

New Data on Sr- and C-Isotopic Chemostratigraphy of the Upper Riphean Type Section (Southern Urals)

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Abstract—New data on Sr- and C-isotopic systematics of carbonate rocks from the Upper Riphean stratotype (Karatau Group of the southern Urals) are obtained for several southwestern sections of the Bashkirian meganticlinorium, which have not been studied before. The results obtained supplement the Sr- and C-isotopic information for the group upper horizons thus detailing chemostratigraphic characterization of the entire succession. Limestone and dolostone samples used to analyze the Sr isotope composition satisfy strict geochemical criteria of the isotopic system retentivity and have been subjected to preliminary treatment in ammonium acetate to remove secondary carbonate phases. Data on 255 samples of carbonate rocks (171 studied for the first time) show that $\delta^{13}\text{C}$ value varies in the Karatau Group succession from -2.8 to $+5.9$ ‰ V-PDB with several in-phase excursions from the general trend in all the sections studied in the area 90×130 km. The $\delta^{13}\text{C}$ variation trend demarcates several levels in the carbonate succession of the Karatau Group suitable for objectives of regional stratigraphy and for C-isotope chemostratigraphic subdivision of the Upper Riphean. The results of Sr isotopic analysis of 121 samples (51 unstudied before) from the Karatau Group imply that rocks in its lower part (the Katav Formation and basal horizon of the Inzer Formation) experienced considerable secondary alterations, while limestones and dolostones of the overlying interval of the group are frequently unaltered. In the “best” samples satisfying geochemical criteria of the isotopic system retentivity, the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio increases from 0.70521–0.70532 in the lower Inzer deposits to 0.70611 in the upper Min’yar carbonates, decreasing to <0.70600 near the top of the latter. Above the regional hiatus separating the Min’yar and Uk formation, this ratio grows from 0.70533 to 0.70605–0.70609 in the limestone succession of the last formation.

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INTRODUCTION

Investigations of last decade enhanced the database of Sr- and C-isotopic chemostratigraphy and feasibility of its application for interregional correlation of Upper Proterozoic deposits and relevant paleogeodynamic considerations. Nevertheless, there are several reasons decelerating scientific progress in these directions. (1) Geochemical criteria used to select carbonate rocks most appropriate for assessment of Sr and C isotope composition in seawater of geological past are not uniform so far, although this is particularly important for the Rb–Sr isotopic system less resistant against epigenetic alterations of rocks than the C isotopic system. (2) The confident C- and Sr-isotopic database for Precambrian carbonate rocks is much less representative than that for the Phanerozoic. (3) Available isotopic-geochronological and biostratigraphic data are often insufficient for compiling the Sr- and C-isotopic char-

acteristics, which are obtained for discrete section intervals in distant regions, into a single trend. As a result, several contradicting curves depicting $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in seawater are suggested even for the Upper Riphean–Vendian interval of the Precambrian that is studied better than others (Derry et al., 1989, 1992; Asmerom et al., 1991; Kaufman and Knoll, 1995; Gorokhov et al., 1995, 1996; Saylor et al., 1998; Walter et al., 2000; Bartley et al., 2001; Melezhik et al., 2001; Kuznetsov et al., 2003; Semikhatov et al., 2004).

Participating in long-lasting research of Riphean deposits in the Urals and Siberia, we have understand methodic requirements, following which one can overcome the above shortcomings (Gorokhov et al., 1995; Kuznetsov et al., 1997, 2003; Melezhik et al., 2001; Semikhatov et al., 2002). The main of them are (1) investigation of thick, predominantly carbonate successions confidently dated with reference to the chronos-

stratigraphic scale, (2) sampling of several concurrent sections in different structures of a region, and (3) application of strict geochemical criteria for evaluation of C- and Sr-isotopic systems' retentivity in carbonates.

The Karatau Group of southern Urals acknowledged as the Upper Riphean stratotype has been the priority object of our research. Rocks of the group are widespread in different facies zones of a vast area, insignificantly altered, well studied in lithologic-facies aspect, having representative isotopic-geochronological and paleontological characterization. First data on C- and Sr-isotopic chemostratigraphy of the group have been obtained for its fragments in four separate sections (Fig. 1): near the town of Min'yar, at the Shubino and Kulmas localities, and in the Manaisu River lower reaches (Semikhatov et al., 1995; Gorokhov et al., 1996; Kuznetsov et al., 1997; Podkovyrov et al., 1998). Unfortunately, sections of the first two localities were misleadingly correlated by compilation of the group succession (Raaben, 2001), and in the group upper part there appeared a gap of unclear duration in the C- and Sr-isotopic characterization of rocks. Besides, data obtained later on showed a considerable hiatus near the group top (Ovchinnikova et al., 1998, 2000; Zaitseva et al., 2000; Kuznetsov et al., 2003). To verify chemostratigraphy of the Upper Riphean stratotype, we studied carbonates of the Karatau Group in five unstudied southwestern sections of the Bashkirian meganticlinorium (Fig. 1), and new results essentially enhanced the former database. Comparing the new and formerly published data, we got opportunity to show the lateral persistence of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values over the area 90×130 km that proves their validity, to divide the group into several chemochrons with different $\delta^{13}\text{C}_{\text{carb}}$ parameters, and to define with a higher precision the variations of Sr isotope composition in seawater of the Late Karatavian time.

LITHOSTRATIGRAPHY AND CHRONOMETRY OF THE KARATAU GROUP

Siliciclastic and carbonate rocks of the Karatau Group 3.5 to 5.5 km thick are exposed in western limb of the Bashkirian meganticlinorium, a large thrust-and-fold structure of the southwestern Urals. Deposits of the group discordantly overlie the Yurmatin Group (the Middle Riphean stratotype) and have unconformable boundary with overlying tillites and terrigenous sediments of the Vendian Asha Group (Garan', 1963; *The Riphean Stratotype...*, 1983; Maslov et al., 2001). In the regional stratigraphic scheme that is adopted at present (*The Riphean Stratotype...*, 1983; Kozlov et al., 1991; Maslov et al., 2001), the Group is divided into six units (from the base upward): the Zilmerdak (siliciclastic deposits 1200 to 3300 m thick), Katav (variegated limestones 150–350 m thick), Inzer (siliciclastic-carbonate succession 300–800 m thick), Min'yar (predominantly dolomite succession 350–800 m thick), Uk (siliciclastic-carbonate sediments 160–300 m thick), and

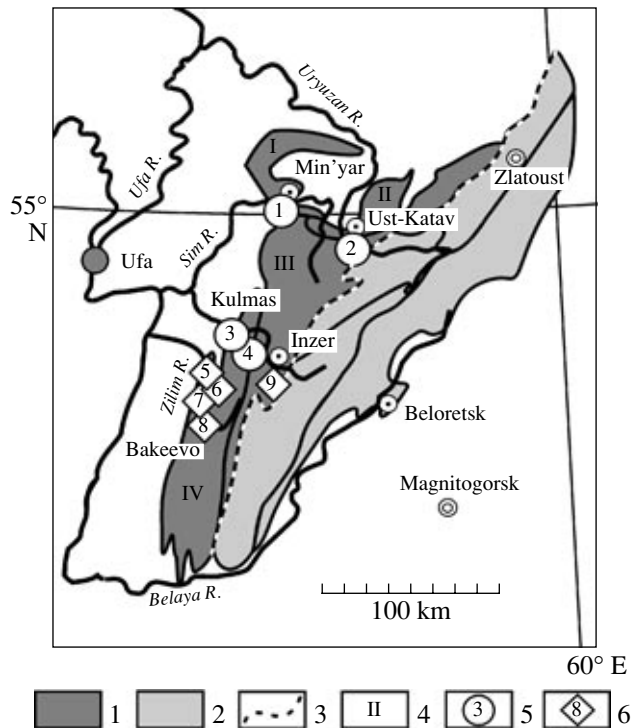


Fig. 1. Localities of the Karatau Group sections studied in the southwest of Bashkirian meganticlinorium: (1) outer facies zone; (2) inner facies zone; (3) boundary between facies zones; (4) structural units of the outer zone; (5) sections studied earlier (Podkovyrov et al., 1998; Kuznetsov et al., 2003); (6) sections studied in this work. Structural units of the outer facies zone: (I) Karatau structural complex; (II) Suleimanovo anticline; (III) Inzer synclinorium; (IV) Alatau anticlinorium. Sections by names numbered in figure: (1) Min'yar; (2) Shubino; (3) Kulmas; (4) Manaisu; (5) Tolparovo-1; (6) Tolparovo-2; (7) Bakeevo; (8) Kurtaza; (9) Usmangali.

Krivaya Luka (siliciclastic rocks up to 560 m thick) formations. The Uk Formation crowns the group section in the western limb of Bashkirian meganticlinorium, and the Krivaya Luka Formation is preserved after the pre-Vendian erosion in the east of the structure only. Three lower formations are interrelated via gradual transitions, whereas stratigraphic unconformities are recorded at the Uk Formation base and locally at the Min'yar Formation base (Bekker, 1961, 1988; Raaben, 1975; Kozlov et al., 1991; Maslov et al., 2001, 2002; Maslov, 2002). The pre-Uk unconformity is regional, whereas the local pre-Min'yar hiatuses signify short-term events of subaerial exposition in separate synsedimentary rises.

Current understanding of the Karatau Group age limits is based on some paleontological data and on isotopic dates of unequal validity. The isochron Pb–Pb date of 836 ± 25 Ma that has been obtained for limestones of the lower Inzer Subformation (Ovchinnikova et al., 1998) is the most reliable one. It defines the time of early diagenesis in the lower Inzer limestones being consistent with the Rb–Sr dates ranging from 835 to

805 Ma, which characterize the authigenic 1M illites from the same subformation and correspond to the age of burial diagenesis (Gorokhov et al., 1995). The Pb–Pb date of 780 ± 85 Ma characterizing dolostones from the middle part of the overlying Min'yar Formation is determined with a rather high uncertainty because of the rock alterations in the course of epigenetic sulfide mineralization (Ovchinnikova et al., 2000). The reliable Rb–Sr and K–Ar isochron ages of 664 ± 11 and 669 ± 16 Ma, respectively, are known for glauconites from the lower Uk Subformation. The Mössbauer spectroscopy showed that epigenetic alterations did not affect the fine structure of glauconites, thus indicating retentivity of their isotopic-geochronological systems (Zaitseva et al., 2000). The K–Ar dates obtained in the 1960s–1980s for mineralogically unstudied glauconites from different horizons of the Karatau Group are less reliable: the Katav–Inzer boundary horizons are dated at 938 Ma; the Inzer Formation lower part at 896–853 Ma; the upper Member of this formation at 790–740 Ma. The dates of 713 to 680 Ma characterize the lower Min'yar Subformation, and values of 658 to 630 Ma (K–Ar) and 688 ± 10 Ma (Rb–Sr) are determined for the lower Uk Subformation (*The Riphean Stratotype...*, 1983; Gorozhanin and Kutuyavin, 1986). The upper age limit of the Karatau Group used to be defined by the isochron Rb–Sr date of 618 ± 13 Ma obtained for glauconite from the lower part of the Asha Group (Kozlov and Gorozhanin, 1993) and by the K–Ar dates of 600 to 557 Ma characterizing glauconites from overlying strata of the group (*The Riphean Stratotype...*, 1983). The attempts to estimate age limits of the Karatau Group using K–Ar dates for whole-rock samples of gabbro-diabases are not convincing: first, the K–Ar isotopic systems of magmatic whole-rock samples are labile, and second, geological relations of the dated gabbro-dabase bodies with the group deposits are inadequately known.

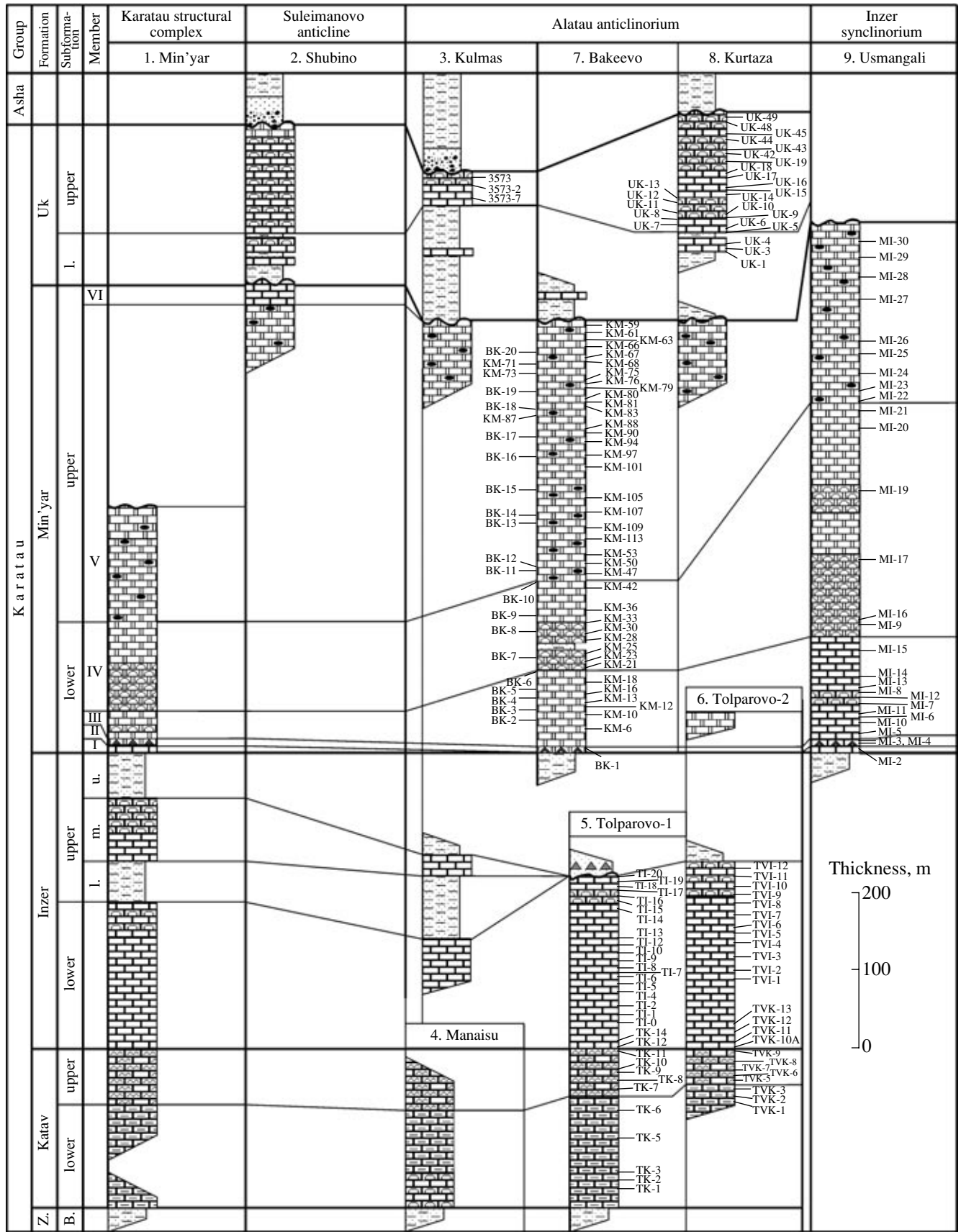
Paleontological data show important changes in composition of organic-walled microfossils in the upper part of Zilmerdak Formation, at the base of its terminal Bederysh Subformation. At this level, transit taxa known from lower horizons of the succession (*Chuarina*, *Navifusa*, *Simia nerujenica*, *Ostiana*, *Poly-spheroides contexus*, *Asperatofilum*, *Taenitrichoides*, *Plicatidium*, *Rectia*, *Botuobia*, *Majaphyton*, *Lakhandinia*, and others) occur in association with acanthomorphic acritarchs *Trachyhystrichosphaera stricta*, *T. truncata*, *Tortunema*, *Glomovertella*, and *Arctacellularia*, which appear for the first time and are typical of the Upper Riphean (Veis et al., 2003). In Siberia, acri-

tarchs of the genus *Trachyhystrichosphaera* define compositional aspect of the well-known Lakhandia microbiota from the Uchur-Maya region and of concurrent (Semikhatov et al., 2002) Derevnya microbiota from the Turukhansk Uplift, which are predated by assemblages similar to those from the pre-Bederysh part of the Karatau Group (German, 1990; Veis et al., 1998). According to available dates obtained for carbonate rocks by the isochron Pb–Pb method, the maximum age limit of the Lakhandia and Derevnya microbiotas is 1030 Ma (Semikhatov et al., 2000; Ovchinnikova et al., 2001). The *Melanocerillium* remains are reported to occur in the middle of the Min'yar Formation (Maslov et al., 1994), though they have not been illustrated and described to our regret. Representatives of this genus attributed to testate amoebae appear in the geological record about 800 Ma ago (Porter and Knoll, 2000). Stromatolites described from the Katav Formation (Krylov, 1963, 1975; *The Riphean Stratotype...*, 1982) are known in Siberia from deposits ranging in age from 1030 to 900 Ma, while their taxa characteristic of the Karatau Group upper part tend to occur in higher Upper Riphean horizons of Siberian sections (Semikhatov and Serebryakov, 1983; Semikhatov and Raaben, 1994). Thus, the Karatau Group interval composed predominantly of carbonate rocks is younger than 1030 and older than 618 ± 13 Ma.

In the western limb of the Bashkirian meganticlinorium, Karatavian deposits of inner and outer facies zones are separated by the Zilmerdak thrust fault (Garan', 1963; Senchenko, 1976; *The Riphean Stratotype...*, 1983). These zones differ from each other in folding style, degree of rocks' alteration, and in proportions of carbonate rocks above the Zilmerdak Formation: about 50% in the inner (eastern) zone and up to 85–90% in the outer one. The degree of rocks' alteration decreases in the same direction: they experienced deep catagenesis and low-T dynamothermal impact in the inner zone and deep to locally initial catagenesis in the outer zone (Anfimov, 1997; Maslov et al., 2001). Sections studied in this work and earlier are situated in four structures of the western facies zone (Fig. 1). Their description is presented below (Fig. 2).

