, the United States. Working temperature was 1450–1650°C. The Sr isotopic ratio in NBS-987 standard is estimated to be 0.710242 ± 0.000012 in average after 10 analyses and 0.710244 ± 0.00001 after 33 additional analyses (2σ uncertainty in both cases) carried out during measurements.

Geochemical results. Geochemical data characterizing carbonate rocks of the Kaltasy Formation recovered by boreholes 133 and 203 (Azino-Pal'nikovo and Bedryazh areas) are presented in Tables 1 and 2. In stoichiometric dolomite Ca/Mg is about 0.60, and carbonates from both boreholes are considered in this work either as dolomitic (Ca/Mg > 0.40) or limestones (Ca/Mg < 0.05). Several samples with Ca/Mg from 0.05 to 0.40 are presumably composed of mixed limestone and dolomite phases. In the section recovered by Borehole 133, the Kaltasy Formation is composed predominantly of dolostones in the lower interval 800 m thick (depth range 3350–2550 m), while in the upper interval 520 m thick (depth range 2550–2030 m) dominant shales are intercalated with subordinate limestone interlayers. In Borehole 203, pure dolostones are confined, in contrast, to the upper 610-m-thick interval (depth range 2950–2340 m), whereas within the lower 1400 m (depth range 4350–2950 m), there are alternating beds of sandstones, shales and dolostones, the latter being dominant again in the lowermost 108 m.

The above lithological changes are consistent in two boreholes with isotopic and geochemical parameters of rocks. Both cores preserve $\delta^{13}C$ values ranging from 0 to –3‰; $\delta^{18}O$ from –4 to –10‰. However in limestones, both parameters are usually lower than in dolostones (Tables 1 and 2). The estimated average values are as follows: $\delta^{13}C$ = –2.3‰ (variation range from –2.0 to –2.7), $\delta^{18}O$ = –8.8‰ (variation range from –7 to –10.9) in limestones versus $\delta^{13}C$ = –0.5‰ (variation range from –0.1 to –1.0), $\delta^{18}O$ = –6.9‰ (variation range from –5.1 to –10.5) in dolostones of Borehole 133 (Azino-Pal'nikovo area); $\delta^{13}C$ = –2.0‰ (variation range from –0.3 to –3.4), $\delta^{18}O$ = –7.6‰ (variation range from –7 to –29.5) in limestones versus $\delta^{13}C$ = –1.1‰ (variation range from –0.4 to –2.8), $\delta^{18}O$ = –4.9‰ (variation range from –3.1 to –8.8) in dolostones of Borehole 203 (Bedryazh area). Variation ranges of Sr concentration are 30–960 ppm in limestones and 9–35 ppm in dolostones. Wider concentration ranges are characteristic of Mn (40–3845 ppm) and Fe (337–55424 ppm) concentrations in limestones, and dolostones are only slightly enriched in both elements.

Assessment of diagenesis. Presence of dolomitic phases, variable C- and O-isotopic parameters, low Sr but high Mn and Fe concentrations, all these characteristics evidence postsedimentary alterations in the Kaltasy carbonates. The degree and factors of diagenesis

Table 1. Trace element concentrations, C-, O- and Sr-isotopic parameters of the Kaltasy Formation carbonates from Borehole 133, Azino-Pal'nikovo area

Sample no.	Depth, m	Phase*	Mg/Ca	Fe, ppm	Mn, ppm	Sr, ppm	$^{87}Sr/^{86}Sr$	$\delta^{13}C$**, ‰	$\delta^{18}O$**, ‰
C133-2047.5	2047.5	P	0.46	20344	1021	45	–	–2.8	–6.5
C133-2068.9	2068.9	P	0.03	6532	478	26	–	–2.7	–9.4
C133-2552.5-1	2552.5	S	0.03	4728	379	39	–	–2.5	–10.9
C133-2552.5-2	2552.5	S	0.03	6178	517	31	–	–2.3	–9.4
C133-2552.5-3	2552.5	P	–	–	–	–	–	–2.0	–7.9
C133-2553.3	2553.3	P	0.03	5422	433	36	–	–2.3	–9.3
C133-2560.3-1	2560.3	P	0.03	6934	519	51	–	–2.4	–9.4
C133-2560.3-2	2560.3	P	0.01	5081	490	49	–	–2.0	–8.3
C133-2565.8B	2565.8	P	0.04	4506	314	55	–	–2.0	–8.7
C133-2571.6-1	2571.6	S	0.01	5330	410	54	0.70763	–2.2	–9.0
C133-2571.6-2	2571.6	P	0.00	5609	413	77	–	–2.2	–7.6
C133-2629	2629.0	P	0.56	7227	420	32	–	–0.7	–7.1
C133-2679.5-1	2679.5	P	0.56	8166	518	22	–	–0.7	–6.6
C133-2679.5-2	2679.5	S	0.53	20477	3845	30	–	–1.0	–10.5
C133-2760.6	2760.6	P	0.55	11666	916	10	–	–0.5	–9.0
C133-2767.5	2767.5	P	0.55	14444	1102	10	–	–0.4	–8.5
C133-2960.1B	2960.1	P	0.61	14452	525	31	–	–0.8	–5.1
C133-3031	3031.0	P	0.62	7963	305	27	–	–0.5	–5.9
C133-3038	3038.0	P	0.62	9240	364	31	–	–0.8	–5.8
C133-3114.5	3114.5	P	0.59	6276	269	28	0.70959	–0.4	–5.9
C133-3177	3177.0	P	0.64	14944	448	35	–	–0.6	–6.3
C133-3252.2	3252.2	P	0.61	8225	309	22	–	–0.5	–7.3
C133-3253.3-1	3253.3	P	0.60	10925	322	24	–	–0.1	–6.3
C133-3253.3-2	3253.3	P	0.59	9995	318	25	–	–0.1	–6.6
C133-3253.3-1B	3253.3	P	0.60	9429	305	21	–	+0.0	–6.3
C133-3253.3-2B	3253.3	P	0.59	8704	313	23	–	–0.2	–6.7
C133-3304	3304.0	P	0.61	8469	271	24	–	–0.4	–7.3

