The Pb–Pb trail dating of carbonates with open U–Pb systems: The Min'yar Formation of the Upper Riphean stratotype, southern Urals

7 authors, including:

Igor Gorokhov
Russian Academy of Sciences
122 PUBLICATIONS   **2,247** CITATIONS

Lev Levskii
Russian Academy of Sciences
173 PUBLICATIONS   **1,010** CITATIONS

Some of the authors of this publication are also working on these related projects:

Geochemistry of the cratonic lithosphere mantle View project

The Pb-Pb Trail Dating of Carbonates with Open U-Pb Systems: The Min'yar Formation of the Upper Riphean Stratotype, Southern Urals

G. V. Ovchinnikova*, I. M. Vasil'eva*, M. A. Semikhatov**, I. M. Gorokhov*,
A. B. Kuznetsov*, B. M. Gorokhovskii*, and L. K. Levskii*

* Institute of Precambrian Geology and Geochronology, Russian Academy of Sciences, nab. Makarova 2,
St. Petersburg, 199034 Russia

** Geological Institute, Russian Academy of Sciences, Pyzhevskii per. 7, Moscow, 109017 Russia

Received January 6, 1999

Abstract – Epigenetic alterations and secondary Pb-Zn mineralization in carbonate rocks of the Min'yar Formation represent a serious problem for the direct measurements of Pb-Pb ages in these upper horizons of the Upper Riphean stratotype (the Karatau Group of southern Urals). In addition to petrographic data, cathodoluminescent analysis, and strict geochemical criteria (Mn/Sr, Fe/Sr, ^{18}O), we paid attention, when selecting samples for Pb-Pb dating, to the minimum difference between $^{87}Sr/^{86}Sr$ ratios measured in secondary carbonate phases leached in the 1N ammonium acetate solution and in primary phases residual after leaching. In order to remove secondary carbonates and microinclusions of Pb-Zn sulfides as carefully as possible, we subjected the preliminary selected samples to a short-term leaching in 0.5 N solution of HBr before their final dissolution in this acid. The Pb-Pb dates estimated for whole rock samples and for residual carbonate phases after the last leaching are equal to 780 ± 200 and 780 ± 110 Ma, respectively. The Pb-Pb date of 470 ± 80 Ma obtained for four carbonate phases (whole rock carbonates, two their fractions leached in 1N NH$_4$OAc and 0.5 N HBr solutions, and the residual phase) of one sample bearing sulfide microinclusions is considered as the age of Pb-Zn mineralization. The model age $t_1 = 770 \pm 220$ Ma is calculated for dolomites on the basis of "isochron t_1-t_2" assuming that $t_2 = 470$ Ma. The weighted average age value for the Min'yar dolomites is 780 ± 85 Ma. This result well fits the formation age limits evaluated on the basis of direct data of isotopic geochronology, paleontology, and chemostratigraphy. The tested procedure of sample selection and isotopic study of carbonate rocks opens a possibility to measure Pb-Pb ages of stratigraphic importance in those cases, when U-Pb systems of rocks were reset in the course of epigenetic sulfide mineralization.

Key words: **U-Pb systematics, carbonate rocks, epigenesis, Upper Riphean, southern Urals.**

INTRODUCTION

Isotopic-geochronological characteristics of the Upper Riphean stratotype (Karatau Group of the western slope of the Urals) are known so far from results of K-Ar and Rb-Sr dating of glauconite inadequately studied in mineralogical aspect and from K-Ar dates obtained for whole rock samples of gabbro-diabase. At the same time, the recent progress in U-Pb and Pb-Pb dating methods offered a possibility to determine age of many Precambrian carbonate-bearing successions (Moorbath *et al.,* 1987; Jahn *et al.,* 1990; Jahn and Cuvellier, 1994; Jahn and Simonson, 1995; Ovchinnikova *et al.,* 1995; Russell *et al.,* 1996). In particular, the Pb-Pb isochron age for limestones from the middle part of the Karatau Group (Inzer Formation) is determined as equal to 836 ± 25 Ma (Ovchinnikova *et al.,* 1998b). This value is interpreted as indicating age of the early diagenesis in carbonate sediments, and the date obtained is consistent with Rb-Sr dates (805-835 Ma) measured in authigenic illite fractions originated in the same formation during the burial diagenesis (Gorokhov *et al.,* 1995).

In this work, we analyzed the U-Pb