The Katav Formation studied in the Min'yar, Kulmas, Manaisu, Tolparovo-1 and Tolparovo-2 sections is divided in two subformations. The lower subformation is composed predominantly of variegated flaggy clayey limestones with rare marl interlayers, while in the Manaisu section the lower 50 m of this subformation are represented by stromatolites *Inzeria tjomusi* and *Jurusania cylindrical*. The Mg/Ca ratio in the subfor-

Fig. 2. Lithostratigraphy of the Karatau Group above the Zilmerdak Formation and sampling levels in sections studied in this work: (1) fine-grained, (2) stromatolitic, (3) clayey and (4) microbial laminated limestones; (5) dolostones; (6) dolostones with cherty nodules; (7) dolostones and limestones with stromatolites *Conophyton miloradovici*; (8) dolostones with cherty nodules; (9) sandy-clayey deposits; (10) sandstones and gravelstones; (11) tillites of the Vendian Asha Group; (12) stratigraphic unconformities; (l) lower; (m) middle; (u) upper; (Z) Zilmerdak; (B) Bederysh; (I–VI) members of the Min'yar Formation (see text); sampling levels in Min'yar, Shubino, and Manaisu sections are given in works by Podkovyrov et al. (1998) and Kuznetsov et al. (2003).



mation rocks is usually not higher than 0.009; rock varieties relatively enriched in Mg ($Mg/Ca = 0.020\text{--}0.027$) appear in the Tolparovo-1 section and at the subformation base in the Monaisu section. Percentage of siliciclastic admixture (SA) consisting of clay and fine silt fractions is 13 to 15% in average, being at the maximum (31.4–31.8%) at the base of the Tolparovo-1 section and at the minimum (6.3–9.2%) in the upper part of the Manaisu section. The subformation is 120–125 m thick in the Min'yar and Manaisu sections and 170 m thick in the Tolparovo-1 section. In the Kulmas and Tolparovo-2 sections, its upper part only is exposed (45 and 20 m, respectively).

The upper Katav Subformation is represented by pale-yellow to pinkish and greenish gray flaggy clayey limestones, characteristic of which is banding and microbial lamination in the upper part. These micritic limestones enclose finest microsparite lenses, which locally contain segregations of sparite and dolosparite sometimes. The Mg/Ca ratio ranges from 0.001 to 0.019 in most rocks and increases to 0.037 near the subformation base in the Tolparovo-1 and Tolparovo-2 sections, and to 0.054–0.076 in the middle 20-m-thick packet of the subformation in the Min'yar section. In the last section, the SA content in limestones declines from 13.5 to 10.2% toward the subformation top; in the Kulmas section, it is almost constant (13.2–13.5%). In the Tolparovo-1 and Tolparovo-2 sections, the SA concentration intervals are 5.5–16.6 and 9.0–15.8%, respectively, with peak values confined to a small Member below the subformation middle and minimum values near the formation top. Quartz, micas, subordinate feldspars, and chlorite are mineral components of the SA. The subformation is 60 m thick in the Min'yar section and 40–50 m thick in the Tolparovo sections. In the Manaisu and Kulmas sections, only lower subformation level, 20 and 40 m respectively, which are well exposed, have been studied. Rocks of the last section are intensively fissured and contain abundant thin (0.2–2.0 mm) veins of secondary calcite.

The Inzer Formation divided in two subformations is studied in the Min'yar, Tolparovo-1, Tolparovo-2, and Kulmas sections, in the last case fragmentarily. The lower Inzer Subformation is composed of dark gray to black limestones with subordinate interlayers of dolomitic limestones and intercalations of stromatolitic limestones and flakestones in the upper part. The Mg/Ca ratio ranges broadly in the subformation sections and over the study area. Being within the range of 0.002–0.013 in the Min'yar and Kulmas sections, it sometimes grows here up to 0.029–0.030. In most samples (70%) of the Tolparovo-1 section, this ratio is not greater than 0.018, although there are some beds with $Mg/Ca = 0.026\text{--}0.072$ and even 0.291 in one case. The Tolparovo-2 section begins with highly dolomitized limestones ($Mg/Ca = 0.215$), but above them this ratio varies from 0.005 to 0.072. Percentage of the SA is low in the studied samples (0.1–1.9%), being occasionally as high as 2.9–3.0% in the Tolparovo-1 section, 3.5–

4.4% in the Kulmas section, and 2.8–6.5% in the Tolparovo-2 section. The SA is concentrated mostly in basal horizons of the subformation, where its mineral composition is similar to that in the Katav Formation, but higher the SA consists of quartz only. Characteristic of the lower Inzer rocks is alternation of thin micrite and microsparite laminae; some of the latter are 1–3 mm thick, displaying relicts of clastic texture and signs of diffuse, early diagenetic dolomitization. In some samples, there are thin lenticules of fine-crystalline calcite. The subformation is 190 m thick in the Min'yar section, 230–240 m thick in the Tolparovo-2 section, and 210–220 m of its lower part are preserved in the Tolparovo-1 section.

In the Min'yar and Kulmas sections, the upper Inzer Subformation includes two members of greenish gray quartz-glaucanite sandstones and siltstones separated by the carbonate Member. Main rock types of the latter are massive microphytolitic micrites intercalated with stromatolitic and clastic limestones in the upper part. The Mg/Ca ratio in carbonate rocks is ≤ 0.020 in general, rising sometimes to 0.031–0.038. The SA content is 2.4–7.0% at the subformation base, decreasing down to 1.3–1.8% near the top. In the Min'yar section, the subformation is 200 m thick in total, with siliciclastic members 70 and 50 m thick and carbonate one 80 m thick. In the Kulmas section, where thickness of the carbonate Member is reduced to 33 m, the subformation is 180 m thick. In the easterly sections, this Member is wedged out.

The Min'yar Formation is the most thick subdivision of the Karatau Group composed predominantly of carbonate rocks and has been studied in the Min'yar, Shubino, Bakeevo and Us mangali sections. In two comparable stratigraphic schemes known from publications, the formation is divided into subordinate units of specific lithology, containing characteristic stromatolite assemblages but lacking a uniform nomenclature (Raaben, 1975, 1981, 1985; Krylov, 1983; *The Riphean Stratotype...*, 1983). The units are described below as members I–VI (Maslov et al., 2001; Maslov, 2002).

Member I overlies the upper Inzer rocks either via gradual transition (Min'yar section), or with a sharp contact (Us mangali section). It is composed of variegated and gray limestones with intercalations of microphytolitic and stromatolitic varieties, flakestones and calcarenites. In micrite to microsparite limestones, the Mg/Ca ratio ranges from 0.009 to 0.035. Upward in the section, the SA content declined from 7.4–10 to 4.7–4.8%. The Member is 12 m thick in the Min'yar section, while its basal interval 3 m thick only is exposed in the Us mangali section. In the Bakeevo section, the Member is missed, and the upper Inzer strata are separated by a sharp boundary from Member II. In the Tolparovo area, the Inzer–Min'yar boundary is unexposed.

Member II corresponds to gray biostromes of stromatolites *Conophyton miloradovici* and associated microbial laminated carbonates. The Member is com-

posed of dolostones (Mg/Ca = 0.607–0.614) in the Min'yar and Bakeevo sections and of limestones (Mg/Ca = 0.010–0.050) in the Usmangali section. The SA content in the rocks is 2.5–4.8%. In the former sections, the Member is 5 m thick. The upper 13.5 m of the Member exposed in the Usmangali section are separated from Member I by unexposed interval 8 m thick, while its contact with overlying Member III is conformable.

Member III includes microphytolitic, stromatolitic and marly carbonates associated with subordinate calcarenites, intraclasites and micrites displaying syneresis cracks. Like in the Member II, these rocks are of dolomitic composition (Mg/Ca = 0.578–0.647) in the Min'yar and Bakeevo sections, being dominated in the Usmangali section by limestones (Mg/Ca = 0.001–0.007) with thin dolomitized laminae (Mg/Ca = 0.050–0.185). The SA content in the rocks is commonly 0.3–4.3% and much higher (10.2–16.5%) in a calcarenite packet within the lower part of the Member. In the Min'yar, Bakeevo and Usmangali sections, the Member is 40–45, 95–100 and 115–120 m thick, respectively.

Member IV is composed of gray to pinkish gray stromatolitic dolostones, which contain thin siltstone and shale laminae. Large bioherms and biostromes of stromatolites *Minjaria uralica* are associated with flakestones and more rare microphytolitic dolostones. The Mg/Ca ratio ranges in dolostones usually from 0.528 to 0.637, being higher in places. The SA content is 0.9 to 4.7% as a rule, increasing sometimes to 5.0–6.9% and even to 17–40% in the Min'yar section, where rocks are enriched in hydromica and silty material. The Member is 100–110 m thick in the Min'yar and Bakeevo sections, and up to 300 m thick in the Usmangali section, where it is exposed fragmentarily.

Member V corresponds to interval of gray massive or thick-bedded dolosparites with abundant interlayers and lentils of black cherts; in its lower part, there are bioherms of *Minjaria uralica*. The Mg/Ca ratio is commonly within the range of 0.601–0.664 or lower sometimes (0.573–0.595). The SA content is about 4%, being higher (7–12%) near the cherty nodules only. In the Min'yar section, we sampled the lower, better-exposed part of the Member that is 120 m thick here. Apparent thickness of the Member is greater in the Bakeevo (330 m) and Usmangali (210 m) sections, where sediments of the Uk Formation overlie it.

Member VI crowning the Min'yar Formation is retained from the pre-Uk erosion in the Shubino section only, being known therefore under synonymous name. Gray flaggy limestones of the Member enclose stromatolitic and microphytolitic interlayers. The Mg/Ca ratio in the rocks is not greater than 0.019 as a rule, but near the Member base it grows up to 0.156. Limestones contain an insignificant admixture of clastic quartz (0.3–3.4%), subangular micrite clasts replaced by sparite, and reveal the syneresis cracks. The Member is about 15 m thick.

The Uk Formation with basal beds and lentils of gravelstone composed of carbonate pebbles overlies discordantly two upper Member of the Min'yar Formation (Maslov et al., 2001). Two subformations of this subdivision are studied in the Shubino, Kulmas and Kurtaza sections. Greenish gray glauconite-quartz sandstones, siltstones and shales of the lower subformation enclose interlayers (0.2–0.4 m) of micritic limestones (Mg/Ca = 0.006–0.012) containing 3 to 8% of siliciclastic material. Thicker packets of carbonate rocks (2–4 m) are confined to the subformation upper half in Kurtaza and Shubino sections, where it is 90 and 60 m thick, respectively. In the Kulmas section, where the subformation is almost lacking carbonate rocks, its thickness is 150 m.

The upper Uk Subformation of light gray stromatolitic, clastic and micrphytolitic limestones (Mg/Ca = 0.002–0.028, in one case 0.042) contains dolomitized interlayers (Mg/Ca = 0.296–0.299) in the Kurtaza section, being crowned by 20-m-thick packet of limy dolostones (Mg/Ca = 0.350) in the Shubino section. The SA content in carbonate rocks is 0.6 to 4.1% in general except for the Shubino section, where it is sometimes as high as 11.4–13.6% in the unit lower half and ranges from 0.6 to 6.0% in the upper one. Stromatolitic limestones are composed of micrite and microsparite with small sparite segregations; clastic varieties are of micritic type. Rock containing poikilitic calcite, dispersed Fe-oxides and hydroxides, and dolomite rhomboids with ferruginate rims are relatively rare. Limy dolostones are composed of dolosparite with lenses of coarse-crystalline dolomite retaining relicts of small micrite clasts (0.1–0.3 mm) and corroded crystals of poikilitic calcite. Depending on the depth of pre-Asha erosion, the subformation thickness changes from 150 and 170 m in the Shubino and Kurtaza sections to 35–40 m in the Kulmas section.

Depositional settings of the Karatau sediments have been interpreted controversially (*The Riphean Strato-type...*, 1983; Krylov, 1983; Khabarov, 1985; Maslov et al., 2001, 2002). Analysis of structure and texture of rocks from the Karatau Group interval above the Zilm-erdak Formation and examination of stromatolite morphotypes suggest that sediments of the Katav Formation, lower Inzer and lower Min'yar subformations accumulated in a lower subtidal zone above the storm wave base. Stromatolites and associated rocks occurring in the upper Inzer Subformation, Min'yar and Uk formations likely represent sediments of an open shelf. Microphytolitic rocks of the Inzer and Uk formations, cross-bedded calcarenites and microphytolitic limestones of Member III in the Min'yar Formation (Usmangali section), and the mid-Min'yar and Uk carbonates with signs of subaerial exposition correspond to sediments deposited in shallowest settings of subtidal and intertidal (in part) zones.

INVESTIGATION PROCEDURE

New data on $\delta^{13}\text{C}_{\text{carb}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in the Karatavian carbonates from the Bakeevo, Kurtaza, Usmangali, Tolparovo-1 and Tolparovo-2 sections studied in 2004–2005 represent an essential addition to results obtained earlier for the Min'yar, Shubino, Manaisu and Kulmas sections (Semikhatov et al., 1995; Gorokhov et al., 1996; Kuznetsov et al., 1997, 2003; Podkovyrov et al., 1998). Intervals between sampling points were commonly 5 to 10 m or greater in the case of less exposed sections. Samples with minimum signs of secondary alterations were divided in two parts: one for petrographic examination and the other one for chemical and isotopic analysis. After decomposition of samples in 1N HCl under room temperature, Ca and Mg contents in carbonate material were determined by the wet chemical method; Mn and Fe concentrations by the atomic absorption technique at the analytical laboratory of the Geological Institute, Russian Academy of Sciences (GIN RAS). Mineralogical composition of siliciclastic admixture was studied by x-ray diffractometry at the Institute of Precambrian Geology and Geochronology (IPGG RAS).

C and O isotopic composition was analyzed by the uniform method (Gostenberger and Herman, 1984) in laboratories of the St. Petersburg State University (SPSU), All-Russia State Institute of Hydrogeology and Engineering Geology (ARIHEG), and Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences (IPGG RAS). To extract CO_2 , powdered aliquots of carbonate rocks about 20 mg in weight were dissolved in concentrated orthophosphoric acid, density 1.89 g/ml, during two (limestones) or 72 (dolostones) hours under temperature 25°C. Mass spectrometers MS-20 (SPSU), MI-1201 (IPGG RAS) and modernized MI-1201B (ARIHEG) were used to determine C- and O-isotope compositions in the extracted CO_2 volume. Working standard MCA-7 ($\delta^{13}\text{C} +2.2\text{‰}$; $\delta^{18}\text{O} -8.8\text{‰}$) used for isotope analysis was attested in the Central Research Institute of Geological Prospecting and All-Russia Institute of Mineral Deposits and calibrated with respect to V-PDB scale by analyzing international standards NBS-18, KH-2 and TKL. The analytical uncertainty of C- and O-isotopic analysis was not greater than $\pm 0.2\text{‰}$ and $\pm 0.4\text{‰}$ at 1σ level. Results of C- and O-isotopic analysis are quoted in this work with reference to standard V-PDB (Table 1).

Rb–Sr isotopic systematics of carbonate rocks was studied by means of stepwise dissolution of samples which included treatment of powdered material (about 100 mg) in 1N solution of ammonium acetate (NH_4OAc) under room temperature and subsequent dissolution of residue in 10% acetic acid (Gorokhov et al., 1995; Montanez et al., 1996; Kuznetsov et al., 1997, 2003; Bailey, 2000; Bartley et al., 2001). Material dissolved in NH_4OAc (designated below as AMA phase) corresponds to the late epigenetic generation of carbonate minerals, and residue dissolved in acetic acid

(ACA phase) is enriched in original carbonate material despite the admissible influence of epigenetic processes. The Rb and Sr concentrations in AMA and ACA phases are measured using the isotopic dilution method and mixed ^{87}Rb – ^{84}Sr spike. The Sr isotope composition is determined in static mode on the multi-collector mass spectrometer Finnigan MAT-261. The normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ averages of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the standard samples SRM 987 and En-1 were 0.71025 ± 0.00001 ($2\sigma_{\text{av}}$, $n = 19$) and 0.70921 ± 0.00001 ($2\sigma_{\text{av}}$, $n = 11$), respectively, during the period of data gathering. Difference between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured in AMA and ACA phases ($\Delta^{87}\text{Sr}/^{86}\text{Sr}$) ranges from 0.0008 to 0.0035 in limestones and from 0.0006 to 0.0022 in dolostones (Table 2), having positive correlation with Mn/Sr ($r = 0.61$, $n = 25$) and Fe/Sr ($r = 0.50$, $n = 25$) ratios. Hence, the results of stepwise dissolution imply dissimilar genesis of Sr isotopic systems in AMA and ACA phases, and allow to use the value $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ as a complementary criterion of the Rb–Sr system disturbance.

Values of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ are of chemostratigraphic significance, if the disturbance degree of original isotopic systems in the rocks are established and samples retaining signature of sedimentation medium are selected. As is shown earlier (Anfimov, 1997; Kuznetsov et al., 1997, 2003; Podkovyrov et al., 1998; Maslov et al., 2001), epigenetic fluids derived from the Zilmerdak clay-sandy and Katav clay-carbonate deposits by the low-T dia- and epigenetic alterations of aluminosilicates represent the main factor responsible for disturbance of initial isotopic signature in carbonates of the Karatau Group. At the burial stage, carbonate phases of rocks tended to be enriched in Mn and especially Fe eluted from the siliciclastic deposits and siliciclastic components of limestones and dolostones. Additional changes of their initial isotopic signature resulted from interaction of carbonate rocks with meteoric waters, which penetrated into the rock succession during its ascent to the surface (Kuznetsov et al., 1997, 2003).