Note: (*) primary (P) and secondary (S) sedimentary phases; (**) uncertainty ±0.2‰ V-PDB for $\delta^{13}C$ and ±0.01‰ V-PDB for $\delta^{18}O$.

can be deciphered from trends in geochemical and isotopic diagrams (Brand and Veizer, 1980, 1981; Veizer, 1983). In the $\delta^{13}C$–$\delta^{18}O$ diagram (Fig. 5), there is seen a considerable decrease of $\delta^{18}O$ values, when $\delta^{13}C$ parameter slightly decrease in the Kaltasy carbonates. Although trends of this kind are typical of carbonate rocks that experienced burial diagenesis (Veizer, 1983), the parameter $\delta^{18}O$ can be quite variable, provided the low water/rock ratio, even if the $\delta^{13}C$ value that is under buffer action of carbonate matrix remains constant (Banner and Hanson, 1990). Oxygen isotope composition in weakly altered marine carbonates of the Precambrian ranges frequently from –3 to –7‰ (Frank and Lyons, 2000; Kah, 2000). It is reasonable to suggest therefore that the Kaltasy carbonates are insignificantly altered by diagenesis, and that variable $\delta^{13}C$ values characterize primary isotopic variations of stratigraphic or facies-dependent type.

The degree of diagenesis can be assessed as well based on Mn, Fe and Sr distribution (Brand and Veizer, 1980; Veizer, 1983; Kuznetsov et al., 1997; Podkovyrov et al., 1998). Being elevated to some extent, concentrations Mn^{2+} are not as high as in the other Precambrian carbonates (Fig. 6), evidencing a satisfactory retentivity of C-isotopic signatures (Bartley et al., 2001). Much higher Fe^{2+} concentrations are nevertheless within the range characteristic of the Precambrian successions (Bartley et al., 2001; Frank et al., 1997). Behavior of Mn^{2+} and Fe^{2+} is controlled by sedimentological factors and conditions of diagenesis (Melezhik et al., 2001a, 2001b, 2002). By the early (near-bottom) diagenesis, microbial decomposition could be responsible for com-

Table 2. Trace element concentrations, C-, O- and Sr-isotopic parameters of the Kaltasy Formation carbonates from Borehole 203, Bedryazh area

