# Sr Isotope Composition in Carbonates of the Karatau Group, Southern Urals, and Standard Curve of <sup>87</sup>Sr/<sup>86</sup>Sr Variations in the Late Riphean Ocean

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Abstract—The presented Rb-Sr systematics of carbonates from the Karatau Group, the Upper Riphean stratotype of southern Urals, elucidates important details of secular variations of <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the Late Riphcan seawater, which have been formerly unknown. Samples selected for analysis satisfy all the strict geochemical criteria characterizing the least altered carbonate rocks (Mn/Sr \_0.2, Fe/Sr \_ 5.0, Mg/Ca = 0.024 in limestones and Mn/Sr \_ 1.2, Fe/Sr \_ 3.0, Mg/Ca \_ 0.608 in dolostones), and they all have been preliminary treated in 1N solution of ammonium acetate for a partial removal of epigenetic carbonate phases. A verified curve of secular variations of <sup>87</sup>Sr/<sup>86</sup>Sr ratio in the Late Riphean ocean is plotted based on new data and Sr isotope parameters formerly known for carbonates of the Upper Riphean key sections. As is established, that ratio was nearly constant. ranging from 0.70519 to 0.70566, within the time span of 1030-810 Ma and next rose up to 0.70611 about 775 Ma ago. Afterward, between 765 and 740 Ma, it decreased down to 0.70561-0.70575 and then, within the time span of 740-690 Ma, it ranged from 0.70646 to 0.70686 with a short-term drop down to 0.70620 about 720 Ma ago. At the end of the Late Riphean (660-640 Ma), the ratio lowered to 0.70538-0.70580 to become growing up to 0.70840-0.70860 during the Vendian and initial Cambrian. The established variations of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio in the Late Riphean ocean have been controlled by a combination of geodynamic factors, magmatic events, sea-level oscillations, and compositional changes in provenances, which were subjected to erosion at that time. An additional influence of climatic fluctuations over supercontinent and its fragments is also admissible.

**Key words:** <sup>87</sup>Sr/<sup>86</sup>Sr ratio in seawater. Late Riphean, carbonate rocks; Karatau, Atar, Shaler, and Akademikerbrecn groups. Bitter Springs Formation.

## INTRODUCTION

Investigation of secular variations of 87Sr/86Sr ratio in paleooceans is an important tool for reconstruction of past geodynamic environments. In addition, this approach elucidates the crustal erosion intensity and terrigenous influx composition at various stages of the Earth evolution, and it may be used as well in correlation of carbonate successions, when the ratio gradients are high. The following aspects define effectiveness of such investigations. (1) At the each moment of geological history, the 87Sr/86Sr ratio is constant in the World Ocean, because the Sr residence time in seawater is three orders of magnitude greater than the stirring time of the whole water mass (Goldberg, 1963; Faure, 1986; Aberg and Wickman, 1987; Hodell et al., 1989). (2) There are three variables that control secular variations of the ratio: the Sr flux with low 87Sr/86Sr ratios from the mantle, the continental runoff intensity, and the Sr isotope composition in the latter (Faure et al., 1965; Veizer and Compston, 1974; Palmer and

Kaufman, 1999; Semikhatov *et al.*, 2002). (3) Ca-bearing minerals of marine origin (carbonates fist of all) inherit the Sr isotope composition of sedimentation medium, and their primary phases are able to retain this isotopic signature until the recent time (Peterman *et al.*, 1970; Tremba *et al.*, 1975; Koepnick *et al.*, 1985). A detailed and internally consistent curve of seawa-

Edmond, 1989; Richter et al., 1992; Jacobsen and

ter <sup>87</sup>Sr/<sup>86</sup>Sr variations has been plotted for the Phanerozoic evolution of the Earth (Burke *et al.*, 1982; Koepnick *et al.*, 1985; Denison *et al.*, 1994; Veizer *et al.*, 1999; McArthur *et al.*, 2001, and references therein). Considerable intervals of this curve arc suitable for stratigraphic correlation and even for high-precision chronological calibration of carbonate successions (DePaolo and Ingram, 1985; McArthur, 1994; Diener *et al.*, 1996; Ebneth *et al.*, 2001; Melezhik *et al.*, 2002). Some extremes of the curve are also found to be corresponding to concrete geodynamic events in the past (Hodell et al., 1990; Richter et al., 1992; Godderis, Francois, 1995).

Investigation of seawater 87Sr/86Sr variations in the Proterozoic ocean that had been initialed later (Veizer, Compston, 1976; Veizer et al., 1983) became active in the last 10-12 years only (Derry et al., 1989, 1992; Asmerom et al., 1991; Pokrovskii and Vinogradov, 1991; Kaufman et al., 1993, 1997; Mirota and Veizer, 1994; Gorokhov et al., 1995, 1996, 1998; Kuznetsov et al., Semikhatov et al., 1998, 2002; 1997: Vinogradov et al., 1998; Walter et al., 2000; Bartley et al., 2001, and references therein). Nevertheless, even the <sup>87</sup>Sr/<sup>86</sup>Sr curve plotted for seawater the Late Riphean interval that is studied better than others is not consistent so far (Melezhik et al., 2001). This is a consequence of the following objective and subjective issues: there are known few well-dated carbonate successions of the Proterozoic; significance of epigenetic alterations in carbonate rocks is underestimated; criteria used to control the preservation state of Rb-Sr isotopic systems in carbonates are not uniform; and the available database is insufficient.

To solve the problem it is necessary to use a comprehensive approach that includes the next procedures: (1) investigation of continuous sedimentary successions with carbonate beds and members; (2) age determination of carbonates based on reliable isotopic-geochronological data; (3) environmental analysis of studied deposits; (4) application of strict geochemical criteria to control the preservation state of isotopic systems in carbonates; and (5) selective leaching of noncogenetic carbonate phases from samples used in analysis. A fragment of seawater 87Sr/86Sr curve that characterizes time of the global Grenville orogeny and Rodinia emergence has been depicted, when this approach was applied to investigation of Middle-Upper Riphean boundary deposits in Siberia (Gorokhov et al., 1995; Semikhatov et al., 1998, 2002). This time span of geological record appears to be well understood now, whereas subsequent evolution of Sr isotope composition in the Late Riphean ocean is known to a first approximation (Kuznetsov et al., 1997; Jacobsen and Kaufman, 1999; Walter et al., 2000) and has been variably interpreted, because it is depicted mostly based on data for discrete intervals of sections in Arctic Canada and Spitsbergen, chronometry of which needs in verification.

Presenting in this work the new data on <sup>87</sup>Sr/<sup>86</sup>Sr ratios in Upper Riphean carbonates from southern Urals, we also summarized and critically revised data of Sr isotope geochemistry, which characterize the key sections in Siberia, southern Urals, Australia, Arctic Canada, and Spitsbergen. We used the results to plot a consistent seawater <sup>87</sup>Sr/<sup>86</sup>Sr curve and to discuss the geodynamic background of Sr isotope evolution in the Late Riphean ocean. New data are obtained for rocks of the Upper Riphean stratotype, the Karatau Group of southern Urals. A considerable stratigraphic range, abundance of slightly altered carbonate rocks, and representative biostratigraphic and isotopic-geochronological characterization are the obvious advantages of the studied sedimentary succession, which distinguish it from the others mentioned above.

## STRATIGRAPHY, AGE LIMITS, AND STRUCTURE OF THE KARATAU GROUP

Thick (3.5 to 5.5 km) terrigenous-carbonate deposits of the Karatau Group are widespread in the 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 (Middle Riphean stratotype) and have unconformable boundary with overlying terrigenous sediments of the Vendian Asha Group. Based on single isotopic dates and presence of tilloids, the lower part of the latter is attributed to the Lower Vendian (*Stratotip rifeya...*, 1983; Bekker, 1988; Maslov *et al.*, 2001, and references therein).

In the regional stratigraphic scheme that is adopted at present (Stratotip rifeya..., 1983; Kozlov et al., 1991; Unifitsirovannye..., 1993; Maslov et al., 2001), the Karatau Group is divided into six units (from the base upward): the siliciclastic Zilmcrdak (1200 to 3300 m thick), variegated Katav (limestone beds 150-350 m thick), compositionally variable siliciclastic carbonate Inzer (300-800 m thick), limestone-dolomitic Min'yar (350-650 m), siliciclastic-carbonate Uk (160-350 m thick), and terrigenous Krivaya Luka (up to 560 m thick) formations. The Uk Formation crowns the group section in the western limb of Bashkirian meganticlinorium, and the last one is preserved after the pre-Vendian erosion in the cast of the structure only. Three lower formations are interrelated, having gradual in-between transitions, whereas stratigraphic unconformities are recorded at the Uk Formation base and locally underneath the Min'yar Formation (Bekker, 1961, 1988; Raaben, 1975; Kozlov et al., 1991; Maslov et al., 2001; Maslov, 2002a). First results of C-isotope chemostratigraphy showed that the studied sections of the Min'yar Formation are lacking horizons with high positive <sup>13</sup>C values, which are characteristic of the upper Upper Riphean in various continents (Kaufman and Knoll, 1995; Kaufman et al., 1997; Kah et al., 1999; Walter et al., 2000). Seeking for explanation, Podkovyrov with colleagues (1998) and Raaben (2001) argued that some intervals of the section could be eroded in the pre-Uk time, although their assumption seemed doubtful, because upper Min'yar horizons are insufficiently exposed in the study region (Raaben, 2001). However, the Min'yar Formation is lacking the mentioned intervals not only in two sections described by Podkovyrov et al. (1998), but also in the section exposed along the Kuzhai Creek upstream of the Bakeevo Village, where it was sampled in detail and then studied in terms of Cisotope chemostratigraphy. In addition, the regional character of the pre-Uk hiatus is evident from certain geological data: the contact between the Min'yar and Uk formations is locally marked by brecciated Fe-Mn accumulations, and basal sandstone beds of the Uk Formation, which enclose gravel and rare conglomerate interlayers, rest on different upper horizons (Shubino Member of limestones) of the Min'yar Formation and locally overlap the pre-Shubino dolostones (Bekker, 1961, 1988; *Stratotip rifeya...*, 1983; Maslov *et al.*, 2001; Raaben, 2000). Thus, we may regard as established a considerable scale of the pre-Uk unconformity. As for the hiatuses traceable at the base and in the middle of the Min'yar Formation, they have been observed in places thus signifying short-term events of subaerial exposition of local sedimentation settings.

Age limits of the Karatau Group are established based on some paleontological data and on isotopic dates of unequal validity. The isochron Pb-Pb date of  $836 \pm 25$  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 (Gorokhov et al., 1995) and correspond to the age of burial diagenesis of sandyclayey sediments underlying the lower Inzer limestones. The Pb-Pb age of dolostones from the middle part of the Min'yar Formation is 780 ± 85 Ma (Ovchinnikova et al., 2000). A rather high uncertainty of this date is connected with an irregular style of epigenetic alterations in the rocks affected by sulfide mineralization. A reliable dating method has been applied as well to glauconites from the lower Uk Subformation. The M ssbauer spectroscopy showed that epigenetic alterations did not affect the structure of the glauconites, and consequently their isotopic-geochronological systems remain intact (Zaitseva et al., 2000). The isochron Rb-Sr and K-Ar ages of these glauconites are  $664 \pm 11$  and  $669 \pm 16$  Ma, respectively. A close age value of  $688 \pm$ 10 Ma has been earlier obtained by the isochron Rb-Sr method for Al-glauconites from the lower Uk strata (Gorozhanin and Kutyavin, 1986). All these dates define the time of early diagenesis in the lower Uk sediments. The K-Ar dates obtained in the 1960s and 1070s for mineralogically unstudied glauconites from different horizons of the Karatau Group are less reliable. They represent a series of age values decreasing upward in the stratigraphic succession from 938 Ma in the upper Katav and lower Inzer strata to 896-853 in the middle and upper parts of the Inzer Formation, and then to 791-740 Ma in the upper member of the latter. Tlie next range of 713-680 Ma characterizes the lower Min'yar Subformation, and final values of 658 to 630 Ma have been measured in the upper Uk Subformation (Stratotip rifeya..., 1983).

The upper age limit of the Karatau Group is defined by the isochron Rb-Sr date of  $618 \pm 13$  Ma obtained for glauconite from the lower part of the Asha Group (Kozlov and Gorozhanin, 1993) and by the range of K-Ar dates (600 to 557 Ma) characterizing the mineralogically unstudied glauconites from overlying strata of the group (*Stratotip rifeya...*, 1983). There were also attempts to estimate age limits of the Karatau Group based on K-Ar dates for whole-rock samples of gabbro-diabases regarded as the pre- and post-Karatavian intrusions (*Stratotip rifeya...*, 1983, and other works). These attempts are not convincing, however: first, the K-Ar isotopic systems of magmatic whole-rocks samples are labile; and second, geological relations of the dated gabbro-diabase bodies with basal and terminal horizons of the group are inadequately known.

Paleontological constraints, first of all the data on succession of organic-walled microfossil assemblages in the Zilmerdak Formation (Veis et al., 2000, 2003), which elucidate chronometric limits of deposits under consideration, are also important. In the lower part of the formation divided into the Biryan, Nugush, and Lemeza subformations, only the middle subdivision is bearing representative microbiota because of the facies control. In addition to small transit forms of simple morphology, the Nugush Subformation yields large and/or relatively complex taxa, such as Chuaria, Navifusa, Simia nerujenica, Ostiana, Polyspheroides con-Asperatofilum, Taenitrichoides, texus, Plicatidium, Botuobia, Majaphyton, Lakhandinia, Caudi-Rectia, osphaera, Pseudodendron, and some other morphotypes. Nearly a half of them is known in the Urals from the Kuzha and/or Tyulma sediments occurring below the Karatau Group (Veis et al., 2000), and almost all the taxa are also characteristic of the overlying Bederysh Subformation that crowns section of the Zilmerdak Formation. Nevertheless, the Bederysh microbiota fundamentally differs from that of the Nugush Subformation, because it includes acanthomorphic acritarchs Trachyhystrichosphaera aimica, T. stricta, T. parva, T. truncata and associated Tortunema, Glomovertella, and Arctacellularia, all appearing for the first time at this level in the southern Urals (Veis et al., 2003). In Siberia, acritarchs of the genus Trachyhystrichosphaera define the compositional aspect of the well-known Lakhanda microbiota from the Uchur-Maya region and of concurrent Derevnya microbiota from the Turukhansk Uplift (German, 1990; Veis et al., 1998, 2000). According to available dates obtained for carbonate rocks by the isochron Pb-Pb method, the maximum age limit of these biotas is 1030 Ma (Semikhatov et al., 2000, 2003; Ovchinnikova et al., 2001). The assemblage of organic-walled microfossils from underlying horizons of Siberian sections mentioned above, i.e., from the Kerpyl Group of the Uchur-Maya region and its analogues in the Turukhansk Uplift, which accumulated 1200-1030 Ma ago (Bartley et al., 2001; Semikhatov et al., 2002), is taxonomically different. It includes a set of taxa characteristic of the Nugush Subformation of the Zilmerdak Formation and of the Kuzha and Tyulma sediments in the southern Urals (Veis et al., 1998, 2000, 2003). Consequently, the pre-Bederysh level in the Uralian succession of organic-

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Fig. 1. Localities of the Min'yar (1), Shubino (2), and Kulmas (3) sections of the Karatau Group.

walled microbiotas corresponds to the pre-Lakhanda level in Siberia, and the Bederysh Subformation of the Zilmerdak Formation is not older than 1030 Ma. On the other hand, silicified microfossils occurring in the Karatau Group above the latter formation are represented by transit taxa (Sergeev, 1992), whereas a specific assemblage of organic-walled forms is recorded here in the lower part of the Inzer Formation only (Veis *et al.*, 2000, 2003). This one is similar to the assemblage from middle horizon of the Akademikerbreen Group of Spitsbergen (Butterfield *et al.*, 1994), but their similarity is unimportant for chronometric calibration of the Karatau Group, because the former group has not been dated by means of isotopic methods.