Ground and meteoric waters are usually depleted in ^{13}C and ^{18}O but enriched in Mn, Fe, and radiogenic ^{87}Sr as compared to seawater (Drever, 1982; Chaudhuri and Clauer, 1993). Accordingly, $\delta^{18}\text{O}$ values and Mn/Sr and Fe/Sr ratios, covariation of these parameters and their correlation with $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ values are suitable criteria for selection of the least altered (“best”) samples of carbonates (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1990; Fairchild et al., 1990; Gorokhov et al., 1995; Gorokhov, 1996; Kuznetsov et al., 1997, 2003). Because of difference between Sr and C concentrations in carbonates and fluids the rocks interact with, the Rb–Sr isotopic systems are less stable under influence of the mentioned factors than C isotopic systems. Consequently, critical values of Mn/Sr and Fe/Sr ratios for the two isotopic systems are essentially different in most cases, but there are no uniform viewpoints on these critical parameters discriminating the

Table 1. Trace element concentrations, content of siliciclastic admixture, C- and O-isotopic composition in carbonate rocks of the Karatau Group, the southern Urals

Sample no.	Subformation, Member ¹	Sampling level ²	Rock types ³	SA ⁴ content, %	Mn, ppm	Fe, ppm	Sr, ppm	Mg/Ca	Mn/Sr	Fe/Sr	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
1	2	3	4	5	6	7	8	9	10	11	12	13
Uk Formation, Kurtaza section												
UK-49	U	165	1	1.5	28	445	155	0.014	0.18	2.9	1.2	-6.1
UK-48	U	162	1	1.1	18	140	123	0.007	0.15	1.1	1.3	-5.7
UK-45	U	142	1	1.2	32	200	110	0.006	0.29	1.8	1.4	-5.5
UK-44	U	137	1	1.2	34	220	118	0.005	0.29	1.9	1.4	-5.8
UK-43	U	125	1	1.4	35	130	182	0.006	0.19	0.71	1.6	-5.5
UK-42	U	120	1	0.9	31	305	154	0.005	0.20	2.0	1.5	-5.3
UK-19	U	112	1	1.3	38	170	159	0.005	0.24	1.1	1.9	-5.8
UK-18	U	92	1	4.1	41	515	202	0.042	0.20	2.6	1.7	-5.6
UK-17	U	87	1	1.1	790	4010	83	0.296	9.5	48.3	1.3	-7.0
UK-16	U	77	1	1.1	49	375	214	0.007	0.28	1.8	2.6	-7.6
UK-15	U	72	1	2.1	22	165	207	0.004	0.11	0.80	2.6	-7.2
UK-14	U	62	1	1.5	230	1610	80	0.299	2.9	20.1	2.1	-6.0
UK-13	U	60	1	1.8	78	195	123	0.004	0.63	1.6	1.9	-5.4
UK-12	U	47	1	0.7	105	270	83	0.003	1.3	3.3	1.3	-5.8
UK-11	U	44	1	1.2	75	170	75	0.005	1.0	2.3	1.4	-5.1
UK-10	U	41	1	1.1	110	250	90	0.003	1.2	2.8	1.3	-5.7
UK-9	U	38	1	1.7	55	325	314	0.005	0.18	1.0	1.7	-7.2
UK-8	U	33	1	2.1	60	385	727	0.006	0.08	0.53	2.7	-6.2
UK-7	U	27	1	1.8	140	505	440	0.007	0.32	1.2	2.6	-5.0
UK-6	U	26	1	2.1	50	275	512	0.008	0.10	0.54	3.2	-5.4
UK-5	U	23	1	3.6	45	330	330	0.008	0.14	1.0	1.4	-5.2
UK-4	L	10	1	3.1	32	225	755	0.006	0.04	0.30	3.4	-4.4
UK-3	L	8	1	7.1	63	1790	170	0.007	0.37	10.5	1.4	-4.7
UK-1	L	3	1	5.5	76	1010	305	0.012	0.25	3.3	1.8	-6.1
Uk Formation, Kulmas section												
3573-1	U	30	1	0.8	66	410	90	0.006	0.73	4.6	1.5	-4.2
3573-2	U	23	1	1.1	64	260	146	0.002	0.44	1.8	2.1	-4.3
3573-7	U	7	1	3.1	27	470	437	0.008	0.06	1.1	2.5	-4.0
Min'yar Formation, Bakeevo section												
KM-59	U-V	560	d	6.7	650	2000	96	0.601	6.8	20.8	-1.1	-6.2
KM-61	U-V	550	d	8.8	665	2150	90	0.643	7.4	23.9	-1.3	-5.3
KM-63	U-V	545	d	3.9	565	2060	99	0.621	5.6	20.6	-1.6	-5.5
KM-66	U-V	535	d	5.5	250	1240	91	0.609	2.8	13.6	-1.4	-5.6
BK-20	U-V	526	d	12.1	320	1540	99	0.623	3.2	15.5	-1.5	-5.4
KM-67	U-V	520	d	2.4	180	990	82	0.595	2.2	12.1	-1.4	-5.0
KM-68	U-V	515	d	5.5	115	1030	98	0.604	1.2	10.5	-1.3	-5.0
KM-71	U-V	500	d	90.4	76	1090	-	0.573	-	-	-1.4	-8.9
KM-73	U-V	490	d	2.6	31	315	118	0.609	0.26	2.7	-1.6	-4.0
KM-75	U-V	485	d	0.8	95	700	99	0.606	0.96	7.1	-0.7	-4.6
KM-76	U-V	480	d	0.9	105	660	92	0.619	1.1	7.2	-0.9	-4.7
BK-19	U-V	477	d	1.0	130	825	103	0.623	1.3	8.0	-0.9	-5.8
KM-79	U-V	465	d	1.7	110	750	88	0.632	1.2	8.5	-1.1	-5.8
KM-80	U-V	460	d	2.9	115	770	82	0.634	1.4	9.3	-1.5	-5.9

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
KM-81	U-V	455	d	1.1	90	630	84	0.639	1.1	7.5	-1.6	-5.5
BK-18	U-V	451	d	2.0	76	710	85	0.601	0.89	8.3	-2.8	-5.7
KM-83	U-V	445	d	2.7	115	750	146	0.664	0.79	5.1	-0.4	-3.4
KM-87	U-V	425	d	1.2	85	550	81	0.611	1.1	6.8	-2.5	-4.2
KM-88	U-V	420	d	4.3	105	620	77	0.648	1.4	8.0	-1.7	-5.6
BK-17	U-V	414	d	1.5	48	170	80	0.604	0.60	2.1	-1.3	-7.6
KM-90	U-V	410	d	1.8	140	430	99	0.633	1.4	4.3	-1.7	-5.9
KM-94	U-V	390	d	2.1	66	495	65	0.645	1.0	7.6	-2.3	-5.3
BK-16	U-V	389	d	1.4	64	165	75	0.626	0.85	2.2	-2.4	-5.7
KM-97	U-V	375	d	2.5	50	255	87	0.616	0.58	3.0	-1.9	-5.3
BK-15	U-V	344	d	2.6	70	115	68	0.644	1.0	1.7	-2.1	-7.0
KM-101	U-V	335	d	7.4	68	460	72	0.641	0.95	6.4	-2.0	-5.8
KM-105	U-V	315	d	1.4	55	180	72	0.646	0.76	2.5	-1.4	-4.8
BK-14	U-V	311	d	3.5	46	155	153	0.624	0.30	1.0	-2.2	-7.8
KM-107	U-V	305	d	2.3	48	110	72	0.622	0.67	1.5	-1.7	-6.5
BK-13	U-V	302	d	5.0	45	260	69	0.609	0.66	3.8	-1.6	-7.2
KM-109	U-V	295	d	6.1	46	180	103	0.636	0.45	1.8	-0.4	-4.9
KM-113	U-V	280	d	6.8	40	265	92	0.612	0.43	2.9	-0.6	-5.3
KM-53	U-V	260	d	1.3	30	280	82	0.601	0.37	3.4	0.0	-5.9
KM-50	U-V	250	d	2.0	30	260	78	0.606	0.38	3.3	1.1	-5.5
BK-12	U-V	248	d	4.9	53	510	66	0.645	0.80	7.7	2.3	-5.5
BK-11	U-V	237	d	7.5	45	550	51	0.629	0.89	11.0	0.9	-6.2
KM-47	U-V	235	d	1.2	43	520	74	0.606	0.58	7.1	0.9	-6.8
BK-10	L-IV	218	d	0.9	70	790	58	0.620	1.2	13.6	1.8	-6.3
KM-42	L-IV	210	d	1.2	55	570	69	0.596	0.80	8.3	0.9	-6.6
KM-36	L-IV	180	d	2.8	30	340	59	0.607	0.51	5.7	1.2	-6.4
BK-9	L-IV	174	d	2.5	70	600	64	0.627	1.1	9.4	-0.6	-7.0
KM-33	L-IV	165	d	6.9	33	375	104	0.617	0.32	3.6	1.4	-5.3
BK-8	L-IV	154	d	1.5	75	480	50	0.637	1.5	9.6	0.2	-7.2
KM-30	L-IV	150	d	5.0	95	1760	47	0.617	2.0	37.4	0.5	-5.9
KM-28	L-IV	140	d	4.5	47	1440	53	0.579	0.88	27.2	0.5	-5.5
KM-25	L-IV	125	d	3.4	153	4690	60	0.528	2.6	78.2	0.5	-6.3
BK-7	L-IV	122	d	3.9	65	1440	65	0.635	1.0	22.2	0.3	-5.9
KM-23	L-IV	115	d	3.4	-	-	-	0.165	-	-	-0.3	-7.9
KM-21	L-IV	105	d	4.6	72	2660	58	0.616	1.2	45.8	-0.6	-6.0
BK-6	L-III	102	d	2.6	95	2390	63	0.594	1.5	37.8	0.2	-5.8
KM-18	L-III	90	d	0.3	110	580	40	0.617	2.8	14.5	0.7	-7.7
BK-5	L-III	81	d	4.3	55	595	81	0.647	0.68	7.4	0.3	-6.5
KM-16	L-III	80	d	0.3	95	695	35	0.598	2.7	19.9	0.9	-7.4
BK-4	L-III	70	d	0.5	95	520	35	0.643	2.6	14.9	1.0	-9.0
KM-13	L-III	65	d	1.4	110	720	136	0.601	0.81	5.3	1.5	-6.8
KM-12	L-III	60	d	0.5	120	330	37	0.615	3.2	8.9	1.0	-7.6
BK-3	L-III	56	d	0.3	98	560	58	0.628	1.7	9.7	1.4	-7.8
KM-10	L-III	50	d	2.2	75	860	71	0.614	1.1	12.1	0.5	-6.9
BK-2	L-III	41	d	0.5	70	335	38	0.626	1.8	8.7	1.0	-8.0
KM-6	L-III	30	d	3.3	155	1830	62	0.578	2.5	29.5	0.5	-6.5
BK-1	L-II	4	d	2.8	145	1230	50	0.614	2.9	24.6	0.2	-6.5

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
Min'yar Formation, Usmangali section												
MI-30	U-V	660	d	2.2	40	165	93	0.601	0.43	1.8	-1.0	-5.0
MI-29	U-V	640	d	4.1	45	135	92	0.620	0.49	1.5	-1.7	-5.3
MI-28	U-V	620	d	10.8	30	330	96	0.611	0.31	3.4	-2.4	-5.0
MI-27	U-V	585	d	3.4	35	175	125	0.578	0.28	1.4	-1.5	-5.8
MI-26	U-V	535	d	1.7	39	85	95	0.616	0.41	0.89	0.4	-8.3
MI-25	U-V	515	d	1.3	19	74	58	0.526	0.33	1.3	2.7	-5.7
MI-24	U-V	490	d	6.0	37	210	50	0.606	0.74	4.2	0.8	-6.2
MI-23	U-V	470	d	11.3	42	445	65	0.606	0.64	6.8	0.6	-7.0
MI-22	U-V	450	d	1.4	37	545	57	0.609	0.65	9.5	1.2	-7.2
MI-21	L-IV	440	d	1.2	29	425	62	0.606	0.47	6.9	2.6	-7.9
MI-20	L-IV	420	d	1.0	37	515	75	0.691	0.49	6.8	3.0	-7.3
MI-19	L-IV	340	d	5.7	50	1480	65	0.615	0.77	22.7	0.1	-7.2
MI-17	L-IV	250	d	1.7	49	820	76	0.587	0.65	10.8	0.9	-7.2
MI-16	L-IV	175	d	3.2	36	1030	67	0.614	0.54	15.4	0.7	-6.5
MI-9	L-IV	165	d	4.7	31	815	50	0.603	0.62	16.3	-0.5	-6.5
MI-15	L-III	130	l	0.8	17	170	301	0.050	0.06	0.56	2.8	-8.3
MI-14	L-III	98	l	2.2	48	1120	115	0.185	0.42	9.7	0.4	-8.7
MI-13	L-III	85	l	1.2	31	680	168	0.053	0.18	4.1	-0.3	-8.4
MI-8	L-III	80	l	0.8	20	150	473	0.014	0.04	0.32	-0.2	-8.9
MI-12	L-III	72	l	3.2	17	1030	655	0.127	0.03	1.6	1.7	-7.8
MI-7	L-III	62	l	3.0	12	165	1060	0.007	0.01	0.16	0.1	-7.3
MI-11	L-III	50	l	1.1	20	1710	290	0.126	0.07	5.9	0.1	-8.5
MI-6	L-III	46	l	16.5	27	1990	410	0.183	0.07	4.9	1.4	-8.1
MI-10	L-III	40	l	10.2	27	2720	365	0.181	0.07	7.5	1.4	-8.2
MI-5	L-III	27	l	1.1	14	385	2450	0.006	0.01	0.16	1.1	-8.6
MI-4	L-II	15	l	4.1	730	815	380	0.050	1.9	2.1	-0.2	-8.8
MI-3	L-II	10	l	2.5	65	505	1086	0.010	0.06	0.47	0.2	-8.3
MI-2	L-I	2	l	7.4	750	1585	165	0.016	4.6	9.6	-0.9	-12.2
Inzer Formation, Tolparovo-1 section												
TI-20	L	225	l	0.2	35	65	205	0.008	0.17	0.32	0.2	-9.6
TI-19	L	220	l	0.1	45	300	225	0.033	0.20	1.3	0.7	-9.3
TI-18	L	215	l	0.4	140	1290	290	0.291	0.48	4.5	2.0	-7.7
TI-17	L	205	l	0.3	25	120	555	0.005	0.05	0.22	1.2	-8.9
TI-16	L	200	l	1.2	30	370	561	0.011	0.05	0.66	1.7	-8.8
TI-15	L	195	l	2.9	34	910	345	0.039	0.10	2.6	2.4	-8.5
TI-14	L	185	l	0.9	28	240	605	0.004	0.05	0.40	2.9	-8.7
TI-13	L	145	l	1.0	47	460	450	0.016	0.10	1.0	2.9	-9.1
TI-12	L	135	l	0.6	30	310	415	0.015	0.07	0.75	2.1	-9.5
TI-10	L	125	l	1.0	15	160	384	0.003	0.04	0.42	2.8	-8.9
TI-9	L	115	l	3.0	105	110	300	0.024	0.35	0.37	3.6	-9.2
TI-8	L	105	l	0.9	25	345	440	0.005	0.06	0.78	2.9	-9.0
TI-7	L	99	l	0.8	19	240	445	0.003	0.04	0.54	2.3	-9.3
TI-6	L	95	l	1.5	33	605	340	0.026	0.10	1.8	2.8	-8.7
TI-5	L	85	l	1.2	26	460	200	0.047	0.13	2.3	2.5	-8.4

Table 1. (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
TI-4	L	75	1	0.9	13	170	510	0.003	0.03	0.33	2.0	-8.6
TI-2	L	55	1	0.5	31	90	490	0.001	0.06	0.18	2.4	-8.7
TI-1	L	45	1	0.9	44	520	532	0.003	0.08	0.98	1.8	-8.7
TI-0	L	35	1	1.1	21	570	495	0.011	0.04	1.2	3.4	-8.6
TK-14	L	10	1	4.8	70	1650	396	0.018	0.18	4.2	2.6	-8.8
TK-12	L	0	1	4.4	115	4620	350	0.072	0.33	13.2	2.9	-7.9
Inzer Formation, Tolparovo-2 section												
TVI-12	L	230	1	2.8	39	730	210	0.047	0.19	3.5	0.8	-7.5
TVI-11	L	220	1	0.3	12	45	225	0.005	0.05	0.20	1.3	-7.6
TVI-10	L	205	1	6.5	23	1060	255	0.055	0.09	4.2	1.7	-7.8
TVI-9	L	195	1	1.6	30	940	440	0.059	0.07	2.1	2.1	-8.1
TVI-8	L	185	1	1.9	26	605	460	0.045	0.06	1.3	3.3	-7.8
TVI-7	L	170	1	1.3	27	510	450	0.032	0.06	1.1	4.0	-7.2
TVI-6	L	155	1	3.3	33	1030	505	0.049	0.07	2.0	3.8	-7.6
TVI-5	L	145	1	4.5	60	1450	250	0.072	0.24	5.8	2.6	-7.4
TVI-4	L	135	1	0.3	13	290	405	0.036	0.03	0.72	2.2	-7.7
TVI-3	L	120	1	1.4	23	1010	310	0.031	0.07	3.3	3.1	-8.1
TVI-2	L	99	1	1.6	10	335	315	0.010	0.03	1.1	2.7	-7.5
TVI-1	L	90	1	0.7	17	330	320	0.014	0.05	1.0	2.4	-7.4
TVK-13	L	19	1	9.5	105	2470	370	0.017	0.28	6.7	2.4	-7.4
TVK-12	L	4	1	8.8	170	1610	390	0.014	0.44	4.1	2.1	-7.6
TVK-11	L	1	1	10.2	240	1640	463	0.014	0.52	3.5	3.0	-8.8
TVK-10A	L	0.2	1	3.2	355	6180	350	0.215	1.0	17.7	2.7	-7.0
Katav Formation, Tolparovo-1 section												
TK-11	U	180	1	5.5	245	1540	210	0.006	1.2	7.3	1.5	-8.2
TK-10	U	155	1	16.6	195	1710	190	0.009	1.0	9.0	0.3	-8.5
TK-9	U	150	1	15.9	205	2750	185	0.037	1.1	14.9	0.6	-7.2
TK-8	U	140	1	13.7	190	1790	223	0.016	0.85	8.0	0.4	-7.5
TK-7	U	130	1	13.1	245	2220	180	0.019	1.36	12.3	0.2	-7.1
TK-6	L	99	1	13.6	200	2230	173	0.025	1.2	12.9	3.1	-7.2
TK-5	L	60	1	14.8	590	2240	205	0.009	2.9	10.9	2.8	-7.9
TK-3	L	16	1	9.3	355	3320	180	0.004	1.9	18.4	2.1	-8.5
TK-2	L	10	1	31.8	635	8190	145	0.020	4.4	56.4	2.0	-8.7
TK-1	L	4	1	31.4	680	7610	150	0.027	4.5	50.7	1.8	-8.5
Katav Formation, Tolparovo-2 section												
TVK-9	U	68	1	9.0	310	1720	190	0.037	1.6	9.1	1.8	-7.3
TVK-8	U	56	1	14.8	315	1580	180	0.009	1.8	8.8	0.4	-7.8
TVK-7	U	45	1	15.8	195	1720	160	0.004	1.2	10.8	0.3	-7.7
TVK-6	U	36	1	12.5	165	1670	205	0.001	0.80	8.2	0.1	-8.5
TVK-5	U	30	1	11.0	155	1540	221	0.006	0.70	7.0	0.7	-7.1
TVK-3	L	20	1	20.0	190	1170	190	0.009	1.0	6.2	0.2	-6.8
TVK-2	L	10	1	–	150	1400	145	–	1.0	9.7	2.1	-6.9
TVK-1	L	3	1	–	350	810	115	–	3.0	7.0	1.7	-7.3

Note: ¹ (L) lower and (U) upper subformations; members are designated by Roman numbers. ² Sampling levels are given in meters above the carbonate succession of formation in the indicated section. ³ (l) limestone and (d) dolostone. ⁴ (SA) siliciclastic admixture.