Sample no.	Depth, m	Phase*	Mg/Ca	Fe, ppm	Mn, ppm	Sr, ppm	$^{87}Sr/^{86}Sr$	$\delta^{13}C$**, ‰	$\delta^{18}O$**, ‰
C203-2339.3-1	2339.3	P	0.58	1588	227	25	–	–1.0	–5.0
C203-2339.3-2	2339.3	P	0.60	1675	226	25	–	–0.9	–4.1
C203-2341	2341.0	P	0.61	1917	220	24	–	–0.7	–4.2
C203-2353	2353.0	P	0.61	1763	142	22	–	–0.8	–4.0
C203-2357.8-1	2357.8	P	0.59	1804	133	28	0.70622	–1.0	–4.3
C203-2357.8-2	2357.8	P	0.61	2150	140	23	–	–1.0	–4.3
C203-2359.6	2359.6	P	0.61	2024	197	16	–	–1.0	–5.6
C203-2359.6-1	2359.6	P	0.59	1146	115	11	–	–0.9	–5.1
C203-2359.6-2	2359.6	S	0.58	4531	515	9	–	–1.1	–8.8
C203-2363.2	2363.2	P	0.56	1653	132	27	–	–0.9	–4.2
C203-2372-1	2372.0	S	0.58	1379	116	22	–	–1.2	–5.7
C203-2372-2	2372.0	P	0.59	1524	143	15	–	–0.9	–4.3
C203-2427.5-1	2427.5	P	0.59	1924	178	15	–	–1.1	–6.4
C203-2430-1	2430.0	P	0.58	1690	122	33	–	–1.0	–3.5
C203-2430-2	2430.0	P	0.60	665	40	30	–	–0.9	–3.1
C203-2450.4	2450.4	P	0.59	961	61	22	–	–0.8	–3.9
C203-2459.8	2459.8	P	0.60	892	70	16	–	–0.6	–4.0
C203-2557.6	2557.6	P	0.59	1668	78	22	0.70961	–0.8	–5.0
C203-2562.7	2562.7	P	0.59	1729	107	15	–	–0.6	–4.3
C203-2650.5-1	2650.5	P	0.58	1751	106	21	–	–0.4	–5.1
C203-2751.5	2571.5	P	0.60	1635	73	19	–	–0.9	–4.9
C203-2958.2-1	2958.2	P	0.58	4473	536	18	–	–2.4	–5.5
C203-2958.2-2	2958.2	S	0.59	7632	899	33	–	–2.8	–7.0
C203-3056.7	3056.7	P	0.01	1081	62	280	0.70463	–3.4	–7.3
C203-3164.6-1	3164.6	P	0.45	5663	169	122	0.70604	–1.7	–4.7
C203-3164.6-1A	3164.6	P	0.47	6015	196	120	–	–1.6	–3.8
C203-3256.8	3256.8	P	0.56	1658	75	24	–	–0.4	–3.6
C203-3259.7	3259.7	S	0.00	337	26	960	–	–0.3	–7.2
C203-3350.5	3350.5	P	0.26	8720	258	169	–	–1.0	–3.8
C203-3506.3	3506.3	P	0.01	3244	392	110	–	–1.9	–7.0
C203-3582	3582.0	P	0.01	2474	346	162	0.70625	–1.6	–8.0
C203-3654	3654.0	P	0.01	3045	335	102	–	–2.2	–7.7
C203-3752.6	3752.6	P	0.02	2224	355	140	–	–1.6	–7.7
C203-3852-1	3852.0	P	0.41	17119	1028	142	–	–1.2	–4.1
C203-3852-2	3852.0	P	0.02	5414	448	145	–	–1.8	–7.9
C203-4078	4078.0	P	0.46	19537	1014	181	–	–1.7	–4.9
C203-4097-A	4097.0	P	0.02	3928	271	287	0.70536	–2.0	–8.4
C203-4097-B	4097.0	P	0.03	3512	251	275	–	–2.1	–8.8
C203-4106	4106.0	P	0.04	4656	262	389	–	–1.9	–9.5
C203-4173.7	4173.7	P	0.42	49623	1642	227	–	–	–
C203-4261.5	4261.5	P	0.27	55424	2005	169	–	–2.7	–7.5
C203-4283.5	4283.5	P	0.30	30664	2115	130	–	–2.4	–6.3
C203-4355	4355.0	P	0.02	6916	885	132	–	–4.0	–9.2
C203-4388	4388.0	P	0.49	33231	1274	236	–	–1.9	–6.0
C203-4392.12	4392.12	P	0.56	40040	1509	216	–	–2.4	–6.3
C203-4413.9	4413.9	P	0.16	8797	456	142	–	–2.0	–8.5
C203-4445.8	4445.8	P	0.40	12617	647	120	–	–1.3	–6.1
C203-4449	4449.0	P	0.26	12095	440	113	–	–1.6	–7.5

Note: (*) primary (P) and secondary (S) sedimentary phases; (**) uncertainty ±0.2‰ V-PDB for $\delta^{13}C$ and ±0.01‰ V-PDB for $\delta^{18}O$.

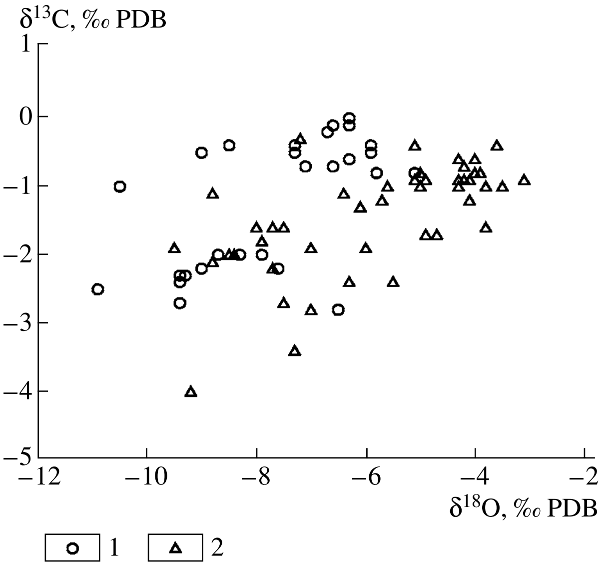

Fig. 5. $\delta^{13}C$–$\delta^{18}O$ diagram for carbonates of the Kaltasy Formation: (1) Borehole 133, Azino-Pal'nikovo area; (2) Borehole 203, Bedryazh area.