It is important for the current consideration that *Mekmocerillium* 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, are known from a series of Upper Riphean sections in North America, West Europe and South Asia, and they appear in the geological record just before 800 Ma (Porter and Knoll, 2000). Thus, the verification of *Melanocerillium* occurrence in the Min'yar Formation should support evaluation of Pb-Pb age of this formation (780  $\pm$  85 Ma).

If the linear dependence between thickness and accumulation time of Karatavian deposits is admissible, then, using the presented radiometric dates and some results of chemostratigraphy considered below, we can estimate the time spans for subdivisions of the group. The estimated ranges are 890-850 Ma for the Katav Formation, 850-810 Ma for the Inzer Formation (850 to 830 and 830 to 810 Ma for its lower and upper subformations, respectively), 810-770 Ma for the Min'yar Formation, and 690-640 Ma for the Uk Formation divided into the lower (690-660 Ma) and upper (660-640 Ma) subformations. These ranges are consistent with data on stromatolite succession in the Karatau Group (Scmikhatov and Raaben, 1994, 1996) and do not contradict the sedimentation rate assessments for Upper Riphean isofacies in the Urals (15 to 20 m/m.y., Maslov *et al.*, 2002b) and Siberia (15 to 30 m/m.y., Semikhatov *et al.*, 2000, 2002; Ovchinnikova *et al.*, 2001). The considerable difference between isotopic dates obtained for the Min'yar and Uk formations confirms a long pre-Uk hiatus.

In the western limb of the Bashkirian meganticlinorium, Karatavian deposits of inner and outer facies zones are separated by the Zilmerdak thrust and associated faults (Stratotip rifeya..., 1983). The zones differ from each other mostly in abundance of terrigenous sediments above the Zilmerdak Formation: up to 50% in the inner (eastern) zone and only 10 to 15% in the outer (western) zone. The degree of epigenetic alterations in sediments decreases in the same direction. We studied three sections of the outer zone characterizing predominantly the carbonate part of the Karatau Group. One is exposed near the town of Min'yar, second one along the Yuryuzan River in the Ust-Katav area upstream of the Shubino Village, and the third section corresponds to a series of road cuts along the Ufa-Beloretsk highway, which are situated near the Kulmas Settlement (Fig. 1). Further, they are termed as the Min'yar, Shubino, and Kulmas sections. In the first one, we studied sediments of the Katav, Inzer, and Min'yar (lower part) formations. Exposed in the second section are rocks of the Min'yar (upper part) and Uk formations, whereas the road cuts exhibit fragments of the Katav, Inzer, and upper Uk successions. Sediments of the formations are described below, and stratigraphic positions of studied samples are shown in Fig. 2.

The Katav Formation conformably resting on siliciclastic Zilmerdak deposits is divided in two subformations. In the Min'yar section, the lower subformation (120 m) is composed of cherry-red flaggy clayey limestones (10 to 24% of siliciclastic components) with rare marl and calcareous shale interlayers, the latter concentrated near the base. Gently inclined cross lamination characteristic of lower strata grades upward into fine horizontal stratification. The upper subformation (60 m) is represented by alternating pale-yellow to pinkish and greenish gray flaggy clayey limestones (10 to 15% of siliciclastic components), characteristic of which is banding and microbial lamination in the upper part. Sediments enclose rare flakestone lentils and slightly dolomitized (Mg/Ca = 0.054) in some members. Micritic matrix of limestones encloses microscopic lenses of microsparite and less abundant segregations (of mm-size scale) and veinlets of fine-grained dolosparite. Cathodoluminescence of micrite and microsparite is weak to moderate, variegated from yel-



Fig. 2. Lithostratigraphy of the Karatau Group, the Min'yar, Shubino, and Kulmas sections: (1) limestone; (2) stromatolitic limestone: (3) clayey limestone; (4) microbial striate limestone; (5) dolostone; (6) stromatolitic dolostone; (7) dolostone with cherty concretions; (8) sandy-clayey deposits; (9) sandstone; (10) sandstone with gravelstone interlayers; (11) stratigraphic unconformity; (12) sample nos. and sampling levels. Abbreviations: (Bak.) Bakeevo; (Zilm.) Zilmerdak; (Ur.) Uryuk; (1) lower; (m) middle; (u) upper.

low to pinkish; it is of the same type though brighter in dolosparite segregations. Fragments of Katav sediments exposed in the Kulmas section do not differ in primary lithology, but the rocks are more intensely fractured here and impregnated by calcite veinlets of late generation.

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The Inzer Formation is also divided in two subformation, the lower of which was known for a while under the name "Podinzer Beds." In the Min'yar section, the lower subformation (ca. 190 m) is represented by dark gray to black limestone weakly dolomitized (Mg up t 1.1%, Mg/Ca = 0.030) in the middle 35-m-

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thick member. Packages of stromatolitic limestones and flakestone lentils are recognizable in the upper part. In the lower 25 to 30-m-thick interval, recrystallization of rock is somewhat stronger than in the Katav Formation. Vaguely laminated micrite with thin microsparite lenses and patchy dolomitization responsible for development of rhombohedral dolomite crystals are established in this interval. However, the main part of the lower Inzer limestones is insignificantly recrystallized, being composed of alternating fine micrite and microsparite laminae, among which there are distinguishable only microscopic lenses of microcrystalline secondary calcite. Microsparite laminae (1 to 3 mm thick) retain the relic clastic structure. Content of siliciclastic fraction is commonly less than 1%, and rare interlayers of clayey limestone (up to 9.6% of siliciclastic components) resembling the Katav Formation rocks are established near the unit base only (Table 1). In distinction from the Min'yar section, rocks in the middle interval of lower Inzer deposits that is fragmentary exposed in the Kulmas section have microcrystalline texture and reveal a system of fine (0.1 to 1.0 mm) fractures filled with late crystalline calcite and presence of microstylolite seams. Limestone sample 373-16 collected near the apparent top of the Kulmas section is of a mosaic texture, with dispersed inclusions of Fehydroxides.

In the Min'yar section, two siliciclastic (gray feldspar-quartz-glauconite sandstones, siltstones and shales) members (70 and 50 m) of the upper Inzer Subformation are separated from each other by the middle carbonate member (80 to 120 m). Rocks of the latter are massive microphytolitic, fine-laminated micritic, stromatolitic, and clastic limestones; two latter varieties appear closer to the subformation top. Fine siliciclastic admixture in the rocks (usually less than 3%) may be concentrated sometimes to a greater extent in some basal horizons. In the Kulmas section, where the succession and lithology of members is unchanged, the total thickness of subformation is decreased (180 m) owing to the carbonate member reduction (Fig. 2). A weak cathodoluminescence is characteristic of limestones in the lower 25 to 30-m-thick part of the Inzer Formation. In other rocks, the bright pinkish to yellow or moderate yellow luminescence is characteristic of the late calcite and dolomite, respectively.

The Min'yar Formation is the thickest (360 to 400 m in the studied sections) and entirely carbonate subdivision of the Karatau Group. In the synonymous section, it is predominantly composed of light to pinkish gray clastic fine-laminated and massive stromatolitic dolostones, which are sandwiched between the basal (12 to 14 m) and terminal Shubino (15 to 20 m) members. In the upper formation interval, the appearance level of dark gray to black lenses and interlayers of early diagenetic cherts is adopted for the boundary between the lower Minka (170-180 m) and upper Byanka (160-180 m) subformations. Near the Minka Subformation base, there is a marker dolostone bed with stromatolites *Conophyton* that has been deposited below the storm wave base. In the middle of that sub-formation, there are some bedding planes marked by desiccation cracks.

Characteristic of the Min'yar dolostones are the narrow range of Mg/Ca ratios (from 0.552 to 0.636) and low content of siliciclastic components (3% in average). Only within the interval from 55 to 90 m above the formation base, percentage of siliciclastic fraction grows up to 17—40%. Stromatolitic varieties of rocks correspond to dolomicrites and dolosparite, and the clastic ones are of the dolosparite type. The rocks retain their primary structures, but they may contain the late crystalline dolomite (5%) filling in the small caverns or thin (0.5 to 2 mm) lenses and veinlets. Dolomite of this generation is mostly localized in the lower 70 to 80-mthick interval of the formation section.

Cherty segregations in the Min'yar dolostones yield silicified microfossils, some of which are in the extraordinary preservation state (Sergeev, 1992). Consequently, the segregations were formed at the earliest stage of diagenesis, immediately after posthumous burial of microorganisms in bottom-surface deposits near the water-sediment interface (Maliva et al., 1989; Sergeev, 1992). Dolomicrite relicts present in some cherty concretions suggest that the early dolomitization of the Min'yar carbonates also begun immediately after precipitation of sedimentary material that likely corresponded in composition to high-Mg calcite. Limestones from the formation lower member are slightly dolomitized (Mg/Ca up to 0.035), composed of micrite and microsparite with microscopic accumulations (0.1 to 0.3 mm across) of rounded micritic clasts. They bear 5 to 10% of siliciclastic admixture.

In the Min'var section, we sampled the Minka to lower Byanka deposits that are 350 m thick and well exposed. Upper horizons of the formation, i.e., the upper Byanka dolostones and Shubino limestones, have been studied in the Shubino section. The Byanka dolostones exposed here are identical to those of the Min'yar section. Characteristic of them is moderate red, sometimes patchy cathodoluminescence. Limestones of the Shubino Member usually consist of pure calcite, and a weak enrichment in Mg (Mg/Ca up to 0.16) is established for them only near the contact with underlying dolostones. These limestones with sporadic desiccation cracks bear an insignificant admixture of clastic quartz (0.5 to 3%), and their micrite to microsparite matrix encloses small accumulations of subangular micritic clasts. Being replaced to some extent by the mosaic sparite or coarse calcite crystals, the latter are surrounded by thin rims with radiolitic texture and/or by Fe-hydroxides. There are also small veins and nests of coarse calcite crystals. In contrast to non-luminescent micrite and microsparite, luminescence of this calcite is bright.

The Uk Formation consists of two subformations. The lower subformation that is 70 m thick in the Shu•

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Sample no.1	Sec- tion <sup>2</sup>	Sampling level <sup>3</sup> , m	Rock type <sup>4</sup>	Siliciclas- tic admix- ture (SA), <sup>5</sup> %	Mg, %	Mn, ppm	Fe, ppm	Sr, ppm	Mg/Ca	Mn/Sr	Fe/Sr	Minerals of SA <sup>6</sup>
Uk Formati	ion			L		1		L	L	l	<u> </u>	I
442-27	SH	195	D	1.8	9.5	110	1120	12	0 350	933	933	I _
442-24	SH	180	L	0.9	1.5	120	220	53	0.040	2.28	42	_
442-23	SH	160	L	0.6	0.5	22	130	313	0.014	0.07	04	-
442-22	SH	150	L	2.9	0.5	31	280	148	0.014	0.07	19	_
442-21	SH	140	L	3.5	0.3	33	340	109	0.008	0.21	31	-
442-18	SH	125	L	3.8	0.3	34	250	106	0.008	0.30	2.4	-
442-16	SH	105	L	6.0	1.1	150	810	117	0.028	1.28	69	-
442-15	SH	90	L	11.4	0.4	80	770	140	0.020	0.56	5.5	O Esp Mc Chl
442-14	SH	85	L	13.6	0.3	82	1010	110	0.007	0.56	9.2	Q, I sp, Mc, Chl
3573	K	84	L	0.8	0.2	66	410	90	0.006	0.73	4.6	-
3573-2	K	78	L	1.1	0.1	64	260	146	0.002	0.44	1.8	-
3573-7	K	62	$\overline{L}$	3.1	0.3	27	470	437	0.008	0.06	1.1	_
442-11	SH	60	$\overline{L}$	1.0	0.1	100	1120	715	0.002	0.14	1.6	_
442-10	SH	45	L	8.1	0.4	603	3450	289	0.010	2.09	11.9	O Fsn
442-9	SH	25	L	5.0	0.4	220	1700	281	0.011	0.78	6.1	-
Min'var Formation												
442-8	SH	362	L	1.6	0.8	385	1420	340	0.019	1 1 1 3	42	1 -
56-16b	SH	361	L	0.3	0.3	130	150	477	0.008	0.27	0.3	
56-16	SH	360	L	2.6	0.1	535	380	346	0.002	1.55	1.1	-
56-15a	SH	359	L	3.2	0.1	445	670	375	0.002	1.18	1.8	0
442-7	SH	358	L	3.4	0.3	1460	660	404	0.007	3.61	1.6	Q Q- Fsn
442-6	SH	343	L	1.6	5.1	2960	1420	230	0.156	12.9	6.2	<b>~</b> • • •
442-3	SH	315	D	3.2	13.4	340	1340	20	0.604	17.1	67.1	-
442-1	SH	300	D	2.1	13.4	102	440	113	0.608	0.90	3.9	-
426-35	М	289	D	2.2	13.4	96	240	68	0.609	1.41	3.5	-
426-33	М	238	D	0.7	13.3	63	150	103	0.636	0.61	1.5	-
426-31	М	213	D	1.6	13.2	68	90	44	0.612	1.55	2.1	-
426-29	М	170	D	8.9	13.2	230	320	28	0.608	8.21	11.4	O. Mc. Chl. FO
426-24	М	144	D	0.9	13.4	51	102	70	0.612	0.73	1.4	-
426-20	Μ	116	D	2.6	13.4	101	150	75	0.606	1.35	2.0	_
426-18	М	102	D	1.8	13.2	44	140	55	0.608	0.80	2.6	-
426-16	М	87	D	17.0	12.2	99	500	57	0.552	1.74	8.7	O. Esp. FO
58-127	М	75	D	0.1	12.7	102	180	44	0.557	2.31	4.1	-
426-14	M	72	D	4.1	13.2	115	220	54	0.601	2.13	4.1	-
426-13	М	65	D	6.6	12.7	98	360	13	0.593	7.54	27.7	O, Fsp, FO
426-12	М	58	D	40.1	12.7	91	410	65	0.575	1.40	6.3	Q, Fsp
426-9	М	54	D	0.7	13.2	140	60	14	0.594	10.1	4.1	-
426-8	М	36	D	0.5	13.3	96	620	28	0.604	3.43	22.1	-
426-6	М	18	D	4.8	13.3	184	450	10	0.607	18.4	45.0	-
426-5	М	6	L	4.8	1.4	138	1370	195	0.035	0.70	7.1	Q, Fsp, Chl
58-10	Μ	4	L	4.7	0.4	125	1470	265	0.010	0.48	5.5	-
58-8	M	3	L	10.0	0.3	130	1670	183	0.009	0.73	9.1	Q, Fsp, Mc, Chl

Table 1. Trace element concentrations and characteristics of siliciclastic admixture in carbonate rocks of the Karatau Group, southern Urals

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Table 1. (Contd.)