Table 2. Rb–Sr analytical data on soluble carbonate phases of limestones and dolostones from the Karatau Group

Sample no.	Members of Min'yar Formation	Rock ¹	Carbonate phase ²	Phase content, %	Rb, ppm	Sr, ppm	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr, measured	⁸⁷ Sr/ ⁸⁶ Sr, initial ³
Uk Formation, Kurtaza section									
UK-48		l	AMA	5.8	0.60	114	0.0154	0.70672	0.70657
			ACA	93.4	0.08	124	0.0019	0.70611	0.70609
UK-43		l	ACA	–	0.19	182	0.0030	0.70607	0.70605
UK-19		l	AMA	5.0	0.76	165	0.0136	0.70697	0.70684
			ACA	93.9	0.32	159	0.0058	0.70615	0.70610
UK-17		l	ACA	–	0.05	83.0	0.0016	0.70711	0.70709
UK-16		l	AMA	7.8	0.52	255	0.0059	0.70680	0.70674
			ACA	90.9	0.18	212	0.0025	0.70638	0.70636
UK-9		l	AMA	5.1	1.09	348	0.0092	0.70653	0.70644
			ACA	93.4	0.21	312	0.0019	0.70588	0.70586
UK-8		l	ACA	–	0.27	727	0.0011	0.70543	0.70542
UK-6		l	AMA	7.6	0.78	548	0.0042	0.70604	0.70600
			ACA	90.4	0.11	509	0.0006	0.70563	0.70562
UK-4		l	ACA	–	0.59	755	0.0023	0.70535	0.70533
Min'yar Formation, Usmangali section									
MI-30	V	d	AMA	2.5	2.75	133	0.0605	0.70699	0.70630
			ACA	95.9	0.23	90.9	0.0073	0.70606	0.70598
MI-28	V	d	AMA	4.3	–	–	–	0.70779	–
			ACA	95.4	0.22	123	0.0050	0.70603	0.70597
MI-27	V	d	ACA	–	0.22	125	0.0051	0.70670	0.70664
MI-25	V	d	ACA	–	0.08	58.3	0.0039	0.70633	0.70629
MI-23	V	d	ACA	–	0.18	65.2	0.0080	0.70609	0.70600
MI-21	IV	d	AMA	1.9	1.60	92.6	0.0506	0.70665	0.70607
			ACA	97.7	0.16	60.6	0.0075	0.70608	0.70599
MI-20	IV	d	ACA	–	0.30	75.2	0.0078	0.70582	0.70573
MI-19	IV	d	ACA	–	0.56	65.1	0.0251	0.70632	0.70604
MI-17	IV	d	AMA	3.3	1.01	92.1	0.0321	0.70722	0.70685
			ACA	95.8	0.12	74.7	0.0049	0.70604	0.70598
MI-16	IV	d	ACA	–	0.42	67.0	0.0183	0.70648	0.70628
MI-15	III	l	AMA	5.0	0.52	274	0.0055	0.70646	0.70646
			ACA	89.4	0.33	305	0.0031	0.70588	0.70584
MI-13	III	l	AMA	6.1	0.61	257	0.0069	0.70610	0.70602
			ACA	88.2	0.10	162	0.0022	0.70577	0.70574
MI-8	III	l	AMA	4.4	0.69	491	0.0041	0.70580	0.70575
			ACA	95.0	0.69	568	0.0036	0.70562	0.70558
MI-7	III	l	AMA	5.4	0.33	830	0.0012	0.70562	0.70561
			ACA	92.4	0.12	1120	0.0003	0.70554	0.70554
MI-5	III	l	AMA	6.2	0.83	1670	0.0015	0.70578	0.70576
			ACA	93.3	0.34	2610	0.0004	0.70550	0.70550
MI-3	II	l	AMA	6.4	0.85	1160	0.0021	0.70577	0.70575
			ACA	90.9	0.10	1080	0.0003	0.70552	0.70552

Table 2. (Contd.)

Sample no.	Members of Min'yar Formation	Rock ¹	Carbonate phase ²	Phase content, %	Rb, ppm	Sr, ppm	⁸⁷ Rb/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr, measured	⁸⁷ Sr/ ⁸⁶ Sr, initial ³
Min'yar Formation, Bakeevo section									
BK-20	V	d	ACA	–	0.15	99.6	0.0045	0.70649	0.70644
KM-73	V	d	ACA	–	0.12	118	0.0030	0.70585	0.70582
BK-19	V	d	ACA	–	0.06	103	0.0017	0.70639	0.70637
BK-18	V	d	ACA	–	0.06	85.2	0.0021	0.70595	0.70593
KM-87	V	d	ACA	–	0.08	81.0	0.0029	0.70590	0.70587
BK-17	V	d	ACA	–	0.15	80.0	0.0055	0.70585	0.70579
BK-16	V	d	ACA	–	0.05	75.4	0.0020	0.70622	0.70620
BK-15	V	d	ACA	–	0.04	68.1	0.0020	0.70682	0.70680
BK-12	V	d	ACA	–	0.11	66.3	0.0050	0.70610	0.70604
BK-9	IV	d	ACA	–	0.06	64.2	0.0028	0.70625	0.70622
BK-6	III	d	AMA	2.1	3.56	107	0.0978	0.70849	0.70740
			ACA	95.7	0.18	62.3	0.0086	0.70625	0.70615
BK-5	III	d	AMA	2.0	0.30	114	0.0077	0.70847	0.70838
			ACA	94.5	0.12	79.6	0.0045	0.70649	0.70644
BK-2	III	d	AMA	2.2	1.37	26.4	0.1520	0.71008	0.70849
			ACA	98.2	0.14	38.4	0.0106	0.70870	0.70858
Inzer Formation, Tolparovo-1 section									
TI-19		1	AMA	6.2	0.06	53.6	0.0034	0.70677	0.70673
			ACA	97.6	0.09	225	0.0012	0.70628	0.70627
TI-17		1	ACA	–	0.20	555	0.0011	0.70537	0.70536
TI-16		1	AMA	4.3	0.57	561	0.0030	0.70599	0.70595
			ACA	94.9	0.07	573	0.0004	0.70547	0.70547
TI-14		1	ACA	–	0.05	605	0.0002	0.70540	0.70540
TI-12		1	ACA	–	0.04	415	0.0003	0.70550	0.70550
TI-10		1	AMA	4.0	0.54	403	0.0039	0.70573	0.70568
			ACA	95.6	0.04	383	0.0003	0.70555	0.70555
TI-7		1	ACA	–	0.25	445	0.0016	0.70545	0.70543
TI-4		1	ACA	–	0.10	510	0.0006	0.70536	0.70535
TI-1		1	AMA	5.3	0.43	513	0.0025	0.70554	0.70551
			ACA	94.0	0.08	533	0.0004	0.70522	0.70521
TI-0		1	ACA	–	0.05	495	0.0003	0.70537	0.70537
TK-14		1	AMA	5.7	3.11	334	0.0273	0.70896	0.70861
			ACA	89.6	0.10	400	0.0007	0.70586	0.70585
Katav Formation, Tolparovo-1 section									
TK-8		1	AMA	5.4	4.80	291	0.0483	0.71236	0.71174
			ACA	81.2	0.24	218	0.0032	0.70888	0.70884
TK-6		1	AMA	4.7	2.19	233	0.0275	0.71250	0.71215
			ACA	81.6	0.70	169	0.0121	0.70973	0.70957

Note: ¹ (l) limestone and (d) dolostone; ² (AMA) carbonate phase soluble in 1N NH₄Oac and (ACA) residue after sample treatment in 1N NH₄Oac solved in 10% CH₃COOH; ³ ⁸⁷Sr/⁸⁶Sr initial ratios are calculated by accepting age values of 870 Ma for Katav Formation, 835 Ma for Inzer Formation, 780 Ma for Min'yar Formation, and 650 Ma for Uk Formation.

altered and “best” carbonate samples in terms of Rb–Sr and C isotopic systematics (Melezhik et al., 2001).

We figured out strict values of discriminative geochemical ratios based on empirical data on Proterozoic carbonate rocks studied in the Urals and Siberia (Gorokhov et al., 1995; Kuznetsov et al., 1997, 2003; Podkovyrov et al., 1998; Semikhatov et al., 2002, 2004). Studying the Rb–Sr systematics of Proterozoic limestones, we believe at present that the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios are appropriate for chemostratigraphic considerations, when the rocks studied fit the following threshold values: $\text{Mn}/\text{Sr} \leq 0.2$, $\text{Fe}/\text{Sr} \leq 5.0$, and $\text{Mg}/\text{Ca} \leq 0.024$. For dolostones, critical values are individual for each formation and can be established only if the above and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are covariant parameters. For instance, we figured out the following threshold ratios for dolostones of the Min’yar Formation: $\text{Mn}/\text{Sr} \leq 1.2$, $\text{Fe}/\text{Sr} \leq 3.0$, and $\text{Mg}/\text{Ca} \geq 0.608$. Using this approach to selecting the least altered samples, we introduced correction for the former variation trends of Sr isotopic composition in seawater of the Middle and Late Rhiphean time (Gorokhov et al., 1996; Kuznetsov et al., 1997, 2003; Semikhatov et al., 2000, 2002). In a series of our works on C isotopic systematics, we accepted the following threshold criteria of retentivity: $\text{Mn}/\text{Sr} \leq 4$, $\text{Fe}/\text{Sr} \leq 10$ for limestones and $\text{Mn}/\text{Sr} \leq 6$, $\text{Fe}/\text{Sr} \leq 15$ for dolostones. The values for dolostones are higher, because crystal lattice of calcite is more suitable for Sr incorporation than that of dolomite (Veizer, 1983), while diagenetic dolomitization of sediment is accompanied by Mn capturing (Brand and Veizer, 1980; Fairchild et al., 1990). Data considered below show however that the above criteria of C-isotopic system retentivity are too strict. As for $\delta^{18}\text{O}$ values in altered carbonates, they are thought to be -10% (Veizer, 1983; Kaufman and Knoll, 1995; Gorokhov et al., 1995).

RESULTS

New information about C- and O-isotopic systematics of the Karatau Group rocks is obtained by analysis of 171 samples (110 of limestones, 61 of dolostones), and the Rb–Sr systematics is added by new data on 51 samples (28 of limestones, 23 of dolostones). In 25 samples, we studied the Rb–Sr systematics of AMA and ACA phases in order to evaluate a possible extent of epigenetic recrystallization; in the other 26 samples, only the ACA phases have been analyzed. All sampling levels are shown in Fig. 2.

Katav Formation. In clayey limestones with rare marl interlayers typical of the lower Katav Subformation in the Tolparovo-1 and Tolparovo-2 sections, Mg/Ca ratio is 0.004 to 0.009, rising up to 0.020–0.027 in two samples only near the subformation base and top (Table 1). In the Tolparovo-1 section, where the greater interval of the subformation is exposed (100 m), the SA maximum content (31.4–31.8%) is established in basal 10–15 m of the unit, and higher in the section it declines down to 9.3–14.8%. In the Tolparovo-2 section, the SA

content in the subformation upper horizons, which are unexposed in the Tolparovo-1 locality, ranges from 16.8 to 20.0%. Maximum Mn (635–680 ppm) and Fe (7610–8190 ppm) concentrations are characteristic of the mentioned basal horizon in the Tolparovo-1 section. Higher, Mn and Fe concentrations decrease here to 200–590 and 2230–3320 ppm, and in the uppermost interval of the unit exposed in the Tolparovo-2 section, they correspond to 115–190 and 810–1400 ppm, respectively. Thus, concentrations of both elements drop by 2.1 and 3.7 times from the base to the top of the subformation. At the same time, averaged Mn and Fe concentrations are notably higher in the Tolparovo-1 than in Tolparovo-2 section (490 versus 230 ppm Mn and 4720 versus 1130 ppm Fe). Both elements are distributed in sections of the lower Katav Subformation with no correlation with either the SA content, or Mg/Ca ratio, and this is probably a consequence of local factors affected the rocks. In limestones of the Tolparovo-1 section, Sr concentration ranges from 145 to 205 ppm (170 ppm in average), being lower (115–190 and 150 ppm in average) in the Tolparovo-2 section. The Mn/Sr ratio in the subformation basal horizon is 4.4–4.5, declining higher to 1.0–3.0, and Fe/Sr ratio decreases simultaneously from 50.7–56.4 to 6.2–12.9.

Interval of Mg/Ca ratios in variegated limestones of the upper Katav Subformation (0.001 to 0.019) is comparable with that of the lower subformation rocks, although in Tolparovo-1 and Tolparovo-2 sections, an upper third of the unit includes dolomitized rock varieties (Mg/Ca = 0.037). On the other hand, the SA content in the upper Katav limestones is lower than in the unit lower part (13 versus 19% in average), ranging from 5.5 to 16.6% in Tolparovo-1 and from 9.0 to 15.8% in Tolparovo-2 sections. The upper subformation is also relatively depleted in Mn: 190–245 ppm in Tolparovo-1 and 155–315 ppm in Tolparovo-2 sections, which are however comparable in terms of average Mn concentrations (215 and 228 ppm, respectively). There is again no correlation of Mn concentration with either the SA content, or Mg/Ca ratio. Averaged Fe concentration is, in contrast, higher in Tolparovo-1 than in Tolparovo-2 sections (2000 versus 1650 ppm); dolomitized limestones are more enriched in this element. Averaged Sr concentration that is 1.2 times higher than in the lower subformation is almost identical (190 and 198 ppm) in both sections. The Mn/Sr ratio ranges from 0.85 to 1.36 in Tolparovo-1 and from 0.7 to 1.8 in Tolparovo-2 sections, and more considerable variations (8.0–14.9 and 7.0–10.8, respectively) are characteristic of Fe/Sr ratio.

Values $\delta^{18}\text{O}$ characterizing lower 16 m of limestones in the lower Katav Subformation of Tolparovo-1 section correspond to $-8.6 \pm 0.1\%$ and grow upward to $-7.6 \pm 0.3\%$ in this section and to $-6.9 \pm 0.1\%$ in the upper subformation exposed in Tolparovo-2 section. In terminal limestone beds of Tolparovo-1 (30–35 m) and Tolparovo-2 sections, $\delta^{18}\text{O}$ is decreased: -8.2 to -8.5% in the first case and -7.1 to -8.5% in the second one. In both sections, $\delta^{13}\text{C}$ varies from $+0.1$ to $+3.1\%$ with a

minimum near the boundary between two subformations. From the formation base to its top, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is lowering from 0.70957 to 0.70884 (Table 2). Hence, the SA content and ratios Mn/Sr, Fe/Sr, $^{87}\text{Sr}/^{86}\text{Sr}$ distinctly decrease upward in the formation sections, while Sr concentration and value $\delta^{18}\text{O}$ vary insignificantly.

Inzer Formation. New data on Rb–Sr and C- isotopic systematics of the Inzer Formation are obtained in Tolparovo-1 and Tolparovo-2 sections, where its lower subformation have been studied. The subformation upper part is truncated by the pre-Vendian erosion in the first section and unexposed in the second one. The deposits under consideration belong to the regional geochemical level (Anfimov et al., 1987; Gareev, 1988) of elevated Sr concentration in carbonates. Above the basal 15- to 20-m-thick interval transitional to the Katav Formation, distinctive features of carbonate rocks are low Mn, Fe, and SA contents.

Limestone samples ($\text{Mg}/\text{Ca} = 0.014\text{--}0.017$) and two dolomitized rocks ($\text{Mg}/\text{Ca} = 0.072$ and 0.215) from basal horizon contain about 7% SA (variation range 3.2–10.2%), 70 to 355 ppm Mn, and 1610 to 6180 ppm Fe (averaged values are 93 ppm Mn and 3135 ppm Fe in Tolparovo-1 section, 218 ppm Mn and 2975 ppm Fe in Tolparovo-2 section). The Sr concentration in the rocks is within the interval of 350–463 ppm (Table 1). As a consequence, Mn/Sr ratio in basal limestones is low: 0.18 to 0.33 in Tolparovo-1 and 0.28 to 2.0 in Tolparovo-2 sections, while Fe/Sr ratio is notably higher: 4.2 to 13.2 and 3.5 to 17.7, respectively.

Carbonate rocks of the lower Inzer Subformation that is 230 to 240 m thick above its basal horizon in the sections studied reveal lateral variations of chemical composition. Pure ($\text{Mg}/\text{Ca} = 0.001\text{--}0.016$) and rare dolomitized ($\text{Mg}/\text{Ca} = 0.024\text{--}0.047$, 0.291 in one case) limestones of Tolparovo-1 section differ from rocks of Tolparovo-2 section, where pure limestones ($\text{Mg}/\text{Ca} = 0.005\text{--}0.014$) are intercalated in the upper part with rather frequent beds of dolomitized varieties ($\text{Mg}/\text{Ca} = 0.031\text{--}0.072$), and the SA content is higher than in Tolparovo-1 section (2.2 versus 1.0%, in average). Averaged Mn concentration is 39 ppm (variation range 13–140 ppm) in Tolparovo-1 section and 26 ppm (variation range 10–60 ppm) in Tolparovo-2 section. In contrast, rocks of Tolparovo-1 are relatively depleted in Fe as compared with the other section (average concentration 385 versus 670 ppm) despite close variation ranges in both cases (65–1290 and 45–1450 ppm). The average Sr concentration in Tolparovo-1 section is somewhat higher than in Tolparovo-2 (410 versus 345 ppm) because of greater abundance of dolomitized rocks in the last case. In the former section, Sr concentration is decreasing, as proportion of dolomite phase is getting higher: in pure limestones ($\text{Mg}/\text{Ca} < 0.016$) it ranges from 384 to 605 ppm, being declined to 200–345 ppm in dolomitic varieties ($\text{Mg}/\text{Ca} = 0.024\text{--}0.291$). A contrary trend is characteristic of Tolparovo-2 section, where Sr concentration is lower in pure limestones

($\text{Mg}/\text{Ca} < 0.014$) than in dolomitic limestones (225–320 versus 250–505 ppm). This situation is likely indicative of different conditions by dolomitization at the early diagenetic stage. Limestones above basal horizon of the lower Inzer Subformation have very low Mn/Sr and Fe/Sr ratios. The first ratio varies between 0.04 and 0.48 (averaged value 1.1) in Tolparovo-1 and between 0.03 and 0.24 (averaged value 0.08) in Tolparovo-2 sections. Parallel ranges of Fe/Sr ratio are 0.18–4.5 and 0.20–5.8 (averaged values 1.1 and 2.2).