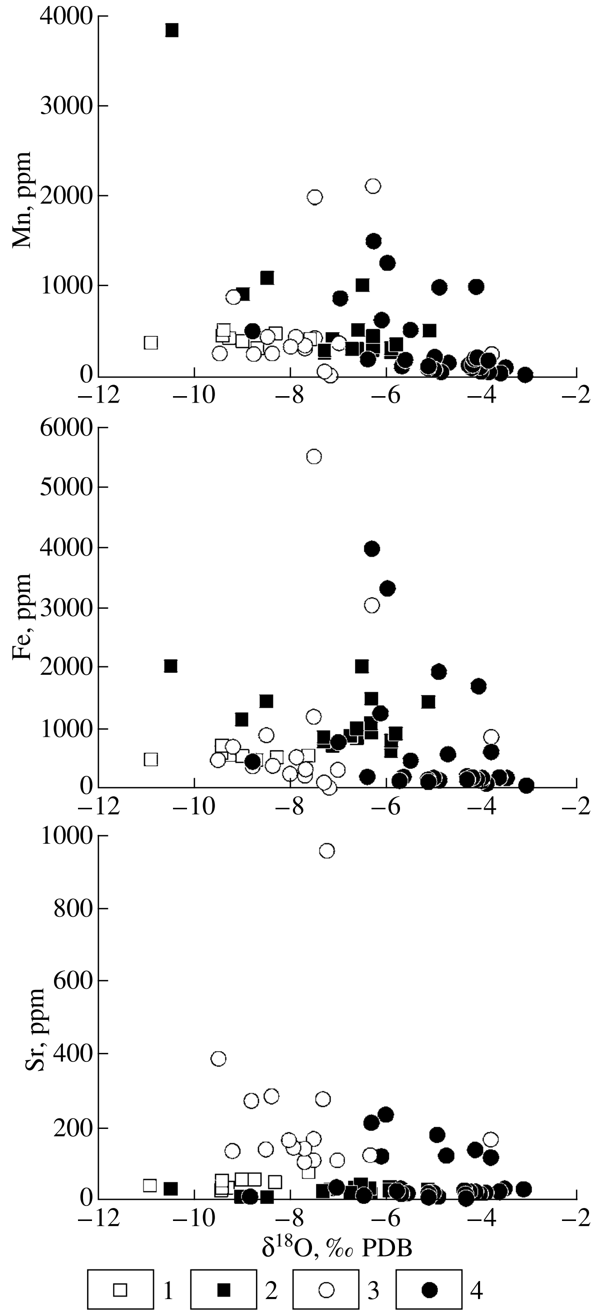

Fig. 6. Carbonates of the Kaltasy Formation in $\delta^{18}O$ versus Mn, Fe and Sr diagrams: (1) limestones from Borehole 133, Azino-Pal'nikovo area, and (2) Borehole 203, Bedryazh area; (3) dolostones from Borehole 133, Azino-Pal'nikovo area, and (4) Borehole 203, Bedryazh area.

paratively high concentrations of both elements in pore fluids. In addition, Mn^{2+} and Fe^{2+} distribution in carbonate sediments is controlled to some extent by tendency of both cations to replace Mg^{2+} and Ca^{2+} in dolomite crystal lattice (Brand and Veizer, 1980). Higher Mn and Fe concentrations in dolostones with $\delta^{18}O >$ –7‰ can be interpreted as evidence of near-bottom dolomitization of sediments with reduced pore fluids, which are almost concurrent to precipitation (Kah et al., 1999).

Strontium concentrations in the Kaltasy carbonates also suggest that trace element distribution was controlled by mineral composition rather than chemical exchange during diagenesis. As Sr concentrations are comparatively higher in limestones of the Kaltasy Formation, we assume partial loss of this element during the early lithification and dolomitization of sediments.

Sr isotopes are commonly most sensitive indicators of diagenesis (Banner and Hanson, 1990). Even in samples with Mn/Sr < 10, Sr-isotopic ratios evidence alterations best explainable in terms of diagenetic impact. As one can see in Fig. 7, there is distinct correlation of Sr concentrations and $^{87}Sr/^{86}Sr$ ratios in the rocks. Two samples from Borehole 133, Azino-Pal'nikovo area, and one from Borehole 203, Bedryazh area, reveal much higher $^{87}Sr/^{86}Sr$ ratios (> 0.70763) than other samples with this parameter ranging from 0.70463 to 0.70625. As all three samples show Mn/Sr ratios (3.5–9.5), which are much higher than values admissible for slightly altered carbonates (Melezhik et al., 2001a), and low Sr concentrations (< 75 ppm), the high $^{87}Sr/^{86}Sr$ ratios may represent in this case a result of epigenetic alterations. In two limestone samples from Borehole 203, Bedryazh area, $^{87}Sr/^{86}Sr$ ratios correspond to 0.70463 and 0.70536. These samples with high Sr concentrations (>250 ppm) and lowest Mn/Sr ratios (<1) apparently characterize better than others the $^{87}Sr/^{86}Sr$ initial ratios in carbonates of the Kaltasy Formation. The rest of samples with $^{87}Sr/^{86}Sr$ ratios from 0.70604 to 0.70625 and Mn/Sr = 1.3–4.7 likely experienced post-sedimentary alterations.