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Sample no. <sup>1</sup>	Sec- tion <sup>2</sup>	Sampling level <sup>3</sup> , m	Rock type <sup>4</sup>	Siliciclas- tic admix- ture (SA) <sup>5</sup> , %	Mg, %	Mn, ppm	Fe, ppm	Sr, ppm	Mg/Ca	Mn/Sr	Fe/Sr	Minerals of SA <sup>6</sup>
Inzer Forma	a <b>tion</b> .	(. <u></u>					4		<u>.</u>			
426-64	М	308	L	1.7	0.5	32	390	175	0.013	0.18	2.2	0
58-1	М	295	L	1.4	1.4	230	1820	118	0.038	1.97	15.4	Q
426-62	М	285	L	1.3	0.6	45	900	169	0.016	0.27	5.3	-
63-6	Κ	270	L	1.8	0.2	43	495	243	0.006	0.17	2.0	-
63-5	Κ	260	L	2.4	0.8	38	570	213	0.020	0.18	2.7	-
426-58	М	245	L	7.0	0.1	51	1510	298	0.002	0.17	5.1	Chl, Mc, Q, Fsp
438-15	М	188	L	0.3	0.2	22	315	545	0.004	0.04	0.6	-
438-12	М	172	L	0.3	0.2	21	310	605	0.005	0.03	0.5	-
438-10	М	158	L	0.4	0.1	15	370	490	0.002	0.03	0.8	-
438-9	М	151	L	0.7	0.2	21	325	521	0.006	0.04	0.6	-
438-6	М	130	L	0.2	0.3	19	220	512	0.006	0.04	0.4	-
438-3	М	110	L	0.8	0.4	23	420	495	0.009	0.05	0.8	-
373-16	K	109	L	3.5	0.4	94	810	151	0.010	0.62	5.4	Q
373-13	K	90	L	4.4	0.4	11	160	590	0.010	0.02	0.3	Q
373-12	K	85	L	0.6	0.5	14	400	417	0.013	0.03	0.9	-
55-47	M	82	L	0.1	0.2	86	646	77	0.004	1.12	8.4	-
441-24	M	80	L	1.7	1.1	37	870	254	0.030	0.15	3.4	Q
373-10	K	70	L	0.6	0.1	18	460	439	0.003	0.04	1.1	-
441-20	М	67	L	0.5	0.1	15	330	423	0.002	0.04	0.8	-
441-18	М	15	L	0.8	0.1	44	420	411	0.003	0.11	1.1	
441-17	М	9	L	4.6	0.1	96	2630	338	0.003	0.28	7.8	Q, Fsp
441-15	М	1	L	9.6	0.2	102	2640	508	0.005	0.20	5.2	Q, Fsp, Mc
Katav Form	nation											•
441-13	M	130	L	10.2	0.4	270	3470	152	0.010	1.78	22.8	Q, Fsp, Mc, Chl
373-9	K	120	L	13.2	0.2	180	3870	240	0.006	0.75	16.1	Q, Mc, Chl, Fsp
63-27	K	105	L	0.4	0.1	225	1210	345	0.002	0.65	3.5	-
441-9	M	95	L	13.5	0.1	220	4360	190	0.002	1.16	22.9	Q, Fsp, Mc, Chl
373-5	K	90	L	13.0	0.6	170	3630	215	0.015	0.79	16.8	Q, Fsp, Mc, Chl
63-17	K	80	L	0.2	0.1	320	2970	255	0.002	1.25	11.6	-
441-5	Μ	70	L	15.1	0.1	240	3970	126	0.002	1.90	31.5	Q, Mc, Chl, Fsp
55-37	Μ	65	L	0.5	0.1	324	3070	155	0.002	2.09	19.8	-
373-3	K	60	L	18.6	0.3	175	2480	160	0.007	1.09	15.5	Mc, Chl, Q, Fsp
441-2	M	40	L	10.5	0.1	234	1560	154	0.002	1.52	10.1	Q, Mc, Chl, Fsp
55-27	М	35	L	0.2	0.1	420	2025	67	0.002	6.30	30.2	-
373-1	K	30	L	23.8	0.1	160	2220	120	0.004	1.33	18.5	Q, Fsp, Mc, Chl

Note: (1) Italicized are data for samples satisfying the accepted geochemical criteria (Mg/Ca \_0.024, Fe/Sr \_5.0, Mn/Sr \_0.2 for limestones and Mg/Ca \_ 0.608, Mn/Sr \_ 1.2, Fe/Sr \_ 3.0 for dolostones). (2) Sections by names: (M) Min'yar, (K) Kulmas, (SH) Shubino. (3) Sampling levels are denoted in meters above the formation base in the generalized succession. (4) Rocks: (L) limestone; (D) dolomite; (5) siliciclastic admixture; (6) Minerals: (Q) quartz, (Mc) mica, (Fsp) Feldspar, (Chl) chlorite, (FO) Fe-oxides, all listed in order of decreasing abundance. (7) Samples of veined calcite or dolomite.

bino section is composed of greenish gray glauconitequartz sandstone, siltstone, and rare shale beds intercalated with separate interlayers (0.2 to 0.4 m) and two members (4-6 and 8-9 m) of micritic limestones, the latter confined to the upper part. Siliciclastic components of limestones (5 to 8%)are represented by quartz and clay minerals. The extent of dolomitization in limestones (Mg/Ca up to 0.04) is variable. Gravelstone at the base of subformation contains clasts of underlying carbonate rocks. The lower 120-m-thick interval of the upper Uk Subformation (140 m) is composed of light gray stromatolitic and rare clastic limestones, which are weakly dolomitized in contrast to dolostones and dolomitic limestones characteristic of the upper 20 to 25-mthick interval. Micrite and microsparite with small sparite segregations are constituents of stromatolitic rock varieties, whereas clastic limestones are predominantly composed of micrite. In some rare rocks, micrite and microsparite are partially replaced by sparite and by medium-grained poikilitic calcite, and dispersed Feoxides and hydroxides appear in their matrix. Small rhombohedral dolomite crystals irregularly distributed in the matrix are surrounded by ferruginate rims. The Mg concentration in limestones from the lower 120-mthick interval of the upper Uk Subformation ranges from 0.2 to 1.5%, and percentage of siliciclastic admixture is usually not greater than 0.1-6%, growing up to 11-14% only near the subformation base. In dolostones and dolomitic limestones crowning the subformation section and containing only 1-2% of siliciclastic fraction, the Mg content ranges from 1.5 to 9.5%. These rocks are composed of dolosparite matrix with irregular segregations and veinlets of coarse-crystalline dolomite, in which there are microscopic micrite relics (0.1 to 0.3 mm) and corroded crystals of poikilitic calcite. The rhombohedral dolomite crystals have regeneration rims and are zonal sometimes. In the Kulmas section, where the Uk Formation is of the same structure in general, its lower subformation increases in thickness up to 150 m and encloses only one limestone package 5 m thick (Fig. 2). In contrast, the upper subformation is thinner (40 m) than in the Shubino section and enriched in microphytolitic limestones. A considerable portion of the upper subformation is likely eliminated by the pre-Vendian erosion. According to cathodoluminescence analysis, the upper Uk carbonates are inhomogeneous. In the non-luminescent micrite to microsparite matrix of limestones, there are seen luminescence of variable intensity that is characteristic of sparite segregations and veins. The patchy luminescence of dolostones indicates that they are composed of several carbonates' generations.

The predominantly carbonate units of the Karatau Group, which are described above, accumulated in a vast sea basin, where, according to conclusion of Maslov *et al.*, (2001), relatively deep environments located below storm wave base were subordinate to dominant subtidal settings. The analyzed structural peculiarities of rocks, widespread among which are

flakestones, and the data on stromatolite morphotypes suggest that the Katav, lower Inzer, and lower Minka carbonates mostly represent sediments of a lower subtidal zone situated close to the storm wave base. Stromatolitic horizons present in these units and in the Uk Formation correspond to the open-shelf deposits. The shallowest origin of carbonates, as compared to others of the Karatau Group, is inferable for their microphytolitic varieties occurring in upper horizons of the Inzer and Uk formations and for those packages of the upper Minka, Byanka and Uk successions, which reveal marks of subaerial exposition.

### INVESTIGATION PROCEDURE

Among 250 samples of carbonate rocks collected from the Karatau Group, we selected for investigation of Rb-Sr systematics only those 70 samples, which were macroscopically homogeneous, lacking obvious signs of secondary recrystallization (53 limestone and 17 dolostone samples; Table 1, Fig. 2). In addition, we analyzed samples of veined calcite from various horizons of the Katav Formation and lower Inzer Subformation and of vein dolomite from the Min'yar Formation. Selected samples were sawed in two parts, one of which was examined by petrographic and cathodoluminescence methods, and the other one was used for the X-ray, chemical, and isotopic analyses. Ca and Mg contents in carbonate fractions were measured by wet chemical method, and the atomic absorption spectroscopy was applied to determine the Mn and Fe concentrations. Mineral composition of siliciclastic admixture is defined by the X-ray diffraction method.

In order to prepare samples for the Rb-Sr isotopic analysis, we removed their epigenetic carbonate phases applying the procedure of selective dissolution that included the preliminary treatment of powdered material in solution of ammonium acetate (NH4OAc) and subsequent dissolution of residue in acetic acid as it is described in work by Gorokhov et al. (1995). After addition of 3 ml of 1N NH<sub>4</sub>OAc, we subjected each sample weighing to ultrasonic machining in UZDN-2T device during 10 minutes and repeated the operation for the residue after centrifuging. After second centrifuging, the precipitate was treated in 10% acetic acid. The carbonate components of limestones dissolved completely after 72 hours, and those of dolostones entered the solution after 72 to 120 hours. Next, the insoluble silicate fraction was separated by centrifuging and rinsed two times in the twice-distilled water. Centrifugates of two treatment stages are designated in this work as the AMA (ammonium acetate) and ACA (acetic acid) phases.

Effectiveness of preliminary sample treatment in ammonium acetate has been demonstrated in a series of works devoted to Rb-Sr systematics of Proterozoic and Phanerozoic carbonates (Gorokhov *et al.*, 1995; Kuznetsov, 1998; Bailey, 2000; Bartley *et al.*, 2001; Semi-khatov *et al.*, 2002). This procedure facilitates a partial

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**Fig. 3.** Diagram showing percentage of AMA phase versus Mg/Ca ratios in the studied samples: (I) limestone; (2) dolostone; (3) veined calcite; (4) veined dolomite.

removal of secondary carbonate phases thus leading to enrichment of samples in primary material. The AMA phase leached from surface of mineral particles represents the latest epigenetic generation of carbonate minerals, whereas the ACA phase corresponds mostly to primary carbonate material with a considerably lesser admixture of epigenetic phases. The completeness of separation and a possibility-in-itself to separate two phases using the selective dissolution depend on degree of epigenetic alterations in primary carbonate sediment.

The Rb and Sr concentrations in AMA and ACA phases are measured using the isotopic dilution method and mixed <sup>87</sup>Rb-<sup>84</sup>Sr spike. Sr isotope composition was determined on the multi-collector Finnigan MAT 261 mass spectrometer using a regime of simultaneous measurements of all isotope currents. The laboratory averages of 0.71025  $\pm$  0.00001 (2 <sub>av.</sub>, n = 38) and 0.70917  $\pm$  0.00002 (2 <sub>av.</sub>, n = 2) were determined for the NIST SRM 987 and USGS EN-I standard carbonates, respectively, during the period of data gathering.

#### Rb-Sr SYSTEMATICS OF NON-COGENETIC CARBONATE PHASES

Percentages of AMA phases range from 3.2 to 6.4% (4.6% in average) in the Karatavian limestones and from 2.0 to 4.7% (3.1% in average) in dolostones. The highest percentage (7.6 to 8.6%) is characteristic of veined calcite, whereas the lowest values are deter-

mined in vein dolomite (2.0%) and in dolostones (2.0 to)2.1%) enriched in siliciclastic material. In general, the content of AMA phase decreases parallel to the Mg/Ca ratio growth (Fig. 3). The ACA and AMA phases differ from each other in terms of Rb-Sr characteristics (Table 2). Concentration of Rb in AMA phases of limestones and dolostones is 34 and 50 times greater, respectively, than in corresponding ACA phases. The Sr concentration is almost equal in both phases of limestones, whereas in dolostones it is two times greater in the AMA than in the ACA phase. This behavior of trace elements formerly established in Riphean carbonates of Siberia implies that the AMA phase is represented in both rock types by secondary calcite and/or by low-Mg dolomite (Gorokhov et al., 1995; Semikhatov et al., 2002). The Sr concentration in bulk carbonate material (Table 1) used to calculate Mn/Sr and Fe/Sr ratios has been assessed as the weighted average based on this element concentrations in AMA and ACA phases and on percentages of the latter in the rocks (Table 2).

The 87Sr/86Sr ratios measured in AMA phases of limestones and dolomites are usually higher than in ACA phases. Difference in this parameter between two phases under consideration is up to 0.0146 in dolostone and not greater than 0.0080 in limestones (Table 2, Fig. 4). The inversed relations are characteristic of veined calcite, and 87Sr/86Sr ratios in ACA phases of this mineral exceed those in AMA phases by values of 0.0001 to 0.0020 (Fig. 4a). All the mentioned distinctions evidence the non-cogenetic character of ACA and AMA phases. In addition, difference between 87Sr/86Sr ratios in these phases of limestones lacking signs of dolomitization (an exception is sample 442-7 taken in proximity to dolostones) is positively correlative with Mn/Sr (correlation coefficient r = 0.67) and Fe/Sr (r =0.88) ratios. This peculiarity means that carbonate rocks became enriched in Mn. Fe. and radiogenic <sup>87</sup>Sr during their partial recrystallization at the late stages of lithogenesis. Even the late veined calcite was partially recrystallized under influence of epigenetic fluids, because its phases are non-cogenetic. However, none of the correlations mentioned above has been established for dolostones, which may indicate deeper recrystallization of these rocks.

Data considered above imply that Rb-Sr systems of ACA and AMA phases in limestones and dolostones have been formed at different stages of lithogenesis. Accordingly, it would be incorrect to calculate the <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios for AMA phases based on the sample age and Rb and Sr concentrations in the bulk carbonate material, because they may turn out to be significantly lower than ratios obtained for the paired ACA phases (Table 2, Fig. 4). Preliminary leaching of samples in ammonium acetate leads to a more confident assessment of <sup>87</sup>Sr/<sup>86</sup>Sr ratios in a paleobasin, as they are estimated in this case based on analytical results obtained for materials enriched in primary carbonates. Thus, all the values of <sup>87</sup>Sr/<sup>86</sup>Sr ratios presented below characterize the studied ACA phases only, if the other

Sample no. <sup>1</sup>	Rock <sup>2</sup>	Carbonate phase <sup>3</sup>	Content of the phase (%)	Rb, ppm	Sr, ppm	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr measured	<sup>87</sup> Sr/ <sup>86</sup> Sr initial			
Uk Formatio	Uk Formation										
442-27	D	AMA	4.7	3.38	96	- 1	-	-			
		ACA	94.0	0.08	7.7	0.0313	0.71080	0.71050			
442-24	L	AMA	4.4	1.00	67	0.0429	0.71239	0.71199			
		ACA	94.3	0.02	52	0.0010	0.71188	0.71187			
442-23	L	AMA	4.8	1.73	343	0.0146	0.70579	0.70565			
	!	ACA	94.4	0.03	311	0.0003	0.70545	0.70545			
442-22	L	AMA	4.5	3.85	190	0.0585	0.70756	0.70702			
	· ·	ACA	92.4	0.19	148	0.0037	0.70598	0.70595			
442-21	L	AMA	5.3	9.51	112	0.1273	0.70785	0.70667			
		ACA	91.3	0.13	111	0.0034	0.70649	0.70646			
442-18	L	AMA	4.4	4.77	121	0.1138	0.70933	0.70827			
		ACA	92.6	0.10	105	0.0028	0.70650	0.70647			
442-16	L	AMA	3.2	13.0	153	0.2460	0.71119	0.70891			
		ACA	91.3	0.20	116	0.0050	0.70725	0.70720			
442-15	L	AMA	3.7	9.75	213	0.1325	0.71107	0.70984			
		ACA	85.3	0.18	138	0.0037	0.70745	0.70742			
442-14	L	AMA	3.7	19.7	48	-	-	-			
		ACA	82.3	0.28	118	0.0069	0.70806	0.70800			
3573	L	AMA	5.4	5.44	116	0.1362	0.70741	0.70615			
		ACA	93.9	0.17	88	0.0056	0.70596	0.70591			
3573-2	L	AMA	5.1	4.03	176	0.0662	0.70696	0.70635			
		ACA	94.0	0.05	144	0.0010	0.70599	0.70598			
<i>3573-7</i> .	L	AMA	5.8	3.07	522	0.0170	0.70578	0.70562			
		ACA	90.9	0.06	431	0.0004	0.70538	0.70538			
442-11	L	AMA	4.6	2.19	771	0.0082	0.70612	0.70604			
		ACA	94.2	0.06	712	0.0002	0.70581	0.70580			
442-10	L	AMA	5.3	9.29	177	0.1522	0.70807	0.70666			
		ACA	86.6	0.15	296	0.0015	0.70596	0.70595			
442-9	L	AMA	4.1	3.82	218	0.0506	0.70694	0.70647			
		ACA	91.4	0.10	282	0.0010	0.70583	0.70582			
Min'yar Forr	nation					•					
442-8	L	AMA	5.7	1.59	410	0.0114	0.70700	0.70689			
		ACA	92.7	0.21	335	0.0017	0.70660	0.70658			
56-16b	L	AMA	4.3	0.53	<sup>°</sup> 465	0.0330	0.70629	0.70626			
		ACA	95.4	0.05	478	0.0003	0.70621	0.70621			
56-16	L	AMA	4.3	3.25	464	0.0203	0.70654	0.70634			
		ACA	93.4	0.06	342	0.0005	0.70608	0.70607			
56-15a	L	AMA	4.8	4.49	463	0.0280	0.70652	0.70624			
		ACA	93.6	0.07	372	0.0005	0.70601	0.70600			
442-7	L	AMA	4.4	4.52	447	0.0262	0.70653	0.70627			
		ACA	92.2	0.08	404	0.0005	0.70608	0.70607			
442-6	L	AMA	4.3	2.37	205	0.0308	0.70701	0.70671			
		ACA	94.0	0.23	230	0.0030	0.70624	0.70621			

Table 2. Rb-Sr isotopic data characterizing carbonate phases of limestones and dolostones of the Karatau Group

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Table 2. (Contd.)