Values $\delta^{18}\text{O}$ in limestones range from -9.5 to -7.9‰ in Tolparovo-1 and from -8.8 to -7.2‰ in Tolparovo-2 localities (Table 1), being in dolomitic varieties ($\text{Mg}/\text{Ca} = 0.215\text{--}0.291$) as high as -7.7‰ in the first case and -7.0‰ in the second one that is characteristic of the early diagenetic dolomitization of calcium carbonate sediments (McKenzie, 1981). The lowest $\delta^{18}\text{O}$ values (-9.6 and -9.3‰) are established in two topmost samples from Tolparovo-1 section. In general, limestones of both sections yield positive $\delta^{13}\text{C}$ values ($+1.2$ to $+4.0\text{‰}$) slightly lower near the subformation top ($+0.2$ to $+0.8\text{‰}$). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in studied limestones is low in most samples, ranging from 0.70521 to 0.70555 (Table 2) in general, but rising to 0.70585 in the basal horizon and to 0.70627 at the level of 5 m below the formation top in Tolparovo-1 section. The Mn/Sr, Fe/Sr, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ value correlate with Mg/Ca ratio.

Min'yar Formation. Trace element concentrations in the formation members depend on dolomitization degree of their rocks (Mg/Ca from 0.01–0.18 to 0.53–0.66).

Member I has been studied only in the Usmanjali section, where the exposed basal interval (3 m) is composed of pure limestones ($\text{Mg}/\text{Ca} = 0.016$) relatively enriched in SA (7.4%), Mn (750 ppm), and Fe (1585 ppm) but depleted in Sr (165 ppm). In the studied sample, Mn/Sr and Fe/Sr ratios are as high as 4.6 and 9.6, respectively, $\delta^{13}\text{C}$ value corresponds to -0.9‰ , and $\delta^{18}\text{O} = -12.2\text{‰}$, the lowest value we have measured.

Member II representing marker bed of stromatolitic rocks is composed of dolostones ($\text{Mg}/\text{Ca} = 0.614$) in the Bakeevo section and of limestones ($\text{Mg}/\text{Ca} = 0.010\text{--}0.050$) in the Usmanjali section. Having the comparable SA content (2.8 and 2.5–4.1%), dolostones and limestones of Member II are dissimilar in geochemical characteristics. Dolostones of the Bakeevo section are enriched in Fe (1230 ppm) and contain 145 ppm Mn, being obviously depleted in Sr (50 ppm), whereas limestones of the Usmanjali section contain 505 to 815 ppm Fe, 65 to 730 ppm Mn and 1086 and 380 ppm Sr. Concentration of the last element is inversely correlated with Mg/Ca ratio. The Mn/Sr and Fe/Sr ratios of 2.9 and 24.6 are respectively characteristic of dolostones and correspond to 0.06–1.9 and 0.47–2.1 in limestones. Parameter $\delta^{18}\text{O}$ ranging from -8.8 to -8.3‰ in limestones increases up to -6.5‰ in dolos-

tones. The $\delta^{13}\text{C}$ variation range of from -0.2 to $+0.2\%$ characterizes rocks of both types. In the "best" limestone sample with lowest $\text{Mg}/\text{Ca} = 0.010$, $\text{Mn}/\text{Sr} = 0.06$, and $\text{Fe}/\text{Sr} = 0.47$, the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio is 0.70552.

Member III composed of dolostones in the Bakeevo section ($\text{Mg}/\text{Ca} = 0.578\text{--}0.647$; 0.614 in average) is represented in the Usmangali section by a packet of alternating dolomitized limestones with different Mg/Ca ratios. Limestones of the first type ($\text{Mg}/\text{Ca} = 0.006\text{--}0.053$; 0.026 in average) contain less than 3% SA, are relatively depleted in Mn and Fe (19 and 310 ppm in average), but obviously enriched in Sr (890 ppm in average). The high Sr concentrations in the rocks likely indicate a high proportion of aragonite in original sediments. In dolomitized limestones of the second type ($\text{Mg}/\text{Ca} = 0.126\text{--}0.185$; 0.160 in average), the SA content is 16.5%, and the rocks comparable in Mn concentration (28 ppm in average) with above limestones are enriched in Fe (1710 ppm in average) but relatively depleted in Sr (365 ppm in average). As compared to limestones of Usmangali section, dolostones of Bakeevo section are relatively enriched in Mn (98 ppm in average) but depleted in Sr (60 ppm in average) and Fe (355 ppm in average). As for Mn/Sr and Fe/Sr ratios, they are much lower in limestones of Usmangali locality than in dolostones of Bakeevo section, corresponding respectively to 0.01–0.42 versus 0.62–3.2 and 0.16–9.7 versus 5.3–37.8. In all limestones of Usmangali section, $\delta^{18}\text{O}$ values are within the range of -8.9 to -7.3% . This may indicate that the early diagenesis and dolomitization of sediments were concurrent and developed under identical conditions. In dolostones of Bakeevo section, $\delta^{18}\text{O}$ values range from -7.8 to -5.8% decreasing to -8.0 and -9.0% in two samples. The variation range of $\delta^{13}\text{C}$ value is wider in Usmangali than in Bakeevo section: -0.3 to $+2.8$ versus $+0.2$ to $+1.5\%$. In Member III, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio equal to 0.70550–0.70584 is established in limestones of Usmangali section. In dolostones of Bakeevo section it is higher, corresponding to 0.70615–0.70644 in the Member upper part and even to 0.70858 in the lower one.

Member IV studied in Bakeevo and Usmangali sections is composed of dolostones ($\text{Mg}/\text{Ca} = 0.587\text{--}0.691$). The lower dolomitization degree ($\text{Mg}/\text{Ca} = 0.165$) is established in one sample only that has been collected near the Member base in Bakeevo section. Average Mg/Ca ratios correspond to 0.570 in the former section and to 0.619 in the second one. The SA content in the rocks is very low: 0.9–6.9% (3.4% in average) in Bakeevo and 1.0–5.7% (2.9% in average) in Usmangali section. The Mn concentration ranging from 29 to 50 ppm (39 ppm in average) in the latter section rises up to 30–153 ppm (70 ppm in average) in the former. The respective Fe concentrations are 425 to 1480 ppm (averaged value 848 ppm) and 340 to 4690 ppm (averaged value 1376 ppm), with concentration maximum established in lower 50 m of the Member in Bakeevo section. Relatively low Sr concentration varies from 50

to 76 ppm in Usmangali and from 47 to 104 ppm in Bakeevo section (averaged values 66 and 62 ppm). Variation ranges of Mn/Sr and Fe/Sr ratios in dolostones of the first locality are 0.47–0.77 and 6.8–22.7, respectively. In Bakeevo section, the Mn/Sr variation range is wider (0.32–2.60), while Fe/Sr ratio varying from 22.2 to 78.2 in lower 50 m declines quickly to 3.6–13.6 in upper 60 m of the Member. In dolostones of Usmangali section, $\delta^{18}\text{O}$ ranges from -7.9 to -6.5% , while in Bakeevo section this parameter is between -7.0 and -5.3% , being as low as -7.9% in one sample ($\text{Mg}/\text{Ca} = 0.165$). The $\delta^{13}\text{C}$ variation ranges in dolostones are -0.5 to $+3.0\%$ in Usmangali and -0.6 to $+1.8\%$ in Bakeevo section. The $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio of 0.70622 is established for one dolostone sample from Bakeevo section, and variation range of 0.70573–0.70628 is determined for rocks of Usmangali section. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70573–0.70599) is characteristic of samples with $\text{Fe}/\text{Sr} < 6.9$ and $\text{Mn}/\text{Sr} < 0.49$.

Member V crowns the Min'yar Formation in Bakeevo and Usmangali sections, because its uppermost horizons are truncated here by pre-Vendian erosion. Carbonate rocks of the Member, which contain intercalations of early diagenetic cherts, are dolomitized to different extent: $\text{Mg}/\text{Ca} = 0.573\text{--}0.664$ (0.621 in average), Bakeevo section; $\text{Mg}/\text{Ca} = 0.526\text{--}0.620$ (0.597 in average), Usmangali section. The SA content approximately equal in all the rocks ranges from 0.8 to 12.2% in Bakeevo and from 1.3 to 11.3% in Usmangali sections (averaged values 3.5 and 4.7%, respectively), one sample from Bakeevo section with 90.4% of silicate material is excluded from calculations. In this section, Mn and Fe concentrations increase from the base to the Member top. The Mn concentration is 30 to 70 ppm (50 ppm in average) in the Member lower beds (160 m), 31 to 180 ppm (102 ppm in average) in the middle interval (115 m), and 250 to 665 ppm (490 ppm in average) in the upper one (35 m). As for Fe concentration, it is 110 to 550 ppm (288 ppm in average) in lower 190 m of the Member section, 315 to 825 ppm (662 ppm in average) in the next interval 85 m thick, and 990 to 2150 ppm (1513 ppm in average) in upper 55-m-thick beds. In Usmangali section, where only lower 210 m of the Member are exposed, Mn and Fe concentrations are low, corresponding respectively to 19–45 ppm (36 ppm in average) and 74–545 ppm (240 ppm in average), thus being comparable to concentration ranges in lower 160–190 m of the Bakeevo section. The considerable upward increase of Mn and Fe concentrations leaves no doubt that these elements were carried in by fluids, which penetrated into rocks during the pre-Uk erosion of the Min'yar Formation. Dolostones of Member V have comparable Sr concentrations in both sections: 51 to 153 ppm in Bakeevo and 50 to 125 ppm in Usmangali localities (in average 88 and 81 ppm, respectively). Minimal Mn/Sr (0.26–1.3) and Fe/Sr (0.89–11.0) ratios are characteristic of dolostones from Usmangali section and from lower beds of Bakeevo section; in upper beds of the lat-

ter (40 m) both ratios are higher: Mn/Sr = 2.2–7.4, Fe/Sr = 12.1–23.9. Variation ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are 0.70579–0.70680 in Bakeevo and 0.70597–0.70664 in Usmangali section; $\delta^{18}\text{O}$ values range from –8.3 to –3.4‰ in the first case and from –8.3 to –5.0‰ in the second one. The $\delta^{18}\text{O}$ variation range in Member V is considerably wider in general than in underlying members lacking cherty inclusions (–5.3 to –9.6‰) that may be indicative of a more complex history of di- and epigenetic alterations in sediments. Positive $\delta^{13}\text{C}$ values (+0.1 to +2.7‰) characteristic of dolostones in the Member lower part give place to negative ones (–2.8 to –0.4‰) higher in the section.

Member VI, the terminal one in the Min'yar Formation, has not been studied in new sections. Data obtained earlier (Podkovyrov et al., 1998; Kuznetsov et al., 2003) show that it is composed of pure limestones (Mg/Ca = 0.002–0.019) with a dolomitized interlayer (Mg/Ca = 0.156) near the Member base. The SA content in limestones is insignificant (0.3–3.4%); Mn and Fe concentrations are variable (130 to 2960 and 150 to 1420 ppm, respectively). The rocks are relatively enriched in Sr (230 to 477 ppm), although decreased concentrations of this element are established near the pre-Uk unconformity and in dolomitized limestone near the Member base. The Mn/Sr ratio ranges from 0.27 to 3.61 in general, being as high as 12.9 at the Member base; Fe/Sr ratio is commonly within the range of 0.3–1.8, being higher near the top (4.2) and at the base (6.2).

Uk Formation. Carbonate–siliciclastic deposits of the lower Uk Subformation discordantly rests on members V and VI of underlying Min'yar deposits. In the Kurtaza and Kulmas sections, the formation includes packets of micritic limestones (Mg/Ca = 0.006–0.012), which contain 3.1 to 5.5% of siliciclastic material, being relatively depleted in Mn (32 to 76 ppm) but enriched in Fe (225 to 1790 ppm) and Sr (170 to 755 ppm). The Mn/Sr and Fe/Sr ranges in the rocks are from 0.04 to 0.37 and from 0.30 to 10.5, respectively; $\delta^{18}\text{O}$ from –6.1 to –4.4‰, and $\delta^{13}\text{C}$ from +1.4 to +3.4‰. Hence, the lower Uk limestones are insignificantly altered by epigenetic fluids. In the “best” limestone sample from the Kurtaza section (Mn/Sr = 0.04, Fe/Sr = 0.30), $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is equal to 0.70533.

The SA content in carbonate rocks of the upper Uk Subformation is very low (0.7 to 4.1%, 1.6% in average). Only lower horizons of this unit have survived the pre-Vendian erosion and are exposed in Kurtaza and Kulmas sections (apparent thickness 150 and 30 to 35 m, respectively). Limestones (Mg/Ca = 0.002–0.008) prevailing in Kurtaza section enclose in their middle interval the 3- to 4-m-thick packets of highly dolomitic varieties (Mg/Ca = 0.296–0.299). In pure limestone, Mn and Fe concentrations are low, ranging from 18 to 140 ppm (averaged value 55 ppm) and from 165 to 515 ppm (averaged value 283 ppm), respectively, in distinction from higher values of 230–790 and

1610–4010 ppm established in dolomitized varieties. The Sr concentration ranges in carbonates from 75 to 727 ppm with peak values (314–727 ppm) confined to lower 15 m of the subformation. Higher it decreases to 75–214 ppm in limestones and to 80–83 ppm in dolomitized varieties. The Mn/Sr ratio commonly ranging from 0.08 to 0.63 is increased (1.0–1.3) in carbonates depleted in Sr. The Fe/Sr range in limestones is 0.53–3.3. The highest Mn/Sr (2.9–9.5) and Fe/Sr (20.1–48.3) ratios are established in dolomitized limestones (Mg/Ca = 0.296–0.299). Value $\delta^{18}\text{O}$ varying usually from –6.2 to –5.0‰ declines in the lower part of the unit to –7.2‰ and more (–7.6 to –7.0‰) near the horizon of dolomitized limestones. In the Kulmas locality, where 30 m of the subformation section are retained, limestones (Mg/Ca = 0.002–0.008) are relatively depleted in Mn (27–66 ppm, 52 ppm in average) and Fe (260–470 ppm, 380 ppm in average), having variable Sr concentrations (90–437 ppm, 224 ppm in average). Limestones of the Kulmas section have the following characteristics: Mn/Sr = 0.06–0.73, Fe/Sr = 1.1–4.6, $\delta^{18}\text{O}$ from –4.3 to –4.0‰, $\delta^{13}\text{C}$ from +1.2 to +3.2‰. In limestones of the Kurtaza section, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio ranges from 0.70542 to 0.70636, rising up to 0.70709 in dolomitic limestone from this section; the $^{87}\text{Sr}/^{86}\text{Sr}$ variation range in the Kulmas section is 0.70538–0.70580 (Kuznetsov et al., 2003). Rising of this ratio indicates partial alteration of rocks under influence of meteoric waters at the time of pre-Vendian hiatus.

SELECTION OF LEAST ALTERED CARBONATE SAMPLES

C-isotopic systematics. In majority (82%), Karataevian carbonates from Tolparovo-1, Tolparovo-2, Usmangali, Bakeevo and Kurtaza sections (Fig. 3) satisfy the geochemical criteria of C-isotope system retentivity accepted for limestones (Mn/Sr \leq 4, Fe/Sr \leq 10, $\delta^{18}\text{O} \geq -10\text{‰}$) and dolostones (Mn/Sr \leq 6, Fe/Sr \leq 15, $\delta^{18}\text{O} \geq -10\text{‰}$). In limestones, which do not satisfy the above criteria, both Mn/Sr and Fe/Sr ratios are higher than threshold values in two samples of clayey limestones from the Katav Formation, Tolparovo-1 section, in which the SA content is over 30%, and in one sample (no. UK-17) of dolomitic limestone from the Uk Formation in Kurtaza section. The Fe/Sr ratio alone is over critical value in 10 samples: six samples with the SA content of 9.3 to 15.9% are from the Katav Formation, two from basal horizon of the lower Inzer Subformation, one from limestone interlayer in siliciclastic lower Uk Subformation, and one more (no. UK-14) from dolomitic limestone interlayer in the upper Uk Subformation, Kurtaza section. Thus, limestones unfitting the retentivity criteria either are enriched in siliciclastic components, or occur near siliciclastic and clay-carbonate beds. For these samples, strict correlation between Mn/Sr and Fe/Sr ratios, on the one hand, and $\delta^{13}\text{C}$ values, on the other, is not established, and covariation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values is also untypical. Con-

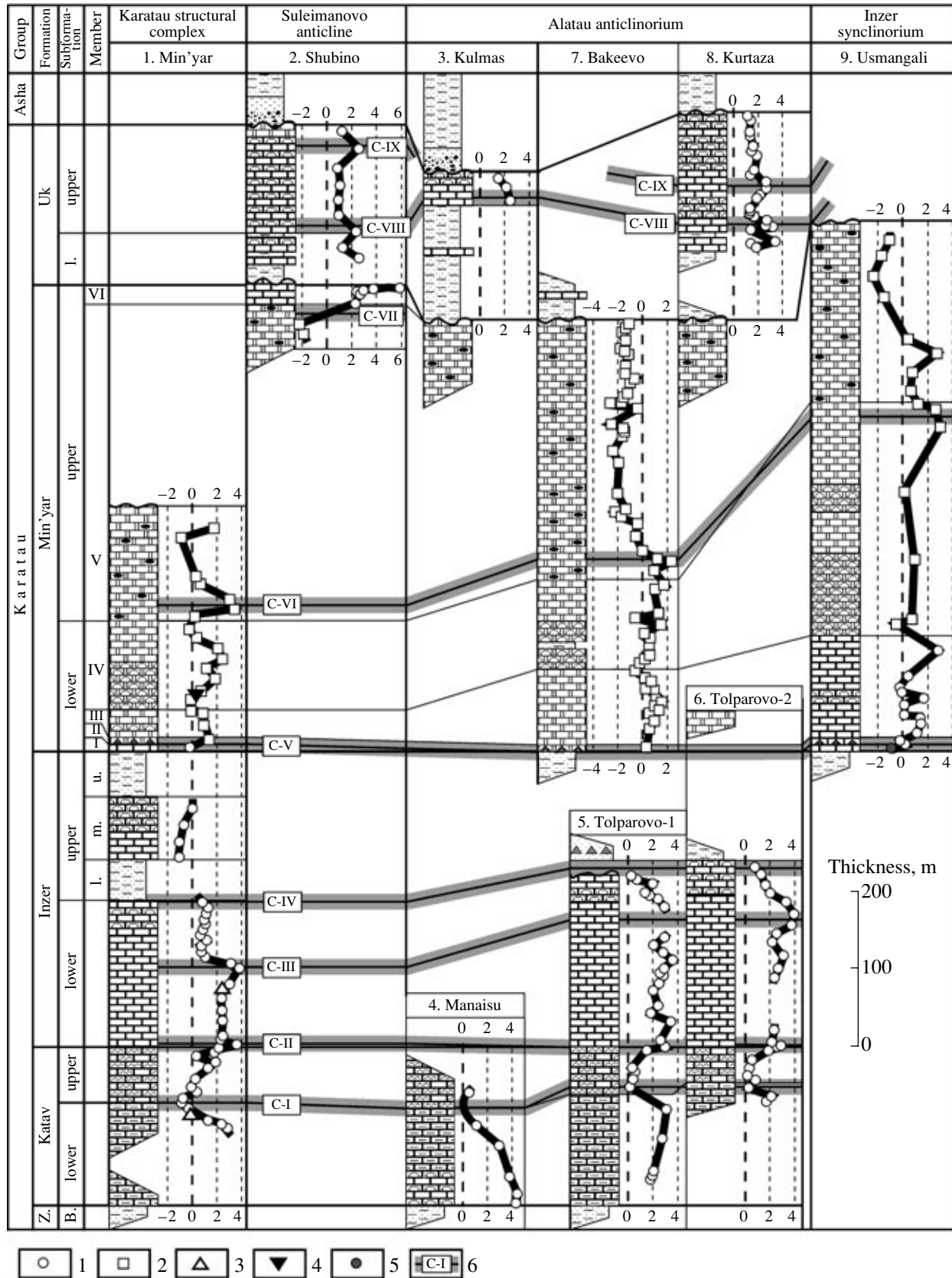


Fig. 3. $\delta^{13}C$ variations in carbonate rocks of the Karatau Group and C-isotopic chemostratigraphic correlation of studied sections: (1) limestones; (2) dolostones; (3) veined calcite; (4) veined dolomite; (5) sample omitted from considerations (see text); (6) C-isotopic correlation levels and their numbers (other symbols as in Fig. 2).

sequently, C-isotopic systems of carbonates under consideration did not experience a considerable disturbance. In samples UK-14 and UK-17 of dolomitized limestones ($Mg/Ca = 0.291$ and 0.299) from the Uk Formation, Mn/Sr and Fe/Sr ratios are independent of $\delta^{13}C$ values, being in covariance with $\delta^{18}O$ values. This is probably a consequence of dolomitization under influence of meteoric waters during the pre-Asha break in sedimentation.