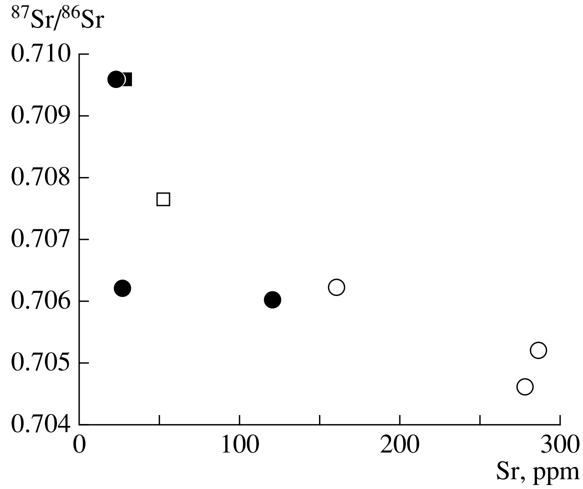

Fig. 7. Carbonates of the Kaltasy Formation in $^{87}Sr/^{86}Sr$ – Sr diagram (symbols as in Fig. 6).

Facies dependence of isotopic parameters. Oxygen isotope composition in the studied dolostones and limestones suggests only limited exchange of rocks with meteoric fluids and/or groundwaters, while trace element concentrations seem to have been controlled primarily by mineral composition. C- and O-isotope compositions in the Kaltasy carbonates are dependent of early diagenetic alterations as is shown above. $\delta^{13}C$ and $\delta^{18}O$ values are positive in dolostones from two studied boreholes, widely ranging in limy dolostones, and negative in limestones (Fig. 8).

Depending on sedimentation settings, limestones and dolostones have different structural patterns and composition. Limestones commonly micritic are of homogeneous texture and form thin interlayers predominantly in clayey intervals of the succession that is indicative of comparatively deep sedimentation settings. In contrast, rocks of dolomitic composition are classed with homogeneous dolomicrites, microturbidites, intraclastic breccias with slump folds, fenestral microbiolites, and grainy rocks; they originated in diverse settings of intermediate shelf to intertidal zone. Dolostones composed of fine crystalline grains (Fig. 4) suggest that dolomitization took place at the early stage of sedimentary lithogenesis. Structure of this kind is commonly a result of the early diagenetic dolomitization of carbonate sediment under influence of seawater or fluid nearly concurrent to sedimentation, and $\delta^{13}C$ values characterize in this case the carbon isotope composition in seawater (Kah, 2000, and references therein). This conclusion is consistent with relatively high Sr concentrations in dolostones of shallow-water marine settings, where the early diagenetic recrystallization took place under conditions of slight evaporation.

The relatively lower $\delta^{13}C$ values (from –2 to –2.5‰) in limestones, as compared to those in associated dolostones, can be explained by influence of several factors. These are (1) geochemical exchange with $\delta^{13}C$-depleted diagenetic fluids, (2) early diagenetic capture of light carbon isotope released by recrystallization of organic sedimentary material, and (3) original C-isotope depth-dependent gradient in seawater. Influence of postsedimentary alterations cannot be excluded as well. Without migration of fluid phase enriched in HCO_3^-, initial dissolution and recrystallization of carbonate phase usually buffer the carbon isotope composition, and radical changes of $\delta^{13}C$ values are hardly probable even in the case of postsedimentary thermal impact (Wickham and Peters, 1993).

Limestones of the Kaltasy Formation, which are apparently of deep-water origin, are frequently intercalated with sediments enriched in organic matter (Fig. 4). It is admissible therefore that the early diagenetic recrystallization in presence of fluids depleted in relevant carbon isotope and derived from decomposing organic substance (Schidlowski et al., 1983; Hayes, 1993) was responsible for lowered $\delta^{13}C$ values in limestones. Some observations show, however, that this is not the case. First, remineralization of dispersed