Sample no. <sup>1</sup>	Rock <sup>2</sup>	Carbonate phase <sup>3</sup>	Content of the phase (%)	Rb, ppm	Sr, ppm	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr measured	<sup>87</sup> Sr/ <sup>86</sup> Sr initial
442-3	D	AMA	2.8	2.09	24	0.1720	0.70816	0.70643
		ACA	94.0	0.03	20	0.0033	0.70682	0.70678
442-1	D	AMA	2.4	6.60	715	0.0270	0.70784	0.70754
		ACA	90.9	0.06	101	0.0017	0.70613	0.70611
		$AMA^5$	3.3	4.10	209	0.0575	0.70766	0.70702
		$ACA^5$	95.0	0.05	103	0.0014	0.70613	0.70611
426-35	D	AMA	2.9	2.08	75	0.0804	0.70737	0.70656
		ACA	95.0	0.07	67	0.0029	0.70628	0.70625
426-33	D	AMA	2.3	12.7	342	0.1088	0.70854	0.70733
		ACA	94.8	0.07	101	0.0020	0.70589	0.70587
		$AMA^5$	2.9	3.90	191	0.0598	0.70811	0.70744
		$ACA^5$	95.8	0.07	102	0.0020	0.70585	0.70583
426-31	D	AMA	3.5	1.84	64	0.0833	-	-
		ACA	94.9	0.45	44	0.0295	0.70614	0.70584
426-29	D	AMA	2.4	9.58	46	0.6115	0.71123	0.70478
		ACA	88.7	0.17	27	0.0184	0.70605	0.70586
426-24	D	AMA	2.4	2.79	142	0.0568	0.70717	0.70656
		ACA	96.9	0.08	66	0.0037	0.70602	0.70598
426-20	D	AMA	3.1	2.72	126	0.0625	0.70812	0.70745
		ACA	94.5	0.06	73	0.0022	0.70615	0.70612
426-18	D	AMA	3.1	2.23	53	0.1226	-	-
		ACA	95.3	0.05	55	0.0024	0.70577	0.70574
426-16	D	AMA	2.0	35.7	105	0.9865	0.72295	0.71210
		ACA	81.6	0.35	56	0.0178	0.70837	0.70817
58-124	D	AMA	2.0	1.31	102	0.0376	0.70882	-
		ACA	97.9	0.08	42	0.0057	0.70820	-
426-14	D	AMA	3.7	15.7	76	0.5950	0.71338	0.70682
		ACA	92.3	0.16	54	0.0084	0.70834	0.70825
426-13	D	AMA	3.5	5.26	19	0.8416	-	-
		ACA	89.9	0.12	12	0.0258	0.70805	0.70776
426-12	D	AMA	2.1	24.0	107	0.6469	-	-
		ACA	58.6	0.67	64	0.0306	0.70847	0.70813
426-9	D	AMA	3.0	1.96	14	0.3998	0.70863	0.70416
		ACA	96.3	0.03	14	0.0063	0.70816	0.70809
426-8	D	AMA	4.0	0.76	43	0.0507	0.70887	0.70830
		ACA	90.3	0.03	28	0.0030	0.70754	0.70753
		AMA <sup>5</sup>	4.6	-		-	0.70883	—
		ACA <sup>5</sup>	89.7	-	—	-	0.70758	-
426-6	D	AMA	3.3	3.25	22	0.4210	-	-
		ACA	95.4	0.05	10	0.0155	0.70819	0.70802
426-5	L	AMA	4.8	7.19	179	0.1160	0.70762	0.70631
		ACA	90.8	0.13	196	0.0020	0.70574	0.70572
58-10	L	AMA	4.9	7.34	229	0.0951	0.70696	0.70589
		ACA	91.0	0.16	267	0.0017	0.70562	0.70560
58-8	L	AMA	5.3	5.62	151	0.1079	0.70746	0.70624
		ACA	88.3	0.14	185	0.0023	0.70571	0.70568

Table 2. (Contd.)

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Sample no. <sup>1</sup>	Rock <sup>2</sup>	Carbonate phase <sup>3</sup>	Content of the phase (%)	Rb, ppm	Sr, ppm	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr measured	<sup>87</sup> Sr/ <sup>86</sup> Sr initial
Inzer Format	ion			· · · ·	·	<u> </u>	·	·
426-64	L	AMA	5.9	2.43	208	0.0438	0.70621	0.70571
		ACA	92.9	0.11	173	0.0017	0.70557	0.70555
58-1	L	AMA	4.1	0.36	175	0.0064	0.70623	0.70616
		ACA	94.9	0.33	115	0.0082	0.70567	0.70558
426-62	L	AMA	5.5	3.18	210	0.0434	0.70628	0.70578
		ACA	93.6	0.09	166	0.0015	0.70565	0.70563
63-6	L	AMA	4.6	0.34	235	0.0041	0.70611	0.70606
	•	ACA	93.9	0.03	260	0.0004	0.70560	0.70560
		AMA <sup>5</sup>	5.7	0.32	170	0.0055	0.70594	0.70587
		ACA <sup>5</sup>	92.7	0.03	235	0.0004	0.70562	0.70562
63-5	L	AMA	3.8	0.21	197	0.0031	0.70623	0.70619
	I	ACA	95.4	0.04	213	0.0005	0.70567	0.70566
426-58	L	AMA	6.4	1.33	241	0.0158	0.70641	0.70622
		ACA	87.3	0.09	302	0.0009	0.70556	0.70555
438-15	L	AMA	5.2	1.35	596	0.0065	0.70555	0.70547
		ACA	94.8	0.15	542	0.0008	0.70539	0.70538
438-12	L	AMA	3.5	0.82	698	0.0030	0.70542	0.70538
		ACA	96.5	0.04	598	0.0002	0.70532	0.70532
438-10	L	AMA	4.9	0.07	564	0.0004	0.70546	0.70546
		ACA	94.1	0.02	517	0.0001	0.70530	0.70530
438-9	L	AMA	4.8	0.71	498	0.0040	0.70542	0.70537
		ACA	94.9	0.03	522	0.0002	0.70525	0.70525
438-6	L	AMA	5.4	0.61	618	0.0022	0.70536	0.70533
		ACA	94.6	0.03	506	0.0002	0.70533	0.70533
		AMA <sup>5</sup>	4.8	0.35	616	0.0017	0.70539	0.70537
		ACA <sup>5</sup>	95.9	0.36	512	0.0021	0.70533	0.70531
<i>438-3</i>	L	AMA	3.7	1.09	650	0.0047	0.70547	0.70541
		ACA	96.0	0.04	491	0.0002	0.70526	0.70526
373-16	L	AMA	5.7	2.28	124	0.0538	0.70742	0.70676
		ACA	91.3	0.12	153	0.0020	0.70648	0.70646
373-13	L	AMA	6.2	0.94	536	0.0052	0.70631	0.70625
		ACA	90.8	0.04	572	0.0002	0.70579	0.70579
		AMA <sup>5</sup>	5.0	1.90	589	0.0094	0.70623	0.70612
		ACA <sup>5</sup>	91.6	0.06	613	0.0003	0.70580	0.70580
373-12	L	AMA	5.2	1.12	387	0.0084	0.70635	0.70624
		ACA	94.5	0.04	418	0.0002	0.70565	0.70565
55-4 <sup>4</sup>	L	AMA	5.1	0.55	110	0.0145	0.70884	-
		ACA	94.9	0.06	76	0.0022	0.70888	-
441-24	L	AMA	4.6	2.39	346	0.0201	0.70579	0.70554
		ACA	94.2	0.06	249	0.0007	0.70536	0.70535
		AMA <sup>5</sup>	4.3	2.57	411	0.0183	0.70554	0.70536
		ACA <sup>5</sup>	94.9	0.04	250	0.0005	0.70539	0.70538
373-10	L	AMA	5.5	1.35	428	0.0091	0.70621	0.70610
		ACA	94.2	0.04	439	0.0002	0.70571	0.70571
441-20	L	AMA	4.3	3.16	532	0.0171	0.70556	0.70535
		ACA	95.4	0.05	418	0.0004	0.70528	0.70528

Table 2.	(Contd.)
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Sample no. <sup>1</sup>	Rock <sup>2</sup>	Carbonate phase <sup>3</sup>	Content of the phase (%)	Rb, ppm	Sr, ppm	<sup>87</sup> Rb/ <sup>86</sup> Sr	<sup>87</sup> Sr/ <sup>86</sup> Sr measured	<sup>87</sup> Sr/ <sup>86</sup> Sr initial
441-18	L	AMA	5.1	2.17	406	0.0154	0.70554	0.70535
		ACA	94.7	0.04	411	0.0003	0.70534	0.70534
441-17	L	AMA	5.4	4.09	345	0.0347	0.70640	0.70596
		ACA	93.1	0.29	338	0.0026	0.70538	0.70536
441-15	L	AMA	4.8	10.2	572	0.0516	0.70658	0.70592
		ACA	85.6	0.18	506	0.0010	0.70541	0.70540
		AMA <sup>5</sup>	3.5	10.8	608	0.0511	0.70658	0.70591
		ACA <sup>5</sup>	87.3	0.19	503	0.0010	0.70541	0.70540
Katav Forma	tion							
441-13	L	AMA	5.4	7.99	168	0.1393	0.70996	0.70823
		ACA	84.4	0.21	151	0.0041	0.70632	0.70627
373-9	L	AMA	5.9	7.29	213	0.1002	0.71185	0.71060
		ACA	81.2	0.19	245	0.0023	0.70756	0.70753
		AMA <sup>5</sup>	5.1	7.88	266	0.0868	0.71200	0.71092
		ACA <sup>5</sup>	81.6	0.19	239	0.0023	0.70755	0.70752
63-24	L	AMA	8.6	0.47	688	0.0020	0.71199	-
ļ		ACA	91	0.08	286	0.0008	0.71243	-
441-9	L	AMA	4.3	15.9	199	0.2338	0.71247	0.70956
		ACA	82.2	0.39	190	0.0060	0.70651	0.70644
373-5	L	AMA	4.9	13.9	214	0.1893	0.71245	0.71010
		ACA	82.1	0.07	216	0.0010	0.70821	0.70820
63-14	L	AMA	8.5	0.60	142	0.0124	- 0.72019	-
		ACA	90.3	0.08	268	0.0008	0.72044	-
441-5	L	AMA	4.3	15.3	162	0.2766	0.71441	0.71097
		ACA	81.0	0.28	123	0.0067	0.70682	0.70674
		AMA <sup>5</sup>	5.8	10.8	125	0.2530	0.71415	0.71100
		ACA <sup>5</sup>	79.7	0.49	125	0.0115	0.70676	0.70662
55-3 <sup>4</sup>	L	AMA	9.2	1.33	111	0.0351	0.72148	-
		ACA	89.9	0.09	160	0.0016	0.72186	-
		AMA <sup>5</sup>	10.0	0.88	115	0.0224	0.72141	-
272.2	т	ACAS	88.7	0.05	159	0.0009	0.72189	-
3/3-3	L	AMA	5.1	18.3	176	0.3052	0.71374	0.70995
441.0	т	ACA	/6.3	0.34	161	0.0063	0.70845	0.70837
441-2	L		6.2	5.35	124	0.1264	0.71253	0.71096
		ACA	83.2	0.24	157	0.0045	0.70714	0.70708
		AMA <sup>3</sup>	5.3	11.2	144	0.2278	0.71319	0.71036
55 04	т	ACA	80.3 7.6	0.19	155	0.0036	0.70718	0.70714
<b>33-</b> 24	L	AMA	/.0	0.41	55	0.0220	0.72272	-
272.1	Ŧ	ACA	91.2	0.24	64	0.0110	0.72472	-
5/3-1	L	AMA	4.7	22.0	154	0.4184	0.71824	0.71304
		ACA	/1.6	0.53	115	0.0135	0.70996	0.70979
		AMA <sup>3</sup>	5.4	1/.6	136	0.3790	0.71767	0.71296
		ACA <sup>3</sup>	70.1	0.52	118	0.0129	0.70991	0.70975

Note: (1) italicized arc data for samples satisfying the accepted geochemical criteria (Mg/Ca \_ 0.024, Mn/Sr \_ 0.2, and Fc/Sr \_ 5 for limestones and Mg/Ca \_ 0.608, Mn/Sr \_ 1.2, Fe/Sr \_ 3.0 for dolostones); (2) limestone (L) or dolostone (D); (3) carbonate material dissolved in 1N NH<sub>4</sub>OAc (AMA phase) and residue after leaching dissolved subsequently in 10% CH<sub>3</sub>COOH (ACA phase); (4) samples of veined calcite or dolomite; (5) data for samples independently treated in 1N NH<sub>4</sub>OAc.

analyzed material is not specified when necessary. Calculating the <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios, we used the following age values: 870 Ma for the Katav Formation, 835 Ma for the Inzer Formation, 780 Ma for the Min'yar Formation, and 650 Ma for the Uk formation. In the case of the Inzer and Min'yar formation, the values correspond to Pb-Pb dates obtained for their rocks. Two other values average out the age intervals adopted for corresponding formations. We did not estimate the <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios for veined calcite and dolomite, because the formation time of veins is unknown.

#### ISOTOPIC-GEOCHEMICAL CHARACTERIZATION OF THE KARATAU GROUP CARBONATES

Katav Formation. Clayey limestones of this formation are composed of calcite with a high percentage of fine siliciclastic admixture (10 to 24%) that consists of illite, chlorite, clastic quartz, and feldspars (Table 1). The carbonate fraction of rocks is rich in Mn and Fe, average concentrations of which correspond to 206 and 3200 ppm, respectively. In contrast, the Sr concentration is rather low, equal to 170 ppm in average and varying from 120 to 240 ppm. Calcite from fine veinlets is almost barren of Mg (<0.1%), being enriched in Mn and depleted in Fe as compared to matrix carbonates. The Sr content in this calcite from the lower part of the formation is slightly lower than in the upper one (67-155 versus 255-345 ppm). The 87Sr/86Sr initial ratios calculated for the Katav clayey limestones are high in general, and their values are higher in the Kulmas section (0.70753-0.70979) than in the Min'var section (0.70627-0.70714). This distinction is likely related to post-sedimentation history of the rocks, which exhibit a high degree of recrystallization, stylolitization, and fracturing in the Kulmas section. Characteristic of both sections is a trend of decreasing-upward 87Sr/86Sr ratios from 0.70714 to 0.70627 in the Min'yar section and from 0.70979 to 0.70753 in the Kulmas section. The same trend is typical of veined calcite. The 87Sr/86Sr ratios in this mineral range from 0.72472 near the formation base to 0.72044-0.72189 in the middle and then to 0.71243 near its top (Table 2).