Among 15 dolostone samples from the Min'yar Formation, Usmanjali section, only three samples from the Member IV have Fe/Sr ratio exceeding the threshold value and ranging from 15.4 to 22.7. In the same formation of Bakeevo section, we collected 61 dolostone samples and established that both Mn/Sr and Fe/Sr threshold ratios are exceeded in two cases. In addition, in eleven samples taken from the lower 30 m of the formation near an argillite interlayer and from the upper 35 m of exposed part of Member V Fe/Sr ratio alone excess the threshold one. In all the dolostone samples studied, there is no correlation between Mn/Sr and Fe/Sr ratios, on the one hand, and parameters $\delta^{18}O$ and $\delta^{13}C$, on the other. The average $\delta^{18}O$ value in dolostones of the Min'yar Formation is by 2.5‰ higher than in concurrent limestones. This difference is close to $\delta^{18}O_{cal.-dol.}$ of the low-T oxygen fractionation in equilibrium calcite–dolomite system (Fritz and Smith, 1970) and coincides with $\delta^{18}O_{cal.-dol.}$ of sedimentary calcium carbonate and cogenetic dolomite (Veizer and Hoefs, 1976; McKenzie, 1981). In such a case, it is reasonable to suggest that dolostones of the Min'yar Formation experienced the early diagenesis in an environment with isotopic parameters close to those in seawater (Kaufman and Knoll, 1995).

Similarity between $\delta^{13}C$ values in the above carbonates unfitting the geochemical criteria and in associated “best” samples (Fig. 3) implies that postsedimentary recrystallization of limestones and dolostones, if it took place, progressed without essential fractionation of carbon isotopes. When the Mn/Sr – $\delta^{13}C$ and Fe/Sr – $\delta^{13}C$ paired correlation is absent, changes in C-isotopic systems cannot be established based on the indicated criteria. It is likely therefore that the accepted threshold values of Mn/Sr and Fe/Sr ratios are lower a priori than those, which could be indicative of critical changes in the original C-isotopic characteristics of the Karatau Group carbonates. The same is evident from the fact that threshold Mn/Sr ratios considered in works dedicated to the problem are thought to be <10 (Knoll et al., 1995; Kaufman and Knoll, 1995; Bartley et al., 2001; Khabarov et al., 2002). As for influence of organic carbon, enriched in light isotope and remobilized during catagenesis, on $\delta^{13}C$ values in the studied whole-rock carbonate samples, it can be ignored under chemostratigraphic considerations in this work, because concentration of organic matter in rocks of the Karatau Group is commonly very low. Data on dolomitic limestones from the Uk Formation show that the late diagenetic dolomitization that increased Mn/Sr ratios and

decreased $\delta^{18}O$ values in the rocks did not change the $\delta^{13}C$ values as compared to those characterizing the associated limestone with “best” geochemical parameters. It is necessary to add as well that $\delta^{13}C$ values in veined and host carbonates of the Min'yar section are close to each other regardless of Mg/Ca ratios in these varieties (Fig. 3). In veined carbonates, $\delta^{13}C$ is equal to $-0.5‰$ in the Katav Formation, $+2.4‰$ in the Inzer Formation, and $+0.5‰$ in the Min'yar Formation, whereas this parameter ranges in rocks of the respective formations from -0.8 to -0.2 , from $+2.4$ to $+3.0$, and from -0.1 to $+0.8‰$. Consequently, epigenetic recrystallization responsible for origin of veined carbonates practically did not influence C-isotopic composition in carbonate sediments. Limestone sample MI-2 with $\delta^{18}O = -12.2‰$ from the Min'yar Formation base in Usmanjali section is the only one that should be excluded from consideration of C-isotopic systematics of sedimentation medium. Thus, all the other samples defined as altered based on too strict threshold values of Mn/Sr and Fe/Sr ratios retain in fact the original C-isotopic characteristics.

Rb–Sr systematics. The accepted geochemical criteria of Rb–Sr system retentivity imply that all the studied samples from the Katav Formation experienced intense secondary alterations (Fig. 4). The Mn/Sr and Fe/Sr ratios in these samples exceed threshold values of <0.2 and <5.0 , respectively, and $^{87}Sr/^{86}Sr$ ratios range widely from 0.70627 to 0.70979 (Kuznetsov et al., 2003). It is plausible to suggest therefore that influence of fluids derived at the burial stage from siliciclastic rocks of Zilmerdak Formation and siliciclastic admixture in Katav carbonates was so intense that resulted in enrichment of the Katav Formation rocks and 10- to 20-m-thick basal horizon of the Inzer Formation in Mn, Fe, and radiogenic ^{87}Sr . Clayey limestones of that horizon are variably enriched in Mn (70 to 355 ppm) and Fe especially (1610 to 6180 ppm), being comparable in this respect with the Katav Formation rocks and inappropriate together with the latter for determination of the $^{87}Sr/^{86}Sr$ initial ratio. The only sample ($Mn/Sr = 0.18$, $Fe/Sr = 4.2$) collected near the horizon top in Tolparovo-1 section is of the least altered type according to formal criteria. However, the $^{87}Sr/^{86}Sr$ ratio in this sample is higher than in concurrent limestones of the Min'yar section (0.70585 versus 0.70536–0.70540). As the latter appear to be altered according to geochemical criteria ($Mn/Sr = 0.20$ – 0.28 , $Fe/Sr = 5.2$ – 7.8), the $^{87}Sr/^{86}Sr$ initial ratio in that sample from basal horizon of the Inzer Formation can be regarded only as a possible upper limit of this ratio in seawater.

The overlying main interval of the lower Inzer Subformation is composed in Tolparovo-1 section predominantly of limestones with low Mn/Sr (0.03 to 0.08) and Fe/Sr (0.22 to 1.2) ratios implying the least altered character of the rocks. The $^{87}Sr/^{86}Sr$ initial ratios ranging in these rocks from 0.70521 to 0.70555 are consistent with the variation range of 0.70525–0.70538 characterizing the “best” limestones from the same subfor-

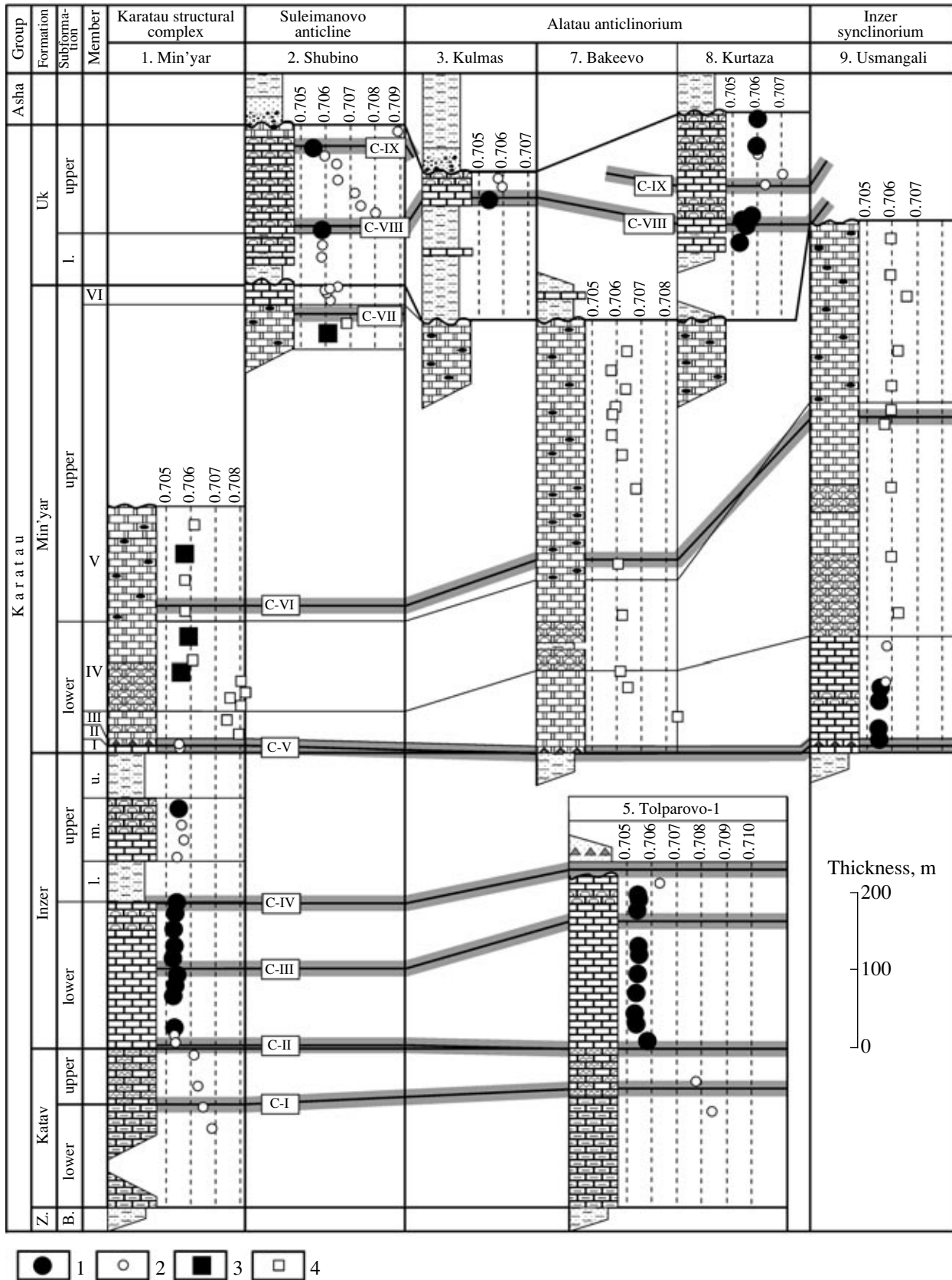


Fig. 4. Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in carbonate rocks of the Karatau Group: (1, 2) limestones satisfying (1) and unsatisfying (2) geochemical criteria of Rb–Sr system retentivity; (3, 4) dolostones satisfying (3) and unsatisfying (4) geochemical criteria of Rb–Sr system retentivity (other symbols as in Figs. 2 and 3).

mation in the Min'yar section (Kuznetsov et al., 2003). The only altered limestone (Mn/Sr = 0.20, Fe/Sr = 1.3, $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70627) is detected near the subformation top, where the ratio increase resulted from influence of meteoric waters during erosion of Karatavian deposits, which are discordantly overlain by Vendian sediments in Tolparovo-1 section.

In the Usmangali section, limestones from members II and III of the Min'yar Formation yielded four samples satisfying the retentivity criteria (Mn/Sr = 0.01–0.06, Fe/Sr = 0.16–0.47). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is equal to 0.70552 in one sample from Member II and ranges from 0.70550 to 0.70558 in three other samples from Member III. The comparable ratios of 0.70560 to 0.70572 (Kuznetsov et al., 2003) have been reported for “altered” limestones (Mn/Sr = 0.43–0.73, Fe/Sr = 5.5–9.1) from Member I of the same formation in the Min'yar section. Two studied samples from Member III of Usmangali section have low Mn/Sr (0.06–0.18) and Fe/Sr (0.56–4.1) but elevated Mg/Ca (0.050–0.053) ratios. Since the early diagenetic dolomitization of Min'yar limestones took place in a medium close in isotopic parameters to seawater (see above), $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios in these rocks (0.70574–0.70584) likely differ insignificantly from this parameter in the early diagenesis medium.

The Mn/Sr and Fe/Sr ratios in the Min'yar dolostones from new studied sections show no correlation with $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Negative and positive correlation between Mg/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is established for dolostones from Usmangali and Bakeevo sections, respectively. The observable situation means compositional difference of fluids, which influenced the Rb–Sr systems of carbonates during di- and epigenetic alterations. Being independent of each other, geochemical characteristics of dolostones are unsuitable for determination of retentivity criteria for Rb–Sr systems in these rocks (Kuznetsov et al., 2003). As postsedimentary alterations of Karatavian carbonates were able to increase but not decrease the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the rocks, we believe that minimum values of this ratio characterize its upper limit in environment of sedimentation and/or early diagenesis of sediments. In dolostones of members IV and V of Usmangali section, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio vary from 0.70573 to 0.70598 and from 0.70597 to 0.70600. In Bakeevo section, the minimum $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in dolostones of Member IV is 0.70622, being lower (0.70573 to 0.70598) in the same Member of Usmangali section, while contrary situation with lowest ratios is characteristic of Member V: 0.70579–0.70593 in the first and 0.70597–0.70600 in the second section. These distinctions likely reflect local isotopic-geochemical peculiarities of epigenetic processes. The above $^{87}\text{Sr}/^{86}\text{Sr}$ ratios characterizing members IV and V are close to these parameters of concurrent least altered rocks studied earlier: 0.70574–0.70598 (Member IV, Min'yar section), 0.70583–0.70611 (Member V, Min'yar and Shubino sections). In Usmangali and Bakeevo sections, Mn/Sr ratio in dolostones with low-

est $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is not greater than 1.1, i.e., below the threshold value of 1.2 figured out for dolostones of the Min'yar Formation (Ovchinnikova et al., 2000; Kuznetsov et al., 2003). However, Fe/Sr ratio in the same rocks exceed frequently the threshold value of 3.0, being sometimes two to three times higher.

The lower Uk Subformation is represented in new collection by a single limestone sample (Mg/Ca = 0.006) satisfying the accepted retentivity criteria (the subformation upper part, Kurtaza section) and having $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70533 that is essentially lower than ratios of 0.70582 to 0.70595 in altered samples of the same subformation from the Shubino section (Kuznetsov et al., 2003). In the upper carbonate subformation, the Kurtaza section, there are three rock packets with differently changed Rb–Sr systems. The least altered limestone samples (Mg/Ca = 0.005–0.008, Mn/Sr = 0.08–0.19, Fe/Sr = 0.53–1.1) characterize basal and terminal thirds of the subformation, while the middle third is composed of “altered” rocks only, which are partly dolomitized and have elevated SA content. The $^{87}\text{Sr}/^{86}\text{Sr}$ variation ranges in the limestone of the first and third packets are 0.70542–0.70586 and 0.70605–0.70609, characterizing Sr isotopic composition in sedimentation medium. In limestones of the middle packet, Mn/Sr (0.28–9.5) and Fe/Sr (1.1–48.3) ratios are above critical values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio correspond to 0.70636, 0.70709 and 0.70610. A possible factor that disturbed Rb–Sr systems in these limestones was influence of meteoric waters during the pre-Vendian hiatus. Nevertheless, it is reasonable to assume that $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio in sedimentation medium was not greater than 0.70610 during accumulation of the middle interval of the subformation.

In Shubino and Kulmas sections, where the Uk Formation has been studied earlier (Kuznetsov et al., 2003), the least altered carbonates (Mg/Ca = 0.002–0.014, Mn/Sr = 0.06–0.14, Fe/Sr = 0.40–1.6) occur near the base and top of the upper subformation. The $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio in basal samples correspond to 0.70538 (Kulmas section) or 0.70580 (Shubino section); in a sample collected higher in last section to 0.70545. C-isotopic chemostratigraphic correlations considered below (Fig. 3) show that in Shubino section the “best” sample ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70545) located near the section top corresponds to a lower stratigraphic level than two “best” samples with ratio of 0.70605 and 0.70609 in the Kurtaza section terminal part (Fig. 4). Altered samples of Kulmas and Shubino sections are mostly confined to the middle and uppermost intervals of the subformation and show $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from 0.70591 to 0.70800 and 0.71050 to 0.71187. Hence, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater declined from the terminal Min'yar to initial Uk time and increased subsequently during the accumulation time of the Uk Formation.

$\delta^{13}\text{C}$ AND $^{87}\text{Sr}/^{86}\text{Sr}$ VARIATIONS IN SEAWATER OF THE KARATAVIAN TIME

Data on distribution of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values in carbonates of the Karatau Group, which are obtained in this work (see above) and published earlier (Semikhatov et al., 1995; Gorokhov et al., 1996; Kuznetsov et al., 1997, 2003; Podkovyrov et al., 1998) clarify some important chemostratigraphic peculiarities of the Upper Riphean stratotype.

C-isotopic characterization. Secular variations of $\delta^{13}\text{C}$ values in the Karatavian carbonates are depicted based on results of 255 analyses, 171 obtained in this work and 84 published earlier (Podkovyrov et al., 1998). Varying from -2.8 to $+5.9\text{‰}$ in general, $\delta^{13}\text{C}_{\text{carb}}$ values characterize successive stratigraphic levels in the Karatau Group with specific C-isotopic parameters, which are not always corresponding to lithostratigraphic subdivisions. These levels C-I to C-IX, as they are designated in this work, correspond either to in-phase extremums of $\delta^{13}\text{C}$ variation curves, which are observable in all the sections studied, or to turning points from negative to positive values and intersection points with zero reference line (Fig. 3).