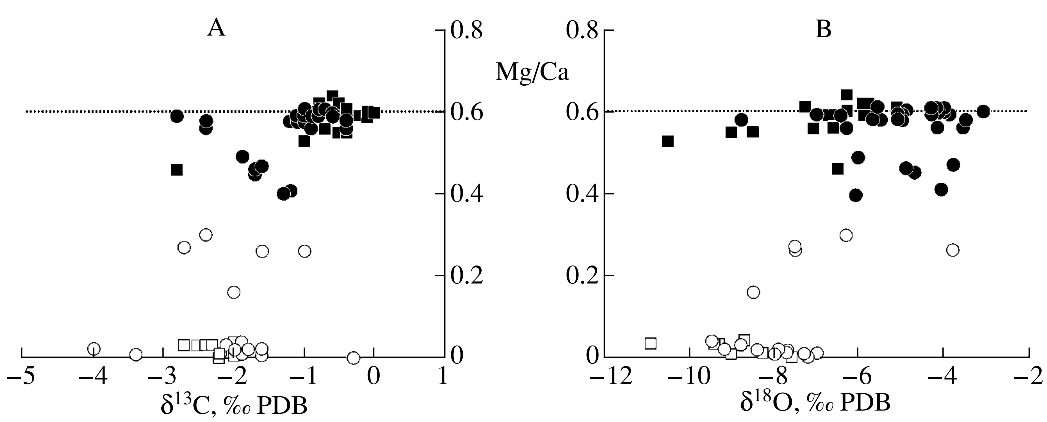

Fig. 8. Carbonates of the Kaltasy Formation in Mg/Ca–$\delta^{13}C$ (A) and Mg/Ca–$\delta^{18}O$ (B) diagrams (symbols as in Fig. 6).

organic matter cannot be the reason of low $\delta^{13}C$ values in those limestones of the Kaltasy Formation, which are so strongly depleted in this material. Second, the values under consideration are remarkably lower in limestones than in dolostones (Tables 1 and 2), including those, which contain relatively considerable amount of organic material. Since the early marine dolomitization is closely interrelated with processes of organic matter decomposition (bacterial sulfate reduction), lowered $\delta^{13}C$ values should be typical of those dolostones as well, but this not the case.

It is more reasonable to assume that depletion of limestones in isotope $\delta^{13}C$ suggest influence of marine isotopic depth gradient in sea basin, where it appears because of comparatively greater influx of organic mater into deep-water environments and its decomposition within the water column that results in imbalance of marine carbon isotope composition, which grows with depth (Kump, 1991). Carbonate that is either precipitated or undergoes very early diagenetic recrystallization in environments affected by this depth gradient will aquire C-isotope composition that record the gradient. The assumption is consistent with both sedimentological and geochemical interpretations of carbonate rocks of the Kaltasy Formation. Dolostones, which are most likely of shallow-water genesis, have the highest $\delta^{13}C$ values, whereas calcic dolomites from intermediate depth zone show variable isotopic parameters, and the highest $\delta^{13}C$ values are recorded in limestones of presumably deep-water origin. If isotopic parameters of core samples from Borehole 203, Bedryazh area, recorded depth-dependent changes of $\delta^{13}C$ values, then the relevant variations should be considered as modifications of carbon isotopic composition in surface water, which introduce uncertainty into chemostratigraphic correlation. In this case, isotopic profile recorded by predominantly shallow-water carbonates, which are recovered by Borehole 133 in the Azino-Pal'nikovo area, could be used for comparison with standard curves, because carbon isotope composition is commonly well averaged in surface seawater. Although the established amplitude of isotopic variations (approximately ±1‰) is insufficient for detailed correlation of stratigraphic sequences, it is appropriate for correlation within wider time spans with the standard Meso–Neoproterozoic C-isotope curve (Kah et al., 1999, 2001).

Chemostratigraphic results. Trends of $\delta^{13}C$ variations in two studied borehole sections are shown in Fig. 9. Almost invariant distribution of carbon isotopes ($\delta^{13}C$ about –1‰) is established in lower 800 m of section penetrated by Borehole 133 in the Azino-Pal'nikovo area (depth range 3350–2550 m), while within 600 m upsection (depth range 2550–2030 m) parameter $\delta^{13}C$ suddenly declines (variations from –2.2 to –2.8‰). Although sampled carbonate horizons are rare in this interval, where they occur, they are dominantly limestone in mineralogy, preserve depositional fabrics indicative of subtidal deposition, and are interbedded with black shale and shaly horizons. Carbon isotope composition in carbonate rocks from Borehole 203, Bedryazh area, is more variable. This section is divisible into several successive intervals: in the basal one 300 m thick (depth range 4450–4150 m), $\delta^{13}C$ values decrease from –1 to nearly –3‰; in the next interval of the same thickness (depth range 4100–3800 m), they increase to –2‰; within the depth range 3800–3300 m, remain relatively constant before growing to values near –0.5‰. After reaching these more positive values, $\delta^{13}C$ values shift abruptly at the next 300 m (depth interval 2900–3200 m) to more negative values (to –3.4‰) in coordination with a change to more shaley, carbonate-poor lithologies. Return of carbonate-rich deposition and appearance of shallow-water depositional fabrics and dolomitic lithologies (560 m of the section, depth range 2900–2340 m), leads to $\delta^{13}C$ increase to 0‰, where it remains for topmost 300 m of the section.

In general, carbon isotope composition in carbonates of the Kaltasy Formation is comparatively constant ($\delta^{13}C \sim -1.0 \pm 1.0$‰). The highest and least variable $\delta^{13}C$ values are characteristic of shallow-water dolostones. The observable variation trends are interpreted as indicative of easily going dolomitization in shallow-water environments of paleobasin with marine carbon isotope depth gradient recorded in the least altered samples.