The high percentage of clay admixture in the Katav limestones can be a factor responsible for enrichment of their carbonate fraction in Mn, Fe, Rb, and radiogenic <sup>87</sup>Sr, because dia- and catagenetic transformations of clay minerals deliberate, as is known, some chemical elements from their structures (Anfimov, 1997). In fact, rather high concentrations of Mn (0.02 to 0.12%) and Fe (0.20 to 0.36%) are characteristic of pore waters in non-consolidated carbonate sediments containing 10 to 15% of clay material (Savin and Epstein, 1970). Nevertheless, <sup>87</sup>Sr/<sup>86</sup>Sr ratios decrease upward in the Katav succession, i.e., away from underlying sandstones and shales of the Zilmerdak Formation, and according to this trend the above factor acted in combination with the other one. It is likely that



Fig. 4. Correlation diagrams for measured (a) and initial (b)  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios in AMA and ACA phases of carbonates from the Karatau Group (symbols as in Fig. 3).

recrystallization of the Katav limestones and enrichment of their carbonate material in trace elements and radiogenic <sup>87</sup>Sr developed also under influence of epigenetic fluids rising from underlying siliciclastic rocks during their burial and at the formation time of fracture systems in the Karatavian succession (Kuznetsov, 1998; Kuznetsov *et al.*, 2002).

*Inzer Formation.* All limestones of this subdivision, except for two samples (441-24 and 58-1) of dolomitized rocks, are composed of low-Mg calcite, in which

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the insignificant (less than 1% in average, Table 1) siliciclastic admixture is represented by clastic quartz. However, the percentage of admixture (quartz in association with clay minerals) grows up to 7-10% near the base of carbonate members occurring in two subformations. Characteristic of Inzer limestones are very low Mn (10 to 50 ppm) and Fe (160 to 900 ppm) concentrations, whereas the Sr concentration is high in the upper subformation (169 to 298 ppm) and especially high in the lower one (411 to 605 ppm). Only dolomitized varieties (samples 441-24 and 58-1), ferruginate limestone (sample 373-16), and basal limestones of both carbonate members exposed in the Min'yar section (samples 441-15, 441-17, and 426-58) are relatively enriched in Mn and Fe. In the last case, the enrichment was likely caused by infiltration of elision fluids derived from the underlying clayey-carbonate sediments of the Katav Formation in the course of their burial.

In the Kulmas section, the 87Sr/86Sr initial ratios in limestones of the lower Inzer Subformation are higher (0.70565 to 0.70646) than in the Min'yar section (0.70525 to 0.70551, Table 2). The extreme value of 0.70646 is established for the ferruginate limestone (sample 373-16) near the apparent top of the Kulmas section. It likely represents the effect of rock interaction with meteoric water, as one can judge from the mosaic structure of the rock displaying presence of Fe-hydroxides and high Mn/Sr and Fe/Sr ratios (Figs. 5a and 5b). Except for the indicated sample, other limestones of the Kulmas and Min'yar sections are similar in terms of such criteria as Mn/Sr and Fe/Sr ratios, although the range of <sup>87</sup>Sr/<sup>86</sup>Sr ratios is greater in the former section latter (0.70525-(0.70565 - 0.70580)than in the 0.70540). This inconsistence seems to be a consequence of patchy recrystallization characteristic of Kulmas limestones, which have microstylolitic seams and crosscutting veinlets (0.1 to 0.5 mm thick) of late crystalline calcite. The high 87Sr/86Sr ratio established for this calcite (0.70888) suggests that late epigenetic fluids were enriched in radiogenic <sup>87</sup>Sr.

In both sections, the <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios in limestones of the upper Inzer Subformation range from 0.70555 to 0.70566 only (Table 2). Moreover, samples of slightly dolomitized limestones (441-24 and 58-1) from upper and lower subformations of the Min'yar section, in which Mn/Sr and Fe/Sr ratios are higher than in neighboring "pure" limestones, do not differ from the latter in terms of <sup>87</sup>Sr/<sup>86</sup>Sr ratios. Accordingly, it is possible to suggest that dolomitization took place at the early diagenetic stage, and that crystal chemistry of dolomite is responsible for difference in trace element concentrations.

*Min'yar Formation.* The average Mg/Ca ratio of 0.608 characterizing dolostones, the main rock types of the formation, is close to that of stoichiometric dolomite (Chilingare *et al.*, 1967). Using the measured ratio range (0.552-0.636), we divided the studied samples in two groups of "high-Mg" (Mg/Ca = 0.608-0.636) and

"low-Mg" (Mg/Ca = 0.552-0.607) dolostones (Table 1). There are also structural and textural distinctions between rocks of two groups. The high-Mg varieties are slightly recrystallized and retain the original sedimentary structures, whereas the low-Mg dolostones are lacking these structures and usually consist of coarsecrystalline dolomite. Rocks of the first group prevail in the Min'var Formation, while low-Mg rocks are characteristic of the 70 to 80-m-thick stromatolitic member of the lower subformation, of interlayers enriched in silty siliciclastic components, and of some small packages below the Shubino Member. In general, the high-Mg dolostones are less rich in Mn (44 to 230 ppm) and Fe (90 to 440 ppm) than the low-Mg rocks (91-340 and 60-1340 ppm, respectively). At the same time, they have more Sr (21 to 113 ppm) and lower <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.70574-0.70678) as compared to low-Mg dolostones (10-65 ppm and 0.70753-0.70825, respectively, Fig. 6). According to Mg/Ca (0.56) and <sup>87</sup>Sr/86Sr (0.70820) ratios, the veined dolomite in the lower formation part (sample 58-12) is similar to low-Mg dolostones (Figs. 5 and 6). It is likely therefore that recrystallization responsible in both cases for decrease of Mg/Ca ratio developed under influence of the same fluids.

In the lower member of Min'yar Formation, slightly dolomitized limestones (Mg/Ca to 0.035) contain 5-10% of siliciclastic admixture represented by quartz, illite, and chlorite. Trace elements (Mn = 130, Fe = 1500, and Sr = 215 ppm in average) are homogeneously distributed in the member (Table 1). In the Shubino Member that is terminal one in the formation section, limestones are composed of calcite except for one sample (442-6, Mg/Ca = 0.16) of mixed calcite-dolomite composition, which has been collected near the contact with underlying dolostones. The insignificant admixture of siliciclastic material (0.5 to 3%) is detected in all samples. The Mn concentration in the rocks is high (130 to 2960 ppm) in contrast to a relatively low Fe concentration (150 to 1420 ppm). Limestones of the Shubino Member contain from 230 to 477 ppm Sr, concentration of which decreases at the member top near the pre-Uk unconformity and in a sample (442-6) of dolomitized limestone collected from the basal 2-mthick strata of the member. The average Fe/Mn ratio characterizing Shubino limestones is equal to 1.2 thus being much lower than in many marine carbonates of the Riphean and Paleozoic, in which this parameter is close to 10 (Kupecz and Land, 1991; Montanez and Read, 1992a; Kuznetsov et al., 1997). According to this distinction, the Shubino Member could be deposited in a partially isolated paleobasin that experienced periodical desiccation (Gorokhov et al., 1998; Kuznetsov et al., 1999) that is consistent with presence of mud cracks in the rocks. At the same time, the mosaic recrystallization and presence of Fe-hydroxides suggest alteration of the rocks under influence of meteoric waters. The <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios in basal limestones of the Miriyar Formation are within the interval of 0.70560-0.70572 that is close to the ratio range in over-



Fig. 5. <sup>87</sup>Sr/<sup>86</sup>Sr ratios in AMA and ACA phases plotted versus Mn/Sr and Fe/Sr ratios in carbonates of the Katav-Inzer (a. b), Min'yar (c, d), and Uk (e. f) formations of the Karatau Group: (1) limestone (micrite or microsparite); (2) limestone with late calcite generations; (3) limestone with clay admixture less than 10%; (4) veined calcite; (5) dolomicrite or dolosparite; (6) dolostone with late dolosparite generations; (7) veined dolomite.

lying high-Mg dolostones (Figs. 5c and 5d). In the Shubino Member, this parameter ranges from the minimum value of 0.70600 in the middle to the maximum ratio of 0.70658 at the top.

*Uk Formation.* Stromatolitic, microphytolitic, and clastic limestones of the formation usually contain not

more than 0.5% Mg, and higher concentrations of this element (1.1 to 1.5%) are detected in some interlayers only (Table 1). Siliciclastic admixture (quartz, feld-spars, illite, and chlorite) ranging in abundance from 0.1 to 14% is mainly characteristic of carbonate members in the lower subformation (5 to 8%) and of basal

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Fig. 6. Sr concentrations (a) and isotopic parameters (b) in dolostones of the Min'yar Formation plotted versus Mg/Ca ratios in the rocks: (I) high-Mg dolostones (Mg/Ca 0.608); (2) low-Mg dolostones (Mg/Ca 0.608); (3) veined dolomite.

beds in the upper one (11 to 14%). Concentration ranges of Mn and Fe are wide. Minimum concentrations of both elements are detected in pure micrites and microsparites (Mn = 22-66 ppm, Fe = 130-470 ppm). In limestones, which are enriched in siliciclastic components or dolomitized, their concentrations are greater (80-150 and 775-1010 ppm, respectively). The maximum concentration values (Mn = 102-603 ppm, Fe = 1120-3450 ppm) are established in carbonate packages of the lower subformation, which are sandwiched between siliciclastic strata, and in basal sandy limestones of the upper subformation (Figs. 5e and 5f). The Sr concentration range of 145-715 ppm characterizes a majority of Uk limestones composed of micrite and microsparite, while lower concentrations (105 to 140 ppm) are measured in limestone varieties containing the late crystalline calcite. An exception is sample 3573 from the top interval of the Kulmas section, in which the Sr concentration is 90 ppm only, although it is composed of micrite and microsparite. Dolostone and dolomitic limestone (samples 442-24 and 442-27) crowning the Shubino section contain 1.5-9.5% Mg, 110-120 ppm Mn, and 220-1120 ppm Fe. The lowermost Sr concentration (12-53 ppm) is a distinctive feature of these rocks.

The <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios range in the Uk limestones from 0.70538 to 0.70800. The minimum values (0.70538-0.70598) are characteristic of micrite to microsparite limestones with low content of siliciclastic components, whereas maximum values are typical of rocks enriched in the latter or bearing poikilitic calcite. A positive correlation of Sr isotopic parameters with Mn/Sr and Fe/Sr ratios, on the one hand, and negative correlation between <sup>18</sup>O values and two latter ratios, on the other (Figs. 5e and 5f), are established for rocks of the last type (Podkovyrov *et al.*, 1998). This is an evidence of rock alteration under influence of meteoric fluids during the pre-Vendian break in sedimentation. The high <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.71050-0.71187) in dolomitic limestones sampled near the formation top suggest that these rocks have been recrystallized under influence of fluids enriched in radiogenic <sup>87</sup>Sr.

Source of epigenetic <sup>87</sup>Sr in the Karatau Group carbonates. Taking into consideration the Karatau Group structure, we assume that epigenetic fluids enriched in radiogenic 87Sr migrated in its carbonate horizons along zones of tectonic decompaction from basal sandy to clayey deposits of the Zilmerdak Formation and from the Katav succession of clayey-carbonate sediments at the time of their burial and diagenesis. This assumption is based on the following facts. (1) Experiencing transformation after burial of siliciclastic and clayey-carbonate deposits, clay minerals are able to deliberate considerable amounts of Mn, Fe, Rb, and radiogenic <sup>87</sup>Sr, which contaminate the associated carbonate sediments. (2) The 87Sr/86Sr ratios in the suited calcite veins decrease upward in the Katav succession, i.e., away from the Zilmerdak Formation top, and directly point to the source of fluids enriched in radiogenic <sup>87</sup>Sr. (3) The 87Sr/86Sr ratio ranges in easily soluble phases leached from clay minerals of the Zilmerdak and Inzer shales 0.7220-0.7225 and 0.7126-0.7181. correspond to respectively (Gorokhov et al., 1995; Kuznetsov et al., 2002). (4) The <sup>87</sup>Sr/<sup>86</sup>Sr ratios measured in late calcite and dolomite from veins in the Karatau Group rocks range from 0.70820 to 0.72472. (5) The 87Sr/86Sr maximum ratios have been detected in surface AMA phases of limestone (0.71292) and dolostone (0.72295) samples from the Karatavian succession. On the other hand, it is also possible that the Karatavian carbonates became additionally enriched in radiogenic 87Sr after interaction with meteoric and ground waters that leached this component from nearby siliciclastic deposits. Influence of this factor is most obvious in terminal

horizons of the Min'yar and Uk formations, especially in the last case.

## POSTSEDIMENTARY TRANSFORMATIONS IN THE KARATAU GROUP CARBONATES AND NEW DATA ON <sup>87</sup>Sr/<sup>86</sup>Sr RATIOS IN THE LATE RIPHEAN SEAWATER

The primary Mn/Sr and Fe/Sr ratios in marine carbonate sediments are low. Chemistry and isotopic composition of sediments change however at the dia- and epigenetic stages, when they interact with elision, ground, and meteoric waters, which are enriched, as compared to seawater, in Mn, Fe, and radiogenic 87Sr leached from associated siliciclastic deposits (Goldberg, 1963; Blatt et al., 1980; Kharaka and Thordsen, 1992; Stueber et al., 1993; Chaudhuri and Clauer, 1993). In addition, postsedimentary chemical transformations in carbonate sediments are controlled by values of water-rock distribution coefficients of trace elements relative to Ca. This coefficient is <1 for Sr, but >1for Mn and Fe (Pingitore, 1978; Kretz, 1982; Banner and Hanson, 1990; Vahrenkamp and Swart, 1990). As a result, carbonate sediments became enriched in Mn and Fe after low-temperature recrystallization, but partially depleted in Sr, the isotopic composition of which also changes therewith (Brand and Veizer, 1980; Yudovich et al., 1980; Gorokhov, 1996). Consequently, the absolute values of Mn/Sr and Fe/Sr ratios proper and dependences between these parameters, on the one hand, and 87Sr/86Sr ratio, on the other hand, are indicative of the secondary alteration degree in Precambrian carbonates (Veizer et al., 1983; Derry et al., 1992; Gorokhov et al., 1995; Melezhik et al., 2001; Semikhatov et al., 2002). As it is demonstrated in practice, a combination of petrographic, lithologic, and geochemical methods is the best way to elucidate secondary alterations in carbonates and to establish the threshold values of geochemical criteria, which enable selection of best preserved samples appropriate for reconstruction of seawater <sup>87</sup>Sr/<sup>86</sup>Sr in the past.

The Rb-Sr systematics of carbonate rocks from type and reference Riphean sections studied in the Urals and Siberia (Kuznetsov *et al.*, 1997; Semikhatov *et al.*, 1998, 2002) allows us to suggest the following critical parameters for selection of the least altered limestones: Mn/Sr  $\_$  0.20, Fe/Sr  $\_$  5.0, and Mg/Ca  $\_$  0.024. Although these parameters can be not universal and applicable in all possible cases of Rb-Sr system transformation in carbonates, they are the strictest among all others suggested so far in publications. In our opinion, they actually ensure a strict selection of the least altered ("best") limestones.