The Katav Formation that begins the carbonate-bearing part of Karatau Group interval with carbonate deposits is divided in two parts by the level C-I corresponding to extreme $\delta^{13}\text{C}$ values of -0.8‰ in Min'yar and $+0.2\text{‰}$ in both Tolparovo sections. The level is detected within 5- to 7-m-thick packet separating lower and upper Katav subformations. In the lower subformation of Tolparovo-1 and Min'yar sections, $\delta^{13}\text{C}$ values increase upward from $+1.8\text{‰}$ near the base to $+2.8\text{‰}$ and then decline quickly to the indicated values of -0.8 and $+0.2\text{‰}$ in the upper third of the unit (Fig. 3). In Manaisu section, $\delta^{13}\text{C}$ values in lower 30 m of the subformation are higher than in correlative interval of Tolparovo-1 section ($+3.8$ to $+4.4$ versus $+1.7$ to $+2.1\text{‰}$). This dissimilarity is probably caused by stromatolitic rocks widespread in lower 50 m of Manaisu section, because cyanobacterial community that built stromatolites in shallow settings favored removal of ^{12}C from seawater and enrichment of carbonate sediments in ^{13}C (Heiskanen and Rychanchik, 1999; Melezhik et al., 1999). An alternative explanation could be disturbance of C-isotopic systems in limestones of Tolparovo-1 section that is inadmissible however, because there is no correlation between Mn/Sr, Fe/Sr, and $\delta^{18}\text{O}$ values in those limestones, on the one hand, and $\delta^{13}\text{C}$, on the other.

Data on Min'yar, Tolparovo-1, and Tolparovo-2 sections show that above C-I level $\delta^{13}\text{C}$ values gradually increase upward, being as high as $+1.5$ to $+1.8\text{‰}$ at the top of the upper Katav Subformation. In lower 2–4 m of the lower Inzer Subformation, they depict a positive extremum, being equal to $+3.6\text{‰}$ in Min'yar, $+2.9\text{‰}$ in Tolparovo-1, and $+3.0\text{‰}$ in Tolparovo-2 sections. That extremum is considered as chemostratigraphic level C-II. Below this level in Min'yar section, $\delta^{13}\text{C}$ in the

4-m-thick packet is as low as $+0.3\text{‰}$, but this decrease has not been detected in Tolparovo sections, where sampling was less detailed.

In the next level C-III established somewhat above the middle of the lower Inzer Subformation, $\delta^{13}\text{C}$ is risen up to $+3.9\text{‰}$ in Min'yar and $+4.0\text{‰}$ in Tolparovo-2 sections. In Tolparovo-1 section, rocks correlative with this level are unexposed, but above and below this gap in outcrops, $\delta^{13}\text{C}$ values of $+2.9\text{‰}$ obviously belong to the same excursion (Fig. 3). In the section interval between levels C-II and C-III, $\delta^{13}\text{C}$ values range in general from $+1.8$ to $+2.9\text{‰}$ with positive fluctuations up to $+3.1\text{‰}$ in Tolparovo-2 and $+3.4$ to $+3.6\text{‰}$ in Tolparovo-1 sections. The Min'yar section is lacking fluctuations of this kind that is probably a consequence of different facies environments of sedimentation.

The terminal part of the lower Inzer Subformation succeeding level C-III corresponds to descending trend of $\delta^{13}\text{C}$ variations, which is different, however, in Min'yar and Tolparovo sections. In the first section, $\delta^{13}\text{C}$ values quickly decrease to lower values ($+0.8$ to $+1.1\text{‰}$) as compared to $+3.9\text{‰}$ characteristic of the level C-III and range afterward from $+0.7$ to $+1.4\text{‰}$ within the relevant interval, declining further near the subformation top. In both Tolparovo sections, the decrease is more gradual, from $+2.9$ to $+3.3\text{‰}$ near the level C-III to values of $+1.3$ to $+2.4\text{‰}$ in the middle and of $+0.2$ to $+0.8\text{‰}$ near the subformation top. The level C-IV that demarkates on top the interval under consideration can be defined tentatively, because above there are siliciclastic deposits of the upper Inzer Subformation. In the middle carbonate Member of this subformation, which has been studied in the Min'yar section only, $\delta^{13}\text{C}$ values grow upward from -1.0‰ to zero. The relevant separate interval of the succession with prevailing negative $\delta^{13}\text{C}$ values is distinct from underlying and overlying interval, where the values are predominantly positive.

The next interval with predominantly low positive $\delta^{13}\text{C}$ values corresponds to members I–IV of the Min'yar Formation. In Min'yar, Bakeevo, and Usmangali sections, $\delta^{13}\text{C}$ values range from -0.2 to $+0.2\text{‰}$ in unaltered rocks of members I–II and from $+0.3$ to $+2.0\text{‰}$ in members III–IV, though being as high as $+2.4$ to $+3.0\text{‰}$ and as low as -0.3 to -0.6‰ in single samples of the last two members. In Usmangali section, where Member III is of maximum thickness (115–120 m) being composed of limestones, fluctuations of $\delta^{13}\text{C}$ values with amplitudes of about 2‰ are more frequent than in dolostones of the same Member in Bakeevo and Min'yar sections. This is likely interrelated with the retentivity extent of initial isotopic signature in limestones and dolostones. The C-isotopic interval distinguished in the lower part of the Min'yar Formation is bounded on top by a positive extremum of the level C-VI with $\delta^{13}\text{C}$ values of $+3.4\text{‰}$ in Min'yar, $+3.0\text{‰}$ in Usmangaly, and $+2.3\text{‰}$ in Bakeevo sections. In

Min'yar and Bakeevo sections, this level is detected respectively 10 and 20 m above the Member V base, while in Usmangali section it is 30 m below the top of Member IV. Consequently, level C-VI characterizes the diachronous character of boundary between lithostratigraphic members IV and V of the Min'yar Formation that has been suggested earlier based on geological data (Maslov, 1997, 2002).

Above the positive extremum determining the level C-VI, $\delta^{13}\text{C}$ values decrease reaching -0.4 to -0.6‰ in Bakeevo, -0.9 to $+0.6\text{‰}$ in Min'yar, and $+0.4\text{‰}$ in Usmangali sections, although values of $+1.3$ and $+2.7\text{‰}$ established for two samples from the latter two sections complicate the general trend. Data on the best studied Bakeevo section show that negative values of -2 to -1‰ characteristic in general of the higher stratigraphic interval are accompanied by local fluctuations attaining -2.8 to -2.4‰ , on the one hand, and -0.7 to -0.4‰ of the other. In Bakeevo section of the Min'yar Formation, interval of Member V with these negative values is 240 m thick, being two times thinner in Usmangali section because of deeper erosion during the pre-Uk hiatus. Youngest rocks of this interval with $\delta^{13}\text{C}$ values of -2.2 to -1.8‰ are exposed in Shubino section. Finally, as is established in the same section, $\delta^{13}\text{C}$ values increase upward to $+1.3$ and $+2.7\text{‰}$ in the thickest Member VI of the Min'yar Formation, being near its top at the maximum of $+5.9\text{‰}$ that is recorded nowhere else in the Karatau Group. Chemostratigraphic level C-VII, the last one in the Min'yar Formation, is determined as characterizing transition from moderately negative $\delta^{13}\text{C}$ values at the top of Member V (-2.2 to -1.8‰) to positive values at the base of Member VI.

It is difficult to detect the C-isotopic boundary between the Min'yar and Uk formations because of unconformity, overlain by basal siliciclastic sediments of the Uk Formation. In Shubino and Kurtaza sections, $\delta^{13}\text{C}$ values in carbonate members of the lower Uk Subformation vary respectively from $+1.4$ to $+2.6\text{‰}$ and from $+1.4$ to $+3.4\text{‰}$. The most complete rock succession of the upper Uk Subformation is preserved after the pre-Vendian erosion in Kurtaza section, where $\delta^{13}\text{C}$ values range in general between $+1.2$ and $+1.9\text{‰}$ with two extremums, one of $+2.7$ to $+3.2\text{‰}$ in the interval of 4 to 10 m above the subformation base and the other one of $+2.6\text{‰}$ in its middle part. A comparable distribution of $\delta^{13}\text{C}$ values has been established earlier in Shubino section (Podkovyrov et al., 1998), where two peak values of $+2.4\text{‰}$ 4–6 m above the base and of $+2.5\text{‰}$ in the upper part of Uk deposits are reported here deviate from the main trend of variations from $+0.7$ to $+1.1\text{‰}$. The indicated extremums can be regarded as corresponding to levels C-VIII and C-IX (Fig. 3). In Kulmas section, the preserved lower horizons of the upper Uk Subformation are adjacent to level C-VIII.

Hence, it is possible to divide the carbonate succession of the Karatau Group into a series of C-isotopic

chemostratigraphic units (chemochrons) separated by the mentioned levels C-I to C-IX. Since the latter are isochronous at least in the regional scale, tracing them in concrete sections, we can establish iso- or diachronism of regional lithostratigraphic subdivisions and estimate relative accommodation rates of concurrent lithostratigraphic units in different structural zones. For instance, position of level C-V in separate sections indicates that boundaries of the marker lithostratigraphic horizon with *Conophyton miloradovici* are time-transgressive to some extent, while level C-VI proves that black cherts used to be considered traditionally as markers of boundary between lower and upper Min'yar subformations are not concurrent in different sections. Another interesting inference is that accommodation rate of members I–IV of the Min'yar Formation was 2.5 times slower in Min'yar (the Karatau structural complex) than in Usmangali section (the Inzer synclinorium). This example and observable difference in thickness of beds between levels C-VIII and C-IX in Shubino (100 m) and Kurtaza (55 m) sections imply that bottom deepening and reduction rate of free space in the Karatau paleobasin have been variable.

Sr-isotopic characterization of the Karatau Group carbonates is based on data obtained in this work for 51 samples and published earlier (70 analyses) for rocks of Min'yar, Shubino, and Kulmas sections (Kuznetsov et al., 1997, 2003).

Around two thirds of the samples studied are unsuitable for chemostratigraphic interpretation because of secondary alterations (Fig. 4). First, these are limestones of the Katav Formation (Min'yar and Kulmas sections) and carbonates of the basal 12- to 15-m-thick interval of the Inzer Formation (Min'yar and Tolparovo-1 sections). Variation ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio correspond to 0.70621–0.70979 in the Katav Formation and 0.70540–0.70585 in the above horizon, thus depicting a tendency of the ratio decrease upward. The main interval of the lower Inzer Subformation above its basal horizon is represented by 18 samples from Min'yar and Tolparovo-1 sections, which satisfy the geochemical retentivity criteria accepted for limestones. The $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio in these samples ranges from 0.70525 to 0.70538 in the first and from 0.70521 to 0.70555 in the second sections and tend to increase upsection. Three "best" samples from the upper Inzer Subformation, which have been collected in Min'yar and Kulmas sections, have similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging within a narrow interval from 0.70555 to 0.70566.

New data essentially enhancing the Sr-isotopic characterization of the Min'yar Formation have been obtained by investigation of rocks from distant Bakeevo and Usmangali sections. In the last section, the formation members I–III are composed of limestones instead of dolostones typical of the formation. Three limestone samples from Member I of the Min'yar section do not satisfy the retentivity criteria accepted in this work, but the minimum value of

0.70560 determines the $^{87}\text{Sr}/^{86}\text{Sr}$ maximum ratio in sedimentation environment (Kuznetsov et al., 2003). In "best" limestone samples from Member II and lower beds of Member III of Usmangali section, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is equal to 0.70552 and 0.70550 to 0.70558, respectively, while in slightly dolomitized limestones from upper beds of the last member it ranges from 0.70574 to 0.70584. We also studied 38 dolostone samples from members III–V of Min'yar, Shubino, Bakeevo, and Usmangali sections, which do not show correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ value with Mn/Sr, Fe/Sr, and Mg/Ca ratios, and retentivity of Rb–Sr systems in these rocks cannot be evaluated therefore. The $^{87}\text{Sr}/^{86}\text{Sr}$ variation ranges in dolostones are 0.70573–0.70858 in Member III, 0.70574–0.70628 in Member IV, and 0.70579–0.70680 in Member V. In limestones of the terminal member VI with geochemical ratios exceeding threshold values, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio varies from 0.70600 to 0.70658, being at maximum near the member top. Thus, according to the retentivity criteria, new rock samples from the Min'yar Formation are appropriate in majority only for evaluation of the ratio upper limits in the media of sedimentation and early diagenesis. It is important, nevertheless, that the $^{87}\text{Sr}/^{86}\text{Sr}$ minimum ratio in dolostones of members IV and V of Bakeevo and Usmangali sections (0.70573–0.70600) is almost identical to ratio in least altered (see above) concurrent dolostones of Min'yar section (0.70574–0.70611). Since the coincidence is established for concurrent stratigraphic horizons in sections of different structural zones (Fig. 1), it is possible to assume that dolostones are altered to a minimum extent and retain initial Sr-isotopic characteristics.

Thus, evolution of Sr-isotopic composition in seawater of the Min'yar time was likely as follows. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was not greater than 0.70560 during accumulation of Member I, corresponded to 0.70552 and 0.70550–0.70558 by deposition of Member II and lower beds of Member III, respectively, increased to 0.70574–0.70598 by accumulation of Member IV, and then was growing from 0.70583 to 0.70611 in formation period of Member V. The lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in altered limestones of Member VI (0.70600–0.70607) suggest that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater decreased to some extent at the end of the Min'yar time. Consequently, it was relatively low during the period in question, slightly increasing from 0.70550 at the beginning to 0.70611 near the end, and dropped below 0.70600 in the terminal stage of Min'yar time.

Limestones of the Uk Formation interacted with meteoric waters during the pre-Vendian hiatus, and only 9 of 23 samples from this unit satisfy geochemical criteria of isotopic retentivity. In sole unaltered sample from the lower Uk Subformation, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is equal to 0.70533, and in five "best" samples collected near the base of the upper subformation it corresponds to 0.70538 in Kulmas section, 0.70580 in Shubino section, and 0.70542–0.70586 in Kurtaza section. Higher in the succession, at the chemostratigraphic level C-IX

in the Shubino section, this ratio in the least altered sample is 0.70545, being risen in Kurtaza section up to 0.70605 and 0.70609, respectively, 48 and 85 m above that level. Compiling the Sr-isotopic data for the Late Karatavian deposits, we can see a notable decline of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater from 0.70600–0.70611 at the end of the Min'yar time to 0.70533 in the early Uk time and subsequent increase from 0.70538–0.70586 in the first third of the late Uk time to 0.70605–0.70609 by the end of that time. Thus the former $^{87}\text{Sr}/^{86}\text{Sr}$ variation trend (Kuznetsov et al., 2003) is supplemented now by the new fragment characterizing the Sr-isotopic variations in seawater of the terminal Karatavian Erathem.

CONCLUSIONS

(1) Investigation of several, predominantly carbonate successions of the Karatau Group in different structural and facies-lithologic zones of a considerable region (90 × 130 km, Fig. 1) enhanced database characterizing the least altered samples suitable for evaluation of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values in sedimentation environment, the facies and chronological variations of these parameters included. Such an approach is undoubtedly valuable for getting insight into variations of C- and Sr-isotopic composition in Proterozoic seawater.

(2) Analyzing trend of $\delta^{13}\text{C}$ variations in carbonates of the Karatau Group, we detected a successive series of in-phase extremums and/or turning points from positive to negative $\delta^{13}\text{C}$ values, which can be regarded as C-isotopic chemostratigraphic reference levels. Based on these levels, the carbonate succession of the Karatau Group separated by the pre-Uk unconformity in two parts can be subdivided into successive chemostratigraphic units (chemochrons). Being isochronous by definition at least in the study region, boundaries of chemochrons not always coincide with lithostratigraphic boundaries. By tracing boundaries of both types in lateral direction, we get an opportunity to establish isochronism or diachronism of lithostratigraphic units and to assess relative sedimentation rates in different structural zones.

(3) In the post-Katav interval of the Karatau Group, $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio in the least altered limestones and dolostones of concurrent lithostratigraphic units is persistent over the studied region. Variation ranges of this parameter established in different sections (named in brackets) are as follows: 0.70525–0.70538 (Min'yar) and 0.70521–0.70555 (Tolparovo-1) for the lower Inzer Subformation; 0.70574–0.70598 (Min'yar) and 0.70573–0.70598 (Usmangali) for Member IV of the Min'yar Formation; 0.70583–0.70586 (Min'yar), 0.70579–0.70593 (Bakeevo), and 0.70597–0.70600 (Usmangali) for the lower part of Member V; 0.70545–0.70580 (Shubino), 0.70538 (Kulmas), and 0.70542–0.70586 (Kurtaza) for the lower part of the upper Uk Subformation. Some local variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in particular lithostratigraphic units are probably caused by somewhat variable, post-diagenetic alter-

ations of rocks, which are imperceptible even by strict geochemical criteria of Rb–Sr system retentivity accepted in this work. Nevertheless, the above consistency of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio characterizing concurrent deposits in different sections proves presence of original carbonate material in the studied samples and correct evaluation of Sr-isotopic composition in sedimentation environment.

(4) New Sr-isotopic data on carbonates from the post-Katav interval of the Karatau Group are consistent with our former conclusion that sediments of the group accumulated in sea basin with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Gorokhov et al., 1996; Kuznetsov et al., 1997, 2003). During accumulation of the Inzer and Min'yar formation, this ratio ranged in general from 0.70521 to 0.70583, being slightly higher (up to 0.70611) in the late Min'yar time, and then it dropped below 0.70600 at the end of this period. After the long-lasting pre-Uk hiatus, it decreased down to 0.70533 to grow again since the mid-Uk time from 0.70538–0.70586 to 0.70605–0.70609.

(5) Owing to representative isotopic-geochronological and paleontological characterization of the Karatau Group, new data of C- and Sr-isotopic chemostratigraphy should be used to verify the standard curve of $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ variations in seawater of the Late Precambrian.