In the least altered limestones of the Kaltasy Formation, $^{87}Sr/^{86}Sr$ ratio is below 0.70625; two lowest values are 0.70536 and 0.70463. In dolostones from two studied boreholes, this ratio is higher, but high Mn/Sr ratios and low Sr concentrations in these rocks imply that initial Sr-isotope composition was changed in the course of epigenetic alterations. The lowest $^{87}Sr/^{86}Sr$ ratios are established in deep-water limestones from Borehole 203, Bedryazh area.

Chemostratigraphic data and age interpretation of the Kaltasy Formation. In large stratigraphic intervals of sections recovered by boreholes 133 and 203 in Azino-Pal'nikovo and Bedryazh areas, variations of carbon isotope composition in carbonates are insignificant: $\delta^{13}C$ values characterizing shallow-water sediments commonly range between 0 and –1‰. The values decreasing approximately to –2.5‰ are facies dependent and best explainable as indicative of the carbon isotope depth gradient in paleobasin. The variation trend of carbon isotope composition in studied carbonates is comparable with the trends characterizing two carbonate succession in Australia: first, in the Bangemall Group that is younger than 1626 ± 10 Ma (U–Pb zircon date obtained by D.R. Nelson and cited in Buick et al., 1995), and second, in the McArthur Group deposited 1640–1600 Ma ago according to U–Pb zircon dates for the lower part of Barney Creek Formation (Page and Sweet, 1998). Similar variation trends are also established in carbonates of the Changcheng and Jixian groups ranging in age from 1624 ± 6 (U–Pb zircon age of extrusive volcanics, Lu and Li, 1991) to approxi-

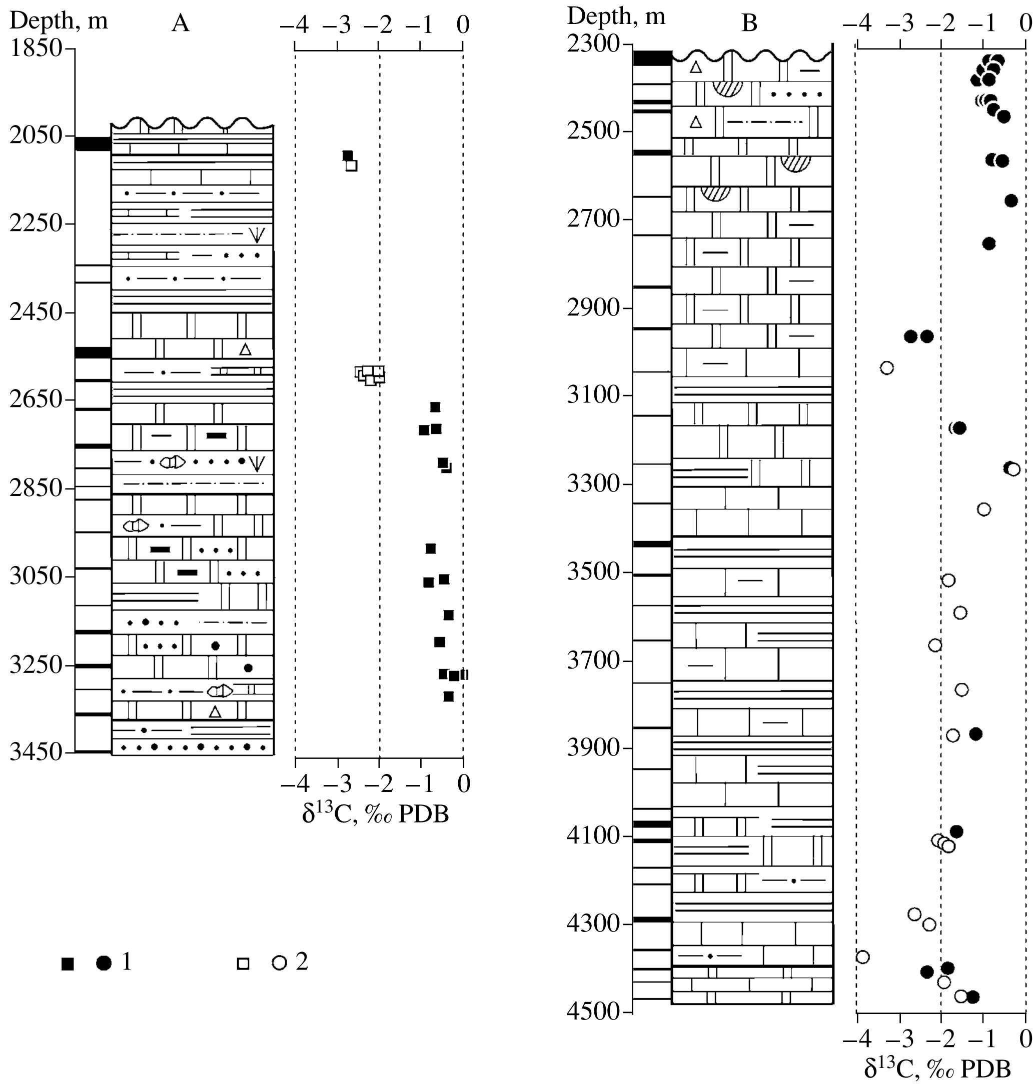

Fig. 9. $\delta^{13}C$ variation trends in the Kaltasy Formation carbonates recovered in the Kama–Belaya aulacogen by boreholes 133, Azino-Pal'nikovo area (A) and 203, Bedryazh area (B): (1) dolostones; (2) limestones (other symbols as in Fig. 2).