Many researchers who studied secular <sup>87</sup>Sr/<sup>86</sup>Sr variations on paleooceans believe that dolostones represent not reliable source of information (Derry *et al.*, 1989, 1992; Asmerom *et al.*, 1991; Kaufman *et al.*, 1993). It is proved now, however, that the early dolomitization of calcareous sediments may develop under seawater influence in shallow-water basins (Ricketts, 1983; Vahrenkamp and Swart, 1990; Land, 1992; Montanez and Read, 1992b; and others), and that these dolostones, if they are lacking signs of intense alteration, are able to retain the Sr isotope signature of sedimentation medium (Kupecz and Land, 1991; Montanez and Read, 1992a; Gorokhov *et al.*, 1995, 1998). Nevertheless, inadequate data on behavior of trace elements during lithogenesis are a serious obstacle for establishing criteria indicative of the least altered dolostones. Data obtained for carbonate rocks of the Karatau Group offer a progress in this direction.

For instance, the studied samples (441-24 and 58-1) from the Inzer Formation imply that a weak earlydiagenetic dolomitization did not change the primary Sr isotope composition in the rocks. Despite an elevated Mg content (1.1-1.4%) exceeding the range of 0.1-0.8% characteristic of other rocks from the stratigraphic interval under consideration, the 87Sr/86Sr ratios in dolomitic varieties do not differ from those in associated "pure" limestones (Table 2). In addition, dolomicrites relicts present in some early-diagenetic cherty concretions from high-Mg dolostones of the Min'yar Formation suggest that dolomitization of calcareous sediments took place immediately after their deposition, and that this process was likely under control of fluids, which were close in chemical and isotopic composition to sedimentation medium of primary carbonate material. Thus, dolostones of this origin can retain the Sr isotopic signature of seawater. It is also important that the high-Mg dolostones of the Min'yar Formation show, in distinction from low-Mg varieties, the betterpreserved sedimentary structures, a lower degree of recrystallization, and a higher Sr content. Accordingly, the above data suggest that the high-Mg dolostones, which originated in the course of the early-diagenetic dolomitization, are lacking serious secondary alterations and preserve primary geochemical characteristics. In contrast, large zonal crystals present in low-Mg dolostones of the Min'yar Formation and low Mg and Sr concentrations typical of these rocks mean that they experienced a partial dedolomitization. In other words, the chemical composition of dolostones is indicative of the preservation extent of their Rb-Sr systems. Critical values of Mg/Ca = 0.608, Mn/Sr = 1.2, and Fe/Sr = 3.0discriminate the high-Mg dolostones from low-Mg varieties (Table 1), and interaction of carbonate rocks with epigenetic fluids added, as is shown above, the radiogenic 87Sr to their composition. Consequently, dolostones with lower Mg/Ca, but higher Mn/Sr and Fe/Sr ratios can be regarded as significantly altered and inappropriate for inference of seawater Sr isotope composition. It is remarkable as well that the above value of critical Mn/Sr ratio is close to that (1.0 to 1.5) formerly accepted for the geochemical criterion discriminating the least- and stronger-altered samples of Upper Proterozoic limestones (Asmerom et al., 1991; Derry et al., 1992; Kaufman et al., 1993).

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Thus, we establish the following threshold values of geochemical criteria applicable for selection of those analyzed samples, which can retain the seawater Sr isotopic signature: Mn/Sr \_ 0.20, Fe/Sr \_ 5.0, and Mg/Ca \_ 0.024 for limestones, and Mn/Sr \_ 1.2, Fe/Sr \_ 3.0, and Mg/Ca \_ 0.608 for dolostones. Analytical results for samples satisfying these criteria are italicized in Tables 1 and 2.

Clayey limestones of the Katav Formation, which are the lowermost carbonate rocks in the Karatavian succession, show a wide range of Sr isotopic parameters and high Mn/Sr and Fe/Sr ratios far-exceeding their threshold values. Accordingly, the Rb-Sr systems of these rocks were reset in the course of postsedimentary alterations, and the corresponding analytical results (Table 2, Fig. 7) are omitted from further consideration as inappropriate for reconstruction of seawater Sr isotopic composition. In distinction, the majority of samples from the Inzer Formation (16 of 22) satisfy the accepted geochemical criteria. The 87Sr/86Sr initial ratios in these 16 samples are within the range of 0.70555-0.70566 in both studied sections. Different ranges of this parameter have been established for the "best" lower Inzer limestones from the Min'yar and Kulmas sections (0.70525-0.70538 and 0.70565-0.70580, respectively; Fig. 7). The higher ratios in rocks of the latter section seem to reflect a more intense recrystallization of corresponding limestones, which bear veins of late calcite with a high <sup>87</sup>Sr/<sup>86</sup>Sr ratio (0.70888). Formally, however, these rocks satisfying criteria ensuring their geochemical retentivity are left as legal for subsequent analysis. Epigenetic alterations are more intense in 25 studied samples from the Min'yar Formation (17 of dolostones and 8 of limestones). As a result, only four samples of high-Mg dolostones appeared to be fitting the accepted geochemical criteria. The 87Sr/86Sr initial ratios, which have been obtained for these samples and represent a series of values increasing upward from 0.70574 to 0.70611, are consistent in general with the upper limit of this parameter in seawater that has been estimated (Fig. 7) based on data for altered limestones sampled near the formation base (< 0.70560) and top (<0.70600). It is likely that the interval of 0.70574-0.70611 adequately characterizes the Sr isotopic composition in seawater of the pre-Shubino interval of the Min'yar time. Rocks of the Uk Formation, which crown the carbonate succession of the Karatau Group and have been deposited in the western limb of the Bashkirian meganticlinorium before the pre-Vendian break in sedimentation, are intensely recrystallized under influence of ground and meteoric waters. Among 15 studied samples from this formation, only three fit criteria of their geochemical retentivity. The 87Sr/86Sr initial ratios in these limestone samples range from 0.70538 to 0.70580. Thus, the Karatau Group is informative with respect to the Sr isotopic composition in seawater only for a limited time span of the Late Riphean (pre-Shubino interval). Constraints in this case are as follows: (1) basal horizons of the group are composed of the

Zilmerdak siliciclastic sediments and of the Katav clayey limestones, which are badly altered; (2) between the Min'yar and Uk Formations there is a hiatus presumably spanning a considerable stratigraphic interval; and (3) the Uk Formation is separated from Vendian basal strata by the terrigenous Krivaya Luka Formation and subsequent hiatus.

#### <sup>87</sup>Sr/<sup>86</sup>Sr RATIO VARIATIONS IN THE LATE RIPHEAN OCEAN AND GEODYNAMIC BACKGROUND

The Lakhanda Group of the Uchur-Maya region and its analogues in the Turukhansk area, which have been deposited in the early Karatavian time (Gorokhov et al., 1995; Semikhatov et al., 1998, 2002), represent, together with the Uralian Inzer, Min'yar, and Uk formations spanning a considerable interval of the Late Karatavian time (Gorokhov et al., 1996; Kuznetsov et al., 1997; Kuznetsov, 1997, and this work), the key subdivisions that enable reconstruction of 87Sr/86Sr secular variations in the Late Riphean seawater. The prime importance of these subdivisions is defined by the fact that they represent predominantly carbonate successions, which have been only slightly altered at the epigenetic stage. In addition, they are rather well calibrated in terms of chronometry, have been studied using a uniform procedure that included the two-stage chemical treatment of samples, which satisfy strict criteria of their geochemical retentivity. Unfortunately, the necessary data have been obtained so far only for three discrete time spans of the Late Riphean (1030-1000, 850-770, and 690-640 Ma) characterizing in sum about 37% of the latter. The Sr isotopic characterization of intervals between these time spans are based either on data published for carbonates from other regions, or partially on interpolation.

The Late Riphean history of seawater 87Sr/86Sr variations followed that of the Middle Riphean, when fluctuations of this parameter were fairly quiet (see Semikhatov et al., 2002, for review and references). According to available data, the seawater 87Sr/86Sr ratio in the early Middle Riphean, 1280-1270 Ma ago, was comparable with that of the Early Riphean time and did not exceed 0.7046-0.7047. Later on, this ratio increased up to 0.7049 1260 Ma ago and then.up to 0.7052-0.7056 1200 Ma ago. That increase was a response to events of the Elsevirian accretionary orogeny, which was of a subglobal significance and commenced about 1300-1250 Ma ago (McLelland et al., 1996; Rivers, 1997; Rivers and Corrigan, 2000). The seawater Sr isotope composition in the period of 1200-1050 Ma is not established yet, although the Shawinigan (1190-1140 Ma) and Ottawan (1080-1020 Ma) collisional impulses of that period (Rivers and Corrigan, 2000; Carr et al., 2000) suggest a further increase of 87Sr/86Sr ratio in the ocean. The Middle Riphean maximum of this ratio (0.70592) is recorded in the Malgina Formation of the Uchur-Maya region (1050-1040 Ma ago,



Fig. 7.  $\frac{87}{87}$ Sr  $\frac{86}{85}$ Sr variations in carbonates of the Karatau Group: (1) limestones satisfying the accepted geochemical criteria (Mn/Sr 0.2. Fe/Sr 5.0. Mg/Ca 0.024); (2) limestones satisfying the accepted geochemical criteria but containing late calcite generation; (3) limestones non-satisfying the accepted geochemical criteria; (4) veined calcite; (5) dolostones satisfying the accepted geochemical criteria; (7) veined dolomite. Horizontal dotted lines denote sampling levels of veined calcite with indicated  $\frac{87}{5}$ Sr/ $\frac{86}{5}$ Sr ratios outside the scale limit; (K) Kulmas, (M) Min'yar, (SH) Shubino sections; other abbreviations and symbols as in Fig. 2.

Semikhatov *et al.*, 2002). By the end of the Middle Riphean (1030 Ma ago), the ratio somewhat decreased down to 0.70567-0.70585 (Sukhaya Tunguska Forma-

tion of the Turukhansk region, Gorokhov *et al.*, 1995). Afterward, at the very beginning of the Late Riphean (1030-1000 Ma), this tendency continued, as it is evi-

dent from data on carbonates from the Lakhanda Group of the Uchur-Maya region and its Turukhansk analogues (Gorokhov et al., 1995; Semikhatov et al., 1998, 2002; Bartley et al., 2001). In the "best" samples from above subdivisions, the 87Sr/86Sr ratio ranges from 0.70519 to 0.70569, decreasing in general to 0.70523-0.70527 in sediments deposited about 1000 Ma ago. It is also remarkable that transition from the ascending Middle Riphean trend to the descending one of the Early Karatavian time took place at the time of the Ottawan (1080-1020 Ma) and Rigolet (1000-980 Ma) collision events of the Grenville orogeny, which resulted in a global-scale collision and in the emergence of the Rodinia supercontinent (Rivers, 1997; Carr et al., 2000; Ketchum and Davidson, 2000; Martignole et al., 2000).

Explanation to the paradoxical seawater 87Sr/86Sr ratio decrease at the time of the Grenville orogeny termination and initial erosion of orogens created by that time was found after analysis of corresponding data of geodynamics, geochemistry, and isotopic geochronology (Semikhatov et al., 2002). Factors responsible for the paradox are as follows. (1) pre-Grenvillian mantle rocks were apparently widespread in the Grenville orogenic structures (Restrepo-Pace et al., 1997; Wareham et al., 1998; Geraldes et al., 2000; Van Schmus, 2000; Dickin, 2000; Carr et al., 2000). (2) A considerable mantle Sr flux into the World Ocean is admissible in connection with the opening and evolution of the Paleo-Asian ocean and its branches at the early Late Riphean time (V. Khain et al., 1997; Khain et al., 1999, 2002, 2003; Khomentovskii and Postnikov, 2001; Khudoley et al., 2001; Fedotova and Khain, 2002) and with concurrent development of the Gaios Ocean within the future Gondwana (1200-800 Ma, Strieder and Suita, 1999) and global Monrovia Ocean around Rodinia (Weil et al., 1998). A high juvenile Sr influx into seawater is inferable also from the Sm-Nd systematics of the Middle-Upper Riphean boundary deposits (Li and McCulloch, 1996; Podkovyrov et al., 2002) and from  $\mu_1 = {}^{238}U/{}^{204}Pb$  calculated for the concurrent carbonate sediments based on the one-stage model of Pb isotope evolution (Ovchinnikova et al., 2002). (3) Peak events of metamorphism are asynchronous in diverse Grenville structures (Andersson et al., 1999; Bruguier et al., 1999; Carr et al., 2000; Martignole et al., 2000) and, what is most important, the erosion rate of the latter was low and not constant. Besides the short-term post-metamorphic peaks, that rate was more than one order of magnitude lower than the upwarping rate in Alps and Himalayas during the last 40 Ma (Cosca et al., 1998; Ketchum and Davidson, 2000; Martignole et al., 2000; Rivers and Corrigan, 2000), when the 87Sr/86Sr ratio sharply increased in the Late Tertiary oceans mainly under influence of this leading factor. (4) In addition to peneplanation of tectonic relief in the eastern Laurentia about 980-920 Ma ago (Cosca et al., 1992; Carr et al., 2000), a vast transgression of the early Karatavian time (Semikhatov and Raaben, 1994, 1996) enlarged the carbonate platform areas favorable for expansion of benthic cyanobacterial ecosystems and thus reduced the continental runoff. (5) As is commonly accepted, phases of an abrupt sea-level rise are interrelated with activation of sea-floor spreading, and contribution of the latter to seawater Sr isotopic parameters could be also perceptible. The development of intense crustal magmatism ( $_{Nd}(t)$  from -2.4 to -11±2) in the West Congolese belt 1000-920 Ma ago (Tack et al., 2001) or collisional events 880-860 Ma ago in the Yenisei Ridge, intrusions of crustal granitoids in Alaska and Taimyr, where they are 950 to 800 Ma old (Vernikovsky and Vernikovskaya, 2001; Vernikovsky et al., 2002; Vernikovskaya et al., 2002), and incipient subduction that developed in the Goianides Ocean 900-850 Ma ago (Brito Nevis et al., 1999) were unable to compensate the effect of factors listed above.

A segment of seawater <sup>87</sup>Sr/86Sr variation curve that corresponds to the Lakhanda Group time span is the best substantiated one for the Proterozoic (Semikhatov et al., 1998, 2002; Bartley, 2001). For the subsequent period of about 150 Ma long, there are only fragmentary data on the Sr isotopic record. First, these are the <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios 0.70570-0.70622 established for altered dolostones of the Shorikha and Turukhansk formations in the terminal part of the Riphean succession of the Turukhansk region and ranging in age approximately from 950 to 900 Ma (Gorokhov et al., 1995). Next, there are Sr isotopic data on limestones and dolostones from members  $I_4$  to  $I_{10}$  of the Atar Group in western Africa (Veizer et al., 1983). Carbonates from these members were intensely recrystallized at the stages of their burial and meteoric diagenesis (Fairchild et al., 1990), as it follows from their highly variable and elevated Mn/Sr, Fe/Sr, and 87Sr/86Sr ratios. The only sample from the base of Member  $I_6$  is acceptable for determination of that ratio upper limit in seawater according to minimal values of Mn/Sr = 0.43 and Fe/Sr = 3.3 measured in it. The Rb-Sr dates obtained for the clay fraction < 2 pm from members  $I_6$  and  $I_5$  are 874  $\pm$  23 and 890 ± 37 Ma, respectively (Clauer, 1981). These age determinations are approximate, however, because the studied fractions contain non-cogenetic illite generations (Gorokhov et al., 1994, 2001). In this work, the age of 870 Ma consistent with data on stromatolites from a lower part of the Atar Group (Bertrand-Sarfati, 1972; Knoll and Semikhatov, 1998) is conventionally adopted for Member I<sub>6</sub>. Using this value in calculations, we obtain the 87Sr/86Sr initial ratio of 0.70558 to characterize limestones of Member I<sub>6</sub>.