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REFERENCES

1. L. V. Anfimov, *Lithogenesis in Riphean Sedimentary Successions of the Bashkirian Meganticlinorium (S. Urals)* (Ural. Otd. Ross. Akad. Nauk, Yekaterinburg, 1997) [in Russian].
2. L. V. Anfimov, A. M. Sul'man, and V. G. Petrishcheva, "Strontium in Riphean Carbonate Rocks of the Southern Urals," in *Geochemistry of Sedimentary Formations in the Urals* (UNTs AN SSSR, Sverdlovsk, 1987), pp. 22–28 [in Russian].
3. Y. Asmerom, S. B. Jacobsen, A. H. Knoll, et al., "Strontium Isotopic Variations of Neoproterozoic Seawater: Implications for Crustal Evolution," *Geochim. Cosmochim. Acta* **55** (10), 2883–2894 (1991).
4. T. R. Bailey, J. M. McArthur, H. Prince, and M. F. Thirlwall, "Dissolution Methods for Strontium Isotope Stratigraphy: Whole Rock Analysis," *Chem. Geol.* **167** (3–4), 313–319 (2000).
5. J. L. Banner and G. N. Hanson, "Calculation of Simultaneous and Trace Element Variations during Water–Rock Interaction with Applications of Carbonate Diagenesis," *Geochim. Cosmochim. Acta* **54** (11), 3123–3137 (1990).
6. J. K. Bartley, M. A. Semikhatov, A. Kaufman, et al., "Global Events across the Mesoproterozoic–Neoproterozoic Boundary: C and Sr Isotopic Evidence from Siberia," *Precambrian Res.* **111** (1–4), 165–202 (2001).
7. Yu. R. Bekker, "Age and Stratigraphic Succession of Deposits in the Karatau Group Upper Part, the Southern Urals," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 9, 49–60 (1961).
8. Yu. R. Bekker, *Precambrian Molasses* (Nauka, Leningrad, 1988) [in Russian].
9. U. Brand and J. Veizer, "Chemical Diagenesis of a Multicomponent Carbonate System-1. Trace Elements," *J. Sediment. Petrol* **50** (4), 1219–1236 (1980).
10. S. Chaudhuri and N. Clauer, "Strontium Isotopic Compositions and Potassium and Rubidium Contents of Formation Waters in Sedimentary Basins: Clues to the Origin of the Solutes," *Geochim. Cosmochim. Acta* **57** (3), 429–437 (1993).
11. L. A. Derry, A. J. Kaufman, and S. B. Jacobsen, "Sedimentary Cycling and Environmental Change in the Late Proterozoic: Evidence from Stable and Radiogenic Isotopes," *Geochim. Cosmochim. Acta* **56** (3), 1317–1329 (1992).
12. L. A. Derry, L. S. Keto, S. B. Jacobsen, et al., "Sr Isotopic Variations in Upper Proterozoic Carbonates from Svalbard and East Greenland," *Geochim. Cosmochim. Acta* **53** (9), 2331–2339 (1989).
13. J. I. Drever, *The Geochemistry of Natural Water* (Prentice-Hall, London, 1982).
14. I. J. Fairchild, J. D. Marshall, J. Bertrand-Sarfati, "Stratigraphic shifts in carbon isotopes from Proterozoic stromatolitic carbonates (Mauritania): Influence of primary mineralogy and diagenesis," *Amer. J. Sci.* **290-A**, 46–79 (1990).
15. P. Fritz and D. G. Smith, "The Isotopic Composition of Secondary Dolomites," *Geochim. Cosmochim. Acta* **34** (11), 1161–1173 (1970).
16. M. I. Garan', "Western Flank and Central Zone of the Southern Urals," in *Stratigraphy of the USSR. Upper Precambrian* (Gosgeoltekhizdat, Moscow, 1963), pp. 114–163 [in Russian].
17. E. Z. Gareev, "Geochemistry and Sedimentation Environments of the Inzer Formation Deposits in the Riphean Stratotype of the Southern Urals," in *Upper Precambrian of the Southern Urals and Eastern Russian Plate* (BNTs UrO AN SSSR, Ufa, 1988), pp. 29–35 [in Russian].
18. T. N. German, *Organic World a Billion Years Ago* (Nauka, Leningrad, 1990).
19. I. M. Gorokhov, "Diagenesis of Carbonate Sediments: Trace Element Geochemistry and Strontium Isotopes," *Litol. Paleogeogr.*, No. 4, 141–164 (1996).

20. I. M. Gorokhov, M. A. Semikhatov, A. B. Kuznetsov, and N. N. Melnikov, "Improved Reference Curve of Late Proterozoic Seawater $^{87}\text{Sr}/^{86}\text{Sr}$," in *Proceedings of the 4th International Symposium on the Geochemistry of the Earth's Surface. Theme 5: Land-Atmosphere-Hydrosphere Interaction, Leeds, 1996*, pp. 714–717.
21. I. M. Gorokhov, M. A. Semikhatov, A. V. Baskakov, et al., "Sr Isotopic Composition in Riphean, Vendian and Lower Cambrian Rocks from Siberia," *Stratigr. Geol. Korrelyatsiya* **3** (1), 3–33 (1995) [*Stratigr. Geol. Correlation* **3** (1), 1–28 (1995)].
22. I. M. Gorokhov, N. N. Melnikov, T. L. Turchenko, et al., "Two Illite Generations in An Upper Riphean Shale: The Rb-Sr Isotopic Evidence," *EUG*, **8**.
23. V. M. Gorozhanin and E. P. Kutuyavin, "Rb–Sr Dating of Glauconite from the Uk Formation," in *Precambrian and Paleozoic of the Southern Urals* (BNTs AN SSSR, Ufa, 1986), pp. 60–63 [in Russian].
24. H. Gostenberger and M. Herman, "KN-2, the New $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ Standard for Mass Spectrometry of Geological Samples," *Geokhimiya*, No. 12, 1939–1940 (1984).
25. S. B. Jacobsen and A. J. Kaufman, "The Sr, C and O Isotope Evolution of Neoproterozoic Seawater," *Chem. Geol.* **161** (1), 37–57 (1999).
26. A. J. Kaufman and A. H. Knoll, "Neoproterozoic Variations in the Carbon Isotopic Composition of Seawater: Stratigraphic and Geochemical Implications," *Precambrian Res.* **73** (1–4), 27–49 (1995).
27. E. M. Khabarov, *Comparative Characterization of Late Precambrian Rift Formations: Sotheaster Siberia, Southern Urals and Timan* (Nauka, Novosibirsk, 1985) [in Russian].
28. E. M. Khabarov, V. A. Ponomarchuk, I. P. Morozova, et al., "Sea-Level Fluctuations and Isotopic Variations of Carbonate Carbon in a Riphean Basin of the Siberian Craton Western Margin (Baikit Anteclyse)," *Geol. Geofiz.* **43** (3), 211–239 (2002).
29. K. I. Heiskanen and D. V. Rychanchik, "The Jatulian (Lower Proterozoic) Carbonates with Abnormally Heavy Carbon: Stratigraphic Position and Paleogeographic Distribution in the Baltic Shield," *Stratigr. Geol. Korrelyatsiya* **7** (6), 14–19 (1999) [*Stratigr. Geol. Correlation* **7** (6), 531–536 (1999)].
30. A. H. Knoll, A. J. Kaufman, and M. A. Semikhatov, "The Carbon-Isotope Composition of Proterozoic Carbonates: Riphean Successions from Northwestern Siberia (Anabar Massif, Turukhansk Uplift)," *Am. J. Sci.* **295** (6), 823–850 (1995).
31. V. I. Kozlov and V. M. Gorozhanin, "To the Problem of Recognizing the Bakevo Formation and Age of Basal Beds in the Asha Group of the Southern Urals," in *Upper Precambrian of the Southern Urals and Eastern Russian Plate* (BNTs UrO AN, Ufa, 1993), pp. 14–23 [in Russian].
32. V. I. Kozlov, A. A. Krasnobaev, E. V. Kozlova, et al., *Stratigraphy of the Riphean Stratotype in the Southern Urals* (BNTs UrO AN SSSR, Ufa, 1991) [in Russian].
33. I. N. Krylov, *Columnar Branching Stromatolites in Riphean Deposits of the Southern Urals and Their Significance for Upper Precambrian Stratigraphy* (Nauka, Moscow, 1963) [in Russian].
34. I. N. Krylov, *Riphean and Phanerozoic Stromatolites of the USSR* (Nauka, Moscow, 1975) [in Russian].
35. I. N. Krylov, "Stratigraphy and Microfossils of the Min'yar Formation, the Southern Urals," *Geol. Geofiz.*, No. 6, 62–71 (1983).
36. A. B. Kuznetsov, I. M. Gorokhov, M. A. Semikhatov, et al., "Strontium Isotopic Composition in the Limestones of the Inzer Formation, Upper Riphean Type Section, Southern Urals," *Dokl. Akad. Nauk* **353** (2), 249–254 (1997) [*Dokl.* **353** (2), 319–324 (1997)].
37. A. B. Kuznetsov, M. A. Semikhatov, I. M. Gorokhov, et al., "Sr Isotope Composition in Carbonates of the Karatau Group, Southern Urals, and Standard Curve of $^{87}\text{Sr}/^{86}\text{Sr}$ Variations in the Late Riphean Ocean," *Stratigr. Geol. Korrelyatsiya* **11** (5), 3–39 (2003) [*Stratigr. Geol. Correlation* **11** (5), 415–449 (2003)].
38. J. D. Marshall and J. Bertrand-Sarfati, "Stratigraphic Shifts in Carbon Isotopes from Proterozoic Stromatolitic Carbonates (Mauritania): Influence of Primary Mineralogy and Diagenesis," *Am. J. Sci.* **290**–A, 46–79 (1990).
39. A. V. Maslov, *Riphean Sedimentary Associations in the Stratotype Area (Evolution of Viewpoints on Accumulation Environments, Lithofacies Zoning)* (Inst. Geol. Geokhim., Yekaterinburg, 1997) [in Russian].
40. A. V. Maslov, "The Upper Riphean Tangaur Subgroup of the Alatau Anticlinorium in the South Urals," *Stratigr. Geol. Korrelyatsiya* **10** (5), 3–22 (2002) [*Stratigr. Geol. Correlation* **10** (5), 421–440 (2002)].
41. A. V. Maslov, Z. M. Abduzaimova, L. A. Karsten, and V. N. Puchkov, "First Finds of *Melanocerillium* in the Riphean Type Sections of Southern Urals," in *State-of-the-Art and Objectives of Geologic Mapping of Precambrian Formations in Russia* (VSEGEI, St. Petersburg, 1994) [in Russian].
42. A. V. Maslov, M. T. Krupenin, E. Z. Gareev, and L. V. Anfimov, *The Riphean in the Western Flank of Southern Urals (Classical Sections, Sedimentogenesis, Minerageny, and Natural Geological Monuments)* (Ural. Otd. Ross. Akad. Nauk, Yekaterinburg, 2001) [in Russian].
43. A. V. Maslov, V. G. Olovyanishnikov, and M. V. Isherskaya, "The Riphean in Eastern, Northeastern and Northern Periphery of the Russian Platform and in Western megazone of the Urals," *Litosfera*, No. 2, 54–95 (2002).
44. J. A. McKenzie, "Holocene Dolomitization of Calcium Carbonate Sediments Form the Coastal Sabkhas of Abu Dabi, U.A.F.: A Stable Isotope Study," *J. Geol.* **89** (2), 185–198 (1981).
45. V. A. Melezhik, A. E. Fallick, P. V. Medvedev, and V. V. Makarikhin, "Extreme $^{13}\text{C}_{\text{carb}}$ Enrichment in Ca. 2.0 Ga Magnesite-Stromatolite-Dolomite-Red Beds Association in a Global Context: A Case for the World-Wide Signal Enhanced by a Local Environment," *Earth Sci. Rev.* **48** (1/2), 71–120 (1999).
46. V. A. Melezhik, I. M. Gorokhov, A. B. Kuznetsov, and A. E. Fallick, "Chemostratigraphy of the Neoproterozoic Carbonates: Implications for 'Blind Experiments'," *Terra Nova* **13** (1), 1–11 (2001).
47. I. P. Montanez, J. L. Banner, D. A. Osleger, et al., "Integrated Sr Isotope Variations and Sea-Level History of Middle to Upper Cambrian Platform Carbonates: Impli-

- cations for the Evolution of Cambrian Seawater $^{87}\text{Sr}/^{86}\text{Sr}$," *Geology* **24**, 917–920 (1996).
48. G. V. Ovchinnikova, I. M. Vasil'eva, M. A. Semikhatov, et al., "U–Pb Systematics on Proterozoic Carbonate Rocks: The Inzer Formation of the Upper Riphean Stratotype (Southern Urals)," *Stratigr. Geol. Korrelyatsiya* **6** (4), 20–31 (1998) [*Stratigr. Geol. Correlation* **6** (4), 336–347 (1998)].
 49. G. V. Ovchinnikova, I. M. Vasil'eva, M. A. Semikhatov, et al., "The Pb–Pb Trail Dating of Carbonates with Open U–Pb Systems: The Min'yar Formation of the Upper Riphean Stratotype, Southern Urals," *Stratigr. Geol. Korrelyatsiya* **8** (6), 3–19 (2000) [*Stratigr. Geol. Correlation* **8** (6), 529–543 (2000)].
 50. G. V. Ovchinnikova, M. A. Semikhatov, I. M. Vasil'eva, et al., "Pb–Pb Age of Limestones of the Middle Riphean Malgina Formation, the Uchur-Maya Region of East Siberia," *Stratigr. Geol. Korrelyatsiya*, **9** (6), 1–25 (2001) [*Stratigr. Geol. Correlation* **9** (6), 527–539 (2001)].
 51. V. N. Podkovyrov, M. A. Semikhatov, A. B. Kuznetsov, et al., "Carbonate Carbon Isotopic Composition in the Upper Riphean Stratotype, the Karatau Group, Southern Urals," *Stratigr. Geol. Korrelyatsiya* **6** (4), 3–19 (1998) [*Stratigr. Geol. Correlation*, 319–335 ()].
 52. S. M. Porter and A. H. Knoll, "Testate Amoebae in the Neoproterozoic Era: Evidence from Vase-Shaped Microfossils in the Chuar Group, Grand Canyon," *Paleobiology* **26** (3), 360–385 (2000).
 53. M. E. Raaben, *Upper Riphean as a Unit of the General Stratigraphic Scale* (Nauka, Moscow, 1975) [in Russian].
 54. M. E. Raaben, "The Min'yar Formation of Southern Urals—a lithostratigraphic Subdivision," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 4, 55–66 (1981).
 55. M. E. Raaben, "New Subdivisions of the Upper Riphean in the Southern Urals," *Sov. Geol.*, No. 5, 88–96 (1985).
 56. M. E. Raaben, "C-Isotope Chemostratigraphic Correlation of the Upper Riphean in the Urals and Arctic Region," *Stratigr. Geol. Korrelyatsiya* **9** (2), 3–14 (2001) [*Stratigr. Geol. Correlation* **9** (2), 107–117 ()].
 57. B. Z. Saylor, A. J. Kaufman, J. P. Grotzinger, and F. A. Urban, "Composite Reference Section for Terminal Proterozoic Strata of Southern Namibia," *J. Sediment. Res.* **68** (6), 1223–1235 (1998).
 58. M. A. Semikhatov and M. E. Raaben, "Dynamics of the Global Diversity of Proterozoic Stromatolites. Article I: Northern Eurasia, China, and India," *Stratigr. Geol. Korrelyatsiya* **2** (6), 10–32 (1994) [*Stratigr. Geol. Correlation* **2** (6), 492–514 (1994)].
 59. M. A. Semikhatov and S. N. Serebryakov, *The Riphean Hypostratotype of Siberia* (Nauka, Moscow, 1983) [in Russian].
 60. M. A. Semikhatov, A. B. Kuznetsov, I. M. Gorokhov, et al., "Low $^{87}\text{Sr}/^{86}\text{Sr}$ Ratios in Seawater of the Grenville and post-Grenville Time: Determining Factors," *Stratigr. Geol. Korrelyatsiya* **10** (1), 3–46 (2002) [*Stratigr. Geol. Correlation* **10** (1), 1–41 ()].
 61. M. A. Semikhatov, A. B. Kuznetsov, V. N. Podkovyrov, et al., "The Yudomian Complex of Stratotype Area: C-isotope Chemostratigraphic Correlations and Yudomian-Vendian Relation," *Stratigr. Geol. Korrelyatsiya* **12** (5), 3–29 (2004) [*Stratigr. Geol. Correlation* **12** (3), 435–459 (2004)].
 62. M. A. Semikhatov, G. V. Ovchinnikova, I. M. Gorokhov, et al., "Isotope Age of the Middle-Upper Riphean Boundary: Pb–Pb Geochronology of the Lakhandu Group Carbonates, Eastern Siberia," *Dokl. Akad. Nauk* **372** (2), 216–221 (2000) [*Dokl.* **372** (4), 625–629 (2000)].
 63. M. A. Semikhatov, V. N. Podkovyrov, D. V. Vinogradov, et al., *A Carbon Isotopic Composition of the Riphean Carbonate: the Type Upper Riphean Succession, the South Urals // Precambrian of Europe: Stratigraphy, Structure, Evolution and Mineralization. MAEGS-9. Abstr.* (IPGG, St. Petersburg, 1995), p. 101.
 64. G. S. Senchenko, *Fold Structures of the Southern Urals* (Nauka, Moscow, 1976) [in Russian].
 65. *The Riphean Stratotype. Paleontology. Paleomagnetism* (Nauka, Moscow, 1982) [in Russian].
 66. *The Riphean Stratotype: Stratigraphy, Geochronology* (Nauka, Moscow, 1983) [in Russian].
 67. A. F. Veis, P. Yu. Petrov, and N. G. Vorob'eva, "Age Transformations of Facies-Ecologic Structure of Precambrian Biotas and Riphean Stratigraphy," *Geol. Geofiz.* **39** (1), 85–96 (1998).
 68. A. F. Veis, V. I. Kozlov, N. D. Sergeeva, and N. G. Vorob'eva, "Microfossils from the Upper Riphean Type Section (the Karatau Group of Southern Urals)," *Stratigr. Geol. Korrelyatsiya* **11** (6), 3–31 (2003) [*Stratigr. Geol. Correlation* **11** (6), 550–572 (2003)].
 69. J. Veizer, "Chemical Diagenesis of Carbonates: Theory and Application of Trace Element Technique," *SEPM* **10** (3), 1–100 (1983).
 70. J. Veizer and J. Hoefs, "The Nature of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ Secular Trends in Sedimentary Carbonate Rocks," *Geochim. Cosmochim. Acta* **40** (11), 1387–1395 (1976).
 71. M. R. Walter, J. J. Veeres, C. R. Calver, et al., "Dating the 840–544 Ma Neoproterozoic Interval by Isotopes of Strontium, Carbon and Sulfur in Seawater and Some Interpretative Models," *Precambrian Res.* **100** (1), 371–433 (2000).
 72. T. S. Zaitseva, T. A. Ivanovskaya, I. M. Gorokhov, et al., "Rb–Sr Age and Nuclear Resonance Spectra of Glaucophanes from the Uk Formation, Upper Riphean, Southern Urals," in *Isotopic Dating of Geological Processes: New Methods and Results* (GEOS, Moscow, 2000), pp. 144–147 [in Russian].