mately 1350 Ma according to the following series of dates: 1496 ± 80 and 1474 ± 52 Ma (Pb–Pb ages of carbonates from the Wumishan Formation); 1392 ± 44 Ma (Pb–Pb age of carbonates in the uppermost Tieling Formation, Jahn and Cuvellier, 1994). The other subdivisions in question are the Luonan Group of China (Xiao et al., 1997), the Carswell Formation of Canada (Abell et al., 1989), and the Belt Supergroup in Montana, the United States (Frank et al., 1997). Similar chemostratigraphic trends have been observed as well in the Lower Riphean Billyakh Group of the Anabar massif (Knoll et al., 1995b), in the Aimchan and Kerpyl (lower part) groups of the Uchur–Maya region in Siberia (Bartley et al., 2001). Basal part of the Ust-Il'ya Formation is of the Early Riphean age according to Rb–Sr (1483 ± 5 Ma) and K–Ar (1459 ± 10 Ma) age of glauconite from this level (Gorokhov et al., 1991). However, K–Ar age of mineralogically unstudied glauconite from the Usmastakh Formation lower part (1260, 1170–1070 Ma, Manuilova, 1968) suggest that sedimentation lasted also in the Middle Riphean. Glauconite and illite from the Aimchan Group is 1260–1200 Ma old (Semikhatov and Serebryakov, 1983), and the minimum age limits of the Kerpyl Group are 1300 Ma (U–Pb date of 1300 ± 5 Ma is obtained for detrital zircon from the Totta Formation, Khudoley et al., 2001). The upper age limit of the Aimchan and Kerpyl groups is inferable from Pb–Pb age of 1025 ± 40 Ma estimated for lower carbonates of the overlying Lakhanda Group (Semikhatov et al., 2000).

In carbonates of the Kaltasy Formation, $\delta^{13}C$ values are lower in general and less variable than in the upper part of Middle and Upper Riphean deposits in the southern Urals (Podkovyrov et al., 1998) and in other regions of the world (Kah et al., 1999, and references therein). The lowest $^{87}Sr/^{86}Sr$ ratio established in the studied carbonates (0.70463) is considerably lower than the ratios reported for Middle and Upper Riphean successions of southern Urals (Gorokhov et al., 1995; Kuznetsov et al., 1997; Podkovyrov et al., 1998; Bartley et al., 2001). Comparable $^{87}Sr/^{86}Sr$ ratios have been reported for limestones of the Lower Riphean Bakal Formation in the southern Urals (0.70456–0.70481; Kuznetsov et al., 2003) and for carbonate rocks of the Belt Supergroup (0.70484–0.70514; Hall and Veizer, 1996) and Lower Riphean Kyutingda Formation of the Olenek Uplift (0.70465; Gorokhov et al., 1995). Consequently, deposits of the Kaltasy Formation and Kyrpy Group should be attributed to the Lower Riphean.

CONCLUSIONS

Siliciclastic and carbonate deposits of the Kyrpy Group, the East European platform, used to be correlated with Lower Riphean deposits of the Burzyan Group, although there was the alternative idea to correlate them with the Middle Riphean Yurmata Group or even the Upper Riphean Karatau Group of the Bashkirian meganticlinorium, the southern Urals. Carbonate rocks of the Kaltasy Formation recovered by boreholes 133 and 203 in Azino-Pal'nikovo and Bedryazh areas of the Kama–Belaya aulacogen retain C- and Sr-isotopic signatures of sedimentation environment and earliest marine diagenesis. Comparatively low $^{87}Sr/^{86}Sr$ ratios and stratigraphically almost invariant $\delta^{13}C$ values established in carbonates of the Kaltasy Formation are incompatible with chemostratigraphic profiles known for Middle and Upper Riphean deposits of the southern Urals and elsewhere, being comparable in these parameters with deposits older than 1300 Ma. Consequently, new chemostratigraphic data approve the Early Riphean age of the Kaltasy Formation and Kyrpy Group.

ACKNOWLEDGMENTS

The work was supported by NASA Exobiology grant NAG5-10666 (L.C.K. and J.K.B). We are grateful to Zheng-Hua-Li (University of Tennessee) and Alice Stagner (State University of West Georgia) for their kind assistance in geochemical study. The manuscript was considerably improved after thoughtful criticism of I.M. Gorokhov, A.B. Kuznetsov (IPGG RAS, St. Petersburg), and M.A. Semikhatov (GIN RAS, Moscow). Our special thanks are to administration of Udmurtneft and Permneft companies for permission to study core samples from boreholes 133 and 203 drilled in Azino-Pal'nikovo and Bedryazh areas.

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