Data on the Inzer Formation of the southern Urals and Bitter Springs Formation of central Australia (Figs. 8 and 9) define termination of the gap in the Sr isotopic record under consideration. The <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios calculated for the "best" limestones from the lower part of the lower Inzer Subformation (850-840 Ma) range from 0.70525 to 0.70534. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios measured in the whole-rock samples of dolostones and sulfates from lower member of the Bitter Springs Formation correspond to 0.70592-0.70611 and 0.70569-0.70610, respectively, and quickly grow upward reflecting either the basin isolation, or epigenetic alteration of samples under influence of meteoric waters (Hill and Walter, 2000; Walter et al., 2000). The Bitter Springs Formation is defined to be 840-830 Ma old based on U-Pb zircon dates (827  $\pm$  6 and 849  $\pm$  9 Ma) for basic dikes comagmatic with volcanic rocks of the formation (Zhao et al., 1994; Wingate et al., 1998; Hill and Walter, 2000). As the values under discussion are obtained for different materials (ACA phases of "best" limestones in one case and whole-rock samples of dolostones and sulfates in the other), we may speak only about their general similarity, bearing in mind that data from the Urals define the 87Sr/86Sr ratio in the Inzer Ocean, whereas data from Australia determine only the upper limit of that ratio in seawater. Materials considered above imply that the 87Sr/86Sr ratios in seawater of the terminal Lakhanda (1000 Ma) and initial Inzer (850 Ma) times were almost identical (0.70523-0.70527 and 0.70525-0.70534), whereas 950-900 to 870 Ma ago they were below the values of 0.70622 and 0.70558, respectively.

insignificantly changeable Persistently low, 87Sr/86Sr ratios in seawater of the early Karatavian time were likely controlled by a high mantle Sr influx into the World Ocean that prevailed over the continental influx almost throughout 200 m.y. Facts in favor of this inference are as follows. (1) Widespread eruptions of plateau basalts with 87Sr/86Sr ratios from 0.7043 to 0.7050 were characteristic of the West Congolese belt 1000-920 Ma ago (Tack et al., 2001). (2) Eruptions of basalts with positive Nd(t) values were related to the first stage of the Adamastor-Brasilide Ocean opening between 950 and 800 Ma ago (Dalziel, 1997; Pedrosa-Soares et al., 2001). (3) Evolution of the Gaios (Strieder and Suita, 1999) and Paleo-Asian oceans (Kovalenko et al., 1999; Khain et al., 2002, 2003; Fedotova and Khain, 2002) was in progress at that time. (4) An island-arc system and ophiolites with low <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios (0.7022-0.7030) and positive  $N_{Nd}(t)$  values appeared at the site of the future Nubian Shield 890-800 Ma ago (Reischmann, 2000). (5) The Goianides Ocean opened 900-850 Ma ago in South America (Brito Nevis et al., 1999) concurrently with origination of ophiolites in Mauritania and Anti-Atlas. (6) An intense rifting and/or intrusion of basaltic dike swarms 890 to 820 Ma old were typical of many large regions (Wingate et al., 1998; Li et al., 1999; Karlstrom et al., 2000; Yarmolyuk and Kovalenko, 2001; Pedrosa-Soares et al., 2001; Sklyarov et al., 2001). (7) Passive margins of the Siberian craton experienced transformation that was followed 850-800 Ma ago by development of extended island arcs along periphery of the Paleo-Asian Ocean (Khain et al., 2003; Fedotova and Khain, 2002). (8) Ophiolite belts of the Central Asian foldbelt originated 800 Ma ago (Kovalenko et al., 1999; Khain et al., 2003). (9) Volcanic island arcs emerged in the Paleo-Asian Ocean at the beginning of the Late

Riphean (Kovalenko *et al.*, 1999; Fedotova and Khain, 2002; Khain *et al.*, 2003). (10) An extensive transgression of the early Karatavian time decelerated erosion of Grenville orogens and reduced influx of continental material into the World Ocean. All these facts evidence not a short-term "mantle event at 900 Ma ago" (Veizer *et al.*, 1983) but a series of large-scale events of the early Karatavian time, which favored influx of low-radiogenic Sr into the ocean (Figs. 8 and 9). Regional accretionary-collisional events and intrusions of post-collisional granitoids (880 to 870 Ma old) (Nozhkin *et al.*, 1999; Vemikovskaya *et al.*, 2002) along the Siberian craton western edge were unable to affect the global situation.

Returning to analysis of data from the Urals, we would like to stress that the Sr isotopic parameters of carbonates from the Inzer and Min'yar formations point to an important change in the character of seawater Sr-isotope variations about 830 Ma ago. The former "quiet," maybe nearly horizontal segment of the variation curve changed into its ascending branch, the origin of which corresponds to boundary horizons between the lower and upper Inzer subformations and termination is at the Shubino Member base. During the corresponding time span (830-775 Ma), the seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratio rose from 0.70555 to 0.70611, and then, at the Shubino time (ca. 770 Ma), it dropped again below 0.70600 (Fig. 9).

Reconstruction of seawater Sr-isotope variations within the subsequent time spans of the Late Riphean is complicated by an ambiguous interpretation of age relationships between three main sources of relevant information—the Shaler Group of Arctic Canada, Akademikerbreen Group of Spitsbergen, and Karatau Group of the southern Urals (Melezhik *et al.*, 2001).

The Shaler Group includes the Glenelg Formation (1400 m) of carbonate-siliciclastic composition and the Reynolds Point (760 m), Minto Inlet (210 m), Wanniatt (590 m), and Kilian (550 m) formations of predominantly carbonate composition. Deposits of the group discordantly overlie basic volcanics bearing baddeleyite that yielded the U-Pb age value of  $1267 \pm 2$  Ma, whereas baddeleyite from dikes crosscutting the group is 723±3 Ma old (Heaman et al., 1990; Rainbird et al., 1994). To precise the maximum age limit, a lower part of the Shaler Group was correlated first with the Ray Group of Arctic Canada, where the U-Pb age of 1080 Ma was obtained for clastic zircons, and next, taking into account palinspastic reconstructions, with an upper part of the Kollanna Group in Australia, where the U-Pb age of a tuff horizon is defined to be 802  $\pm$ 10 Ma (Rainbird et al., 1994). Data of C-isotope chemostratigraphy seem to be more informative in this respect. They show that <sup>13</sup>C values from +3 to +5‰ PDB, which are typical of the Reynolds Point Formation, are followed by higher values of +6 to +8‰ PDB of the overlying Minto Inlet and Wanniatt formations (Asmerom et al., 1991; Kaufman and Knoll, 1995).

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Fig. 8. Sr-chemostratigraphy and age characterization of key sections of the upper Upper Riphean and Lower Vendian. Lithology: (1) limestone; (2) stromatolitic limestone; (3) clayey limestone; (4) dolostone; (5) stromatolitic dolostone; (6) dolostone with cherty concretions; (7) sulfates (evaporites); (8) tillites; (9) sandy-clayey deposits; (10) sandstone; (11) sandstone with gravelstone interlayers; (12) stratigraphic unconformity; (13) isotopic age (see explanations in the text). Samples in terms of geochemical criteria accepted in this work: (14,15) limestones satisfying (14) and non-satisfying (15) the criteria; (16,17) dolostones satisfying (16) and non-satisfying (17) the criteria; (18) sulfates. Abbreviations: (Baklund.) Baklundtoppen; (Gil.) Gillen; (Dr.) Draken; (Zilm.) Zilmerdak; (Inz.) Inzer; (Kt.) Katav; (M) Minto Inlet; (Min.) Min'yar; (Polar.) Polarisbreen; (Svanb.) Svanbergfjellet; (H.) Heavitree; (Elb.) Elbobreen.

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Fig. 9. Standard curve of <sup>87</sup>Sr/<sup>86</sup>Sr in the Late Riphean seawater: (1) Kerpyl and Lakhanda groups and their analogues in the Turukhansk region (Gorokhov *et al.*, 1995; Semikhatov *et al.*, 1998, 2002; Bartley *et al.*, 2001); (2) Shorikha and Turukhansk formations of the Turukhansk region (Gorokhov *et al.*, 1995; Bartley *et al.*, 2001); (3) Membar of the Atar Group (Veizer *et al.*, 1983); (4) Inzer Formation of the Karatau group (this work; Kuznetsov *et al.*, 1997); (5) Bitter Springs Formation (Walter *et al.*, 2000; Hill and Walter, 2000); (6) Min'yar Formation of the Karatau Group (this work); (7) Shaler Group (Asmerom *et al.*, 1991); (8) Akademikerbreen Group (Derry *et al.*, 1989, 1992); (9) Uk Formation (this work); (10) Polarisbreen Group (Kaufman *et al.*, 1993); (11) Nama and Vitvley groups (Kaufman *et al.*, 1993); symbols as in Fig. 8.

When evaluated in the global context (Jacobsen and Kaufman, 1999; Kah *et al.*, 1999; Bartley *et al.*, 2001), these values suggest that the Reynolds Point Formation is younger than 850-800 Ma. On the other hand, carbonates of the Min'yar Formation yield <sup>13</sup>C values mostly ranging from -2.2 to +2.7‰ PDB (Podkovyrov *et al.*, 1998), though its terminal horizons correspond to an ascending trend of this parameter with a maximum value of +5.9‰ PDB at the top of the Shubino Member. This trend seems to be implying that carbonate sediments of the Reynolds Point, Minto Inlet, and Wanniatt formations were deposited in the post-Min'yar time 770-730 Ma ago. It is reasonable to remind therewith that deposits of this age are unknown in the southern Urals.

<sup>87</sup>Sr/<sup>86</sup>Sr 0.709 г

0.708

Data on the Sr isotope composition in the Shaler Group are known for 17 limestone and dolostone samples from three middle formations of this subdivision (Fig. 8). The Mn/Sr and <sup>87</sup>Sr/<sup>86</sup>Sr ratios widely range in these samples from 0.12 to 9.3 and from 0.70561 to 0.70876, respectively (Asmerom et al., 1991). Only two limestone samples from the Wanniatt Formation satisfy criteria of geochemical retentivity accepted in this work. The 87Sr/86Sr initial ratios calculated for the bulk carbonate material of this samples are equal to 0.70575 and 0.70674. However, a minimum value of this ratio (0.70561) is established for an altered limestone sample (Mn/Sr = 0.67) from the lower part of the Minto Inlet Formation (Fig. 8). If, despite the altered status of the rock, the last value reflects nevertheless the Sr isotope composition in sedimentation medium, then we may compare this and above values with data on

carbonates from the Min'yar Formation, which immediately predate the indicated carbonates of the Shaler Group. Such a comparison shows that the seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios decreased gradually from 0.70600 to 0.70561 since the end of the Min'yar time during the subsequent 10-15 m.y., and afterward, at the deposition time of the upper Wanniatt Formation, they became growing again and attained the level of 0.70674 at about 730 Ma ago (Fig. 9).

The next interval of the standard curve of seawater 87Sr/86Sr variations can be elucidated based on data for the Akademikerbreen Group of Spitsbergen (Derry et al., 1989, 1992). The successive Grusdievbreen (650 m), Svanbergfjellet (500 m), Draken (250 m), and Baklundtoppen (500 m) carbonate formations of the group conformably rest on the terrigenous Veteranen Group, and, according to recent data (Fairchild and Hambrey, 1995; Kaufman et al., 1993, 1997; Harland, 1997), their eroded top is overlain with a hiatus by the Polarisbreen Group. Near the base of the latter, there are tillites of the Varangerian Glaciohorizon that is 600-590 Ma old in opinion of many researchers (Knoll and Walter, 1992; Knoll, 2000; Semikhatov, 2000, and references therein). To our regret, isotopic dates for rocks of the Akademikerbreen Group have not been obtained. In the 1970s, the group was correlated, based on microphytoliths and stromatolites, with the Riphean stratotype of the Urals (Raaben and Zabrodin, 1972; Raaben, 1975), but the results obtained need to be verified. As is established (Semikhatov, 1974; Khomentovskii, 1976; Yakshin, 1985), stratigraphic significance of microphytoliths used for correlation is negligi-

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ble, and stromatolites of the group are represented mainly by endemics and taxa identified in an open nomenclature. In the 1980s, some horizons of the group were dated based on silicified microfossils, but these results need in a verification as well. Thus, the location of the Akademikerbreen Group in stratigraphic scale strongly depends on chemostratigraphy.

Postsedimentary alterations in carbonate rocks of the Akademikerbreen Group are insignificant (Derry et al., 1989, 1992). Among 12 limestone and 5 dolostone samples, which have been studied, 8 limestone samples are satisfying our criteria of geochemical retentivity. The 87Sr/86Sr initial ratios range in these limestone samples mostly from 0.70646 to 0.70686 and decrease down to 0.70620 in the lower part of the Svanbergfjellet Formation only (Fig. 8). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.70646-0.70677) and <sup>13</sup>C values (+5.9‰ PDB) in middle carbonate strata of the Grusdievbreen Formation are practically identical to these parameters (0.70662-0.70674 and +5.0 to +6.0% PDB) characterizing a terminal part of the Wanniatt Formation of the Shaler Group (Derry et al., 1989; Asmerom et al., 1991). This concordance chemostratigraphic characteristics between suggests that the above formations are correlative, and that the middle Grusdievbreen strata were deposited about 730 Ma ago immediately after accumulation of the Wanniatt Formation. The exact isotopic age of terminal horizons of the Akademikerbreen Group is unknown. This group is separated from the basal carbonate Member E1 of the Polarisbreen Group by a hiatus, the time span of which is unknown (Fairchild and Hambrey, 1995; Harland, 1997). Chemostratigraphic data on the Karatau Group suggest that accumulation of the Akademikerbreen Group terminated ca. 690 Ma ago, at the time of initial deposition of the Uralian Uk Formation. Actually, carbonates of the Baklundtoppen Formation crowning the Akademikerbreen Group are characterized by <sup>87</sup>Sr/<sup>86</sup>Sr initial ratios of 0.70662 to 0.70686 and by <sup>13</sup>C values of +4.2 to +8.4‰ PDB, whereas these parameters in the lower Uk carbonates deposited 690-660 Ma ago are much lower: 0.70582 to 0.70595 and + 1.4 to +2.6‰ PDB, respectively. In the upper Uk carbonates with the age range of 660-640 Ma, the same parameters decrease further and are within the intervals of values from 0.70538 to 0.70580 (Fig. 9, Table 2) and from +0.7 to +2.5‰ PDB (Podkovyrov et al., 1998).

Consequently, the Uk Formation and upper horizons of the Akademikerbreen Group cannot be regarded as age equivalents because of a considerable distinction between their Sr- and C-isotope parameters. On the other hand, the former also differs in these parameters from the carbonates of Member E1 at the base of the Polarisbreen Group, characteristic of which are the  $^{87}Sr/^{86}Sr$  initial ratios equal to 0.70661-0.70683 and predominantly high (+5  $\pm$  1‰) <sup>13</sup>C values (Knoll *et al.*, 1986; Kaufman *et al.*, 1993; Fairchild and Spiro, 1987). The negative <sup>13</sup>C values have not been established in Member E1 underlying the lower tillites of the Varangerian Glaciohorizon of Spitsbergen, but they are

typical of Member 19 below the same tillites of Greenland, and this discrepancy has been regarded as evidence in favor of a hiatus below tillites of Spitsbergen (Fairchild and Hambrey, 1995; p. 223). It is likely therefore that sediments of the Uk Formation were deposited in the period of that hiatus between the Akademikerbreen and Polarisbreen groups, which was presumable as long as 60-70 m.y. Nevertheless, it is impossible to suggest a confident Sr-isotopic characterization of corresponding time span, because the lower Uk interval is predominantly composed of siliciclastic deposits intercalated with carbonates, which have been significantly altered at the epigenetic stage (Fig. 7). The corresponding time span that was presumably as long as 30 m.y. separates the "best" upper carbonates of the Akademikerbreen Group from those of the upper Uk Subformation.

Turning now to consideration of geodynamic and other factors, which controlled the 87Sr/86Sr ratio variations in seawater of the Late Karatavian time, we should remind that a distinct ascending trend of that ratio is recorded in "best" carbonates samples from the upper Inzer and Min'yar strata deposited 830-775 Ma ago. It is logical to assume that this trend is interrelated with a series of accretionary and collisional events of that time. These events and associated granitoid magmatism are detectable in many regions. A collision of microcontinent with island arcs or continent happened about 850-800 Ma ago in the northwestern Alaska-Taimyr region (Vernikovsky and Vernikovskaya, 2001). The Tarim massif basement originated 829  $\pm$  60 Ma ago in connection with a collision between two microcontinents (Guo et al., 2001). In the Tuva-Mongolia belt, continental blocks collided 800 Ma ago either with each other and/or with the Siberian craton margin, and these events were accompanied by development of an island-arc system in oceanic peripheral zone (Salnikova et al., 2001; Sklyarov et al., 2001; Fedotova and Khain, 2002). Events of collision, accretion, and local subduction 830-800 Ma ago characterize an important stage in evolution of the Paleo-Asian Ocean (Khain et al., 2002, 2003). Syntectonic granitoids of the BaikaI-Muya fold belt originated 800 Ma ago in connection with a powerful collision that terminated the Early Baikalian tectogenesis in the southeast of Siberia (Rytsk et al., 2001). In the Baikal-Vitim branch of that ocean, a microcontinent subducted under Siberian craton and island arc fragments became docked with a (micro)continent 850 Ma ago (Khomentovskii and Postnikov, 2001), while in South America the Gaios Ocean closure is dated back to 800 Ma (Strieder and Suita, 1999). The mantle flux of low-radiogenic Sr, intrusions of mafic dikes with a mantle isotopic signature, and expansion of carbonate platforms along passive continental margins counterbalanced the continual growth of seawater <sup>87</sup>Sr/86Sr ratio in the period from 830 to 770 Ma. Nevertheless, the net Sr influx into the World Ocean was enriched in radiogenic isotope at that time.

In response to global geodynamic changes around 770 Ma ago, the ascending trend of seawater 87Sr/86Sr ratio turned for a short but significant period (from ca. 775 to 740 Ma) into the descending one. The latter is recorded in rocks of the Shubino Member (less than 0.70600) and in lower horizons of the Shaler Group, in which the ratio decreases from 0.70611 down to 0.70561-0.70575. A subglobal extension that commenced at that time (Powell et al., 1993; Hoffman, 1991; Karlstrom et al., 2000; Prave, 1999; Brito Nevis et al., 1999) triggered a series of the following important events. (1) East Gondwana (Australia, India and Antarctic) split off from Laurentia 750 Ma ago, and this resulted in emergence of the Paleo-Pacific Ocean and in a later (700-720 Ma ago) intense rifting in South America (Powell et al., 1993; Colporn et al., 2002; Brito Nevis et al, 1999). (2) In the western (present-day coordinates) margin of Laurentia, a high-scale development of extended rift structures up to 2500 km long was associated 760-720 (or 780-720) Ma ago with activation of basaltic magmatism that was very intense in places and with emergence of basins floored by oceanic crust (Ross, 1995; Hoffman, 1991; Colporn et al., 2002). (3) Volcanic island arcs and ophiolites appeared in the future Arabia-Nubian Shield, East Egyptian desert, and Taimyr correspondingly 770-736, about 780, and 750-720 Ma ago (Reischmann, 2000; Loizenbauer et al., 2001; Vernikovsky and Vernikovskaya, 2001; Vernikovsky et al, 2002). (4) A volcanic arc of the Andean type (750  $\pm$  2.5 Ma old) emerged along the eastern margin of Gondwana (Torsvik et al., 2001). (5) Partition of East Gondwana, South China continental block, and Laurentia took place at about 700 Ma ago (Li et al., 1996). (6) Rifting and associated intrusions of basic dikes and sills were characteristic 770-720 Ma ago of the South China platform, Tuva, South Africa, and North Canada (Heaman et al., 1990; Hoffman et al., 1996; Li et al., 1999; Yarmolyuk and Kovalenko, 2001). It should be mentioned that Asmerom et al. (1991) who rightfully connected the Shaler event with an intense development of juvenile crust and largescale oceanic rifting attributed all phenomena to the period of 840-810 Ma ago. According to recent results (Karlstrom et al, 2000), these events took place later, however, within the time span of 762-723 Ma. Concurrent events of opposite significance can be exemplified by collision and post-collisional granitoids of the Yenisei Ridge, which are 750-720 Ma old, by the microcontinent-island arc collision 740 Ma ago in the north of the Mozambique belt, and by the intra-plate granitoids of eastern Egypt, which are 780 Ma old (Reischmann, 2000; Loizenbauer et al., 2001; Vernikovsky et al., 2002; Vernikovskaya et al., 2002). Contribution of these events to the total substance balance in World Ocean likely was negligible.

Somewhat higher seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios (0.70646-0.70686) characterize the next period of the Late Riphean history (from 740 to 690 Ma), i.e., the accumulation period of upper horizons in the Wanniatt

Formation of the Shaler Group and of a greater portion of the Akademikerbreen Group (boundary horizons of the Grusdievbreen and Svanbergfjelet formations excluded). These elevated ratios are in a harmony with the following geodynamic events of that time. In the indicated period, or more precisely between 736 and 715 Ma, oceanic basins of the future Arabia-Nubian Shield closed, and, after convergence of India and East Africa 740-720 Ma ago, first the Mozambique and then the Farusian oceans disappeared (Reischmann, 2000; Torsvik et al., 2001; Brito Nevis et al., 1999). In the Paleo-Asian Ocean, it was a time of disappearance of large island arcs and back-arc basins and of a concurrent (735-715 Ma) intensification of supra-subduction magmatism (Sklyarov et al., 2001; Fedotova and Khain, 2002; Khain et al., 2003). In some regions, these led to intrusion of crustal granites and to replacement of basaltic volcanism by calc-alkaline magma eruptions (Kovalenko et al., 1999; Reischmann, 2000; Loizenbauer et al., 2001; Kuzmichev, 2001; Fedotova and Khain, 2002). In particular, extended ensialic island arcs with abundant eruptions of andesitic, dacitic, and rhyolitic magmas originated along the periphery of Prileo-Asian Ocean 730-700 Ma ago (Kuzmichev et al., 2001; Khain et al., 2003). Less significant events of the same type are exemplified by accretion of island arcs around continental blocks in the Urals-Mongolian belt and by a microcontinent collision with the Siberian craton 760-720 Ma ago, or by post-collisional intrusions of crustal granites in the Yenisei Ridge, which are 730 to 718 Ma old according to results of U-Pb dating (Vernikovsky et al, 2002; Vernikovskaya et al, 2002; Sklyarov et al., 2001; Khain et al., 2003).

The paleoclimatic factor could be also responsible for the seawater 87Sr/86Sr ratio growth during the Late Karatavian time. According to paleomagnetic data, the Rodinia fragments migrated across a set of latitudes during the Late Karatavian time. That migration must control the annual precipitation and intensity of weathering and erosion in continental provenances, in other words, the continental runoff value. A tight interrelation between the seawater 87Sr/86Sr ratios and climate humidity is convincingly demonstrated for the Late Permian and Triassic (Korte et al., 2003). To our regret, the idea of an increased continental runoff during the Late Karatavian time is inconsistent with data implying that abundance of carbonate stromatolitic formations was at that time twice greater than in the Early Karatavian time (Raaben and Semikhatov, unpublished data). It is logical to think that these data suggest a lateral expansion of carbonate sedimentation and concurrent reduction of settings with siliciclastic deposits. Unfortunately, the comparative data on corresponding terrigenous formations are unknown.

It is more difficult to explain a negative excursion of <sup>87</sup>Sr/<sup>86</sup>Sr ratios from 0.70646 to 0.70620 that is established based on three samples from boundary horizons of the Grusdievbreen and Svanbergfjelet formations and happened, as inferred above, about 720-710 Ma

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ago (Figs. 8 and 9). If the inferred age is correct, the excursion is concurrent to the Sturtian glaciation that must unavoidably result in a large glacioeustatic sealevel drop (as large as 100 m according to assessment of N.M. Chumakov). An immediate consequence would be intensification of continental runoff and a considerable growth rather than decline of seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios.

If the situation under discussion is not an artefact, one may assume, to explain it, that the mantle flux of low-radiogenic Sr was extraordinary high 720-700 Ma ago owing to global extension events, and that exactly these events controlled the Sr isotopic balance in the World Ocean during 20 m.y. However, the evaluated intensity of events implies that such an assumption is highly improbable. In order to solve the posed problem, it is necessary to specify age relationships between that excursion and Sturtian glaciation, to seek for marks of glacioeustatic sea-level drop in the Akademikerbreen Group succession, and to elucidate stratigraphic relations between these marks and <sup>87</sup>Sr/86Sr ratios in "best" carbonates of the group. Work of Fairchild and Hambrey (1995) devoted to the overlying Polarisbreen Group and Varangerian glaciation is a good example of such an analysis.

The terminal segment of the proposed standard curve of 87Sr/86Sr ratio variations in the Late Riphean ocean is mainly based on data obtained for the Uk Formation of southern Urals. This segment characterizes a quick decline of that ratio within the time span of 690-640 Ma from the range of 0.70662-0.70682 established for upper horizons of the Baklundtoppen Formation to values ranging from 0.70585 to 0.70592 in altered limestones of the lower Uk Subformation and from 0.70538 to 0.70580 in "best" limestones of the upper one. Such a considerable drop of <sup>87</sup>Sr/<sup>86</sup>Sr ratios reflects a regime of tectonic extension in many regions, the concurrent development of new island arcs, and an intense magmatic activity, that of the mantle origin included. In such geodynamic circumstances, the Baltia split off from Laurentia about 650-630 Ma ago. This event was initiated by rifting and intrusions of tholeiitic dike swarms of mantle origin first in the western margin of Scandinavia and somewhat later in Labrador and Appalachians (Hoffman, 1991) and terminated 620-605 Ma ago with the opening of the future Iapetus Ocean (Torsvik et al., 1996; Svenningsen et al., 2001): In the Paleo-Asian Ocean, it was a formation time of extended volcanic arcs: a vast belt of extension and associated pyroxene-gabbro intrusions 630 to 620 Ma old, which yield Nd(t) mantle values (Fedotova and Khain, 2002), are situated now in the Transbaikal region; corresponding island-arc complexes  $637 \pm 5$  Ma old and somewhat older (697  $\pm$  4 Ma) granitoids with a mantle Sm-Nd signature and 87Sr/86Sr ratio of 0.70385 are established in the Yenisei ophiolite belt (Vernikovsky et al., 2001). In the Nubian Shield, acid volcanic eruptions took place 670-618 Ma ago (Reischmann, 2000). Island arcs of the Tocantins belt in South America originated 640 Ma

ago, partially after reworking of older continental and oceanic crust (Brito Nevis *et al.*, 1999). The Cadomian island arc that is extraordinary long (from New Scotland and Avalon to the Polar and, maybe. Central Urals) also originated within the time span under consideration, as it is evident from dates ranging around 675 Ma and characterizing basic magmatism and ophiolites of this structure (Scarrow *et al.*, 2001).

mentioned and analogous events in other The regions controlled the seawater 87Sr/86Sr ratio decrease. At the same time 660-640 Ma ago, some regional events acted in opposite direction. For instance, a gradual convergence of Gondwanan fragments and their collision 664 ± 20 Ma ago gave rise to the syncollisional calc-alkaline magmatism in the East Egyptian desert (Loizenbauer et al., 2001). It was also a time of active collision in the Baikal-Vilyui branch of the Paleo-Asian Ocean (Khomentovskii and Postnikov, 2001). As is established in the Tocantins province (Pedrosa-Soares et al., 2001), a series of terranes and island arcs became docked somewhat later, 630-620 Ma ago, with a continental massif just formed in the Adamastor Ocean that closed 600-570 Ma ago.

These and other large-scale events were a preamble of the global Panafrican orogeny that gave rise to the sharp unprecedented rise of <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the Vendian and Early Cambrian seawater (Kaufman *et al.*, 1993). This rise is however out of the scope of this paper.

#### CONCLUSIONS

(1) Carbonate sediments of Karatau Group have been insignificantly altered after deposition, especially in northwestern sections (town of Min'yar and Shubino Settlement) of the Bashkirian meganticlinorium of the southern Urals. During burial and tectonic deformations, isotopic-geochemical systems in lower limestones of the group and in low-Mg dolostones of the Min'yar Formation have been disturbed under influence of elision fluids derived from sandy-clayey sediments (from the Zilmerdak Formation rocks and from siliciclastic constituents of the Inzer Formation). In addition, carbonates of the Uk Formation and upper strata of the Min'yar Formation were partly recrystallized under influence of meteoric waters.

(2) The Sr isotope variations in the Upper Riphean carbonate rocks are studied much better than in other stratigraphic intervals of the Proterozoic. Nevertheless, there is no standard curve, which can be adopted broadly to characterize these variations in the Late Riphean seawater. This is a consequence of the following reasons: the available curves are plotted based on data obtained for discrete carbonate successions, correlation between which is not unambiguous; significance of epigenetic alterations in carbonate rocks is underestimated; criteria used to control the geochemical retentivity of studied carbonates are not uniform; and the

procedure of selective dissolution and removal of epigenetic carbonate phases have been used in exceptional cases only.

(3) The new standard curve of <sup>87</sup>Sr/86Sr ratio variations in the Late Riphean ocean is predominantly based on analytical results obtained for the Karatau Group carbonates from the southern Urals and for the Lakhanda Group carbonates from the Uchur-Maya region and for age equivalents of the latter from the Turukhansk region. These subdivisions have a confident chronometric calibration, and their rocks are slightly altered and satisfy strict criteria of geochemical retentivity. In addition, the studied samples have been subjected to preliminary chemical treatment in order to remove the late diagenetic carbonate phases. The resultant curve of detailed seawater 87Sr/86Sr variations are plotted for three intervals of the Late Riphean ranging from 1030 to 1000, from 850 to 770, and from 660 to 640 Ma. The intermediate intervals are characterized based on critical evaluation of published Sr isotope parameters of corresponding rocks and partially on interpolation. Such an approach made it possible to present a modified version of the standard curve of <sup>87</sup>Sr/<sup>86</sup>Sr variations in the Late Riphean seawater, which, in distinction from earlier variants, is lacking several inconsistence and former disadvantages.

(4) During the first half of the Late Riphean (1030-810 Ma) the seawater  ${}^{87}Sr/{}^{86}Sr$  ratio was low, ranging from 0.70519 to 0.70566. Later on, up to about 775 Ma ago, that ratio rose to 0.70611, but afterward, during the subsequent 30 m.y., it decreased again down to 0.70561-0.70565. Within the time span of 740-690 Ma, the ratio in question ranged from 0.70646 to 0.70686 with a short-term drop down to 0.70620 about 720 Ma ago. At the end of the Late Riphean (660-640 Ma), the ratio lowered to 0.70538-0.70580 to become growing up to 0.70840-0.70860 during the Vendian and earliest Cambrian.

(5) Secular variations of Sr isotope composition in paleooceans depend not only on balance between the mantle and continental Sr flux into the World Ocean, but also on compositional changes in provenances, on the character of volcanism, and/or on changeable intensity of weathering and erosion under influence of paleoclimatic events and changes in the atmosphere composition (CO<sub>2</sub>-O<sub>2</sub> balance is of prime importance). Consequently, these variations are sensitive indicators of secular variations in proportions between various microelements and nutrients brought into the World Ocean. The noticeably higher values and fluctuation amplitudes of 87Sr/86Sr ratio in seawater of the late Late Riphean, as compared to these parameters of the earlier intervals of the Proterozoic, reflect changes of a comparable scale in seawater composition. These changes influenced for sure the Precambrian biota on the eve of the Vendian and Phanerozoic. In other words, data on seawater 87Sr/86Sr variations in the World Ocean allow

us to analyze secular trends of global biosphere evolu-tion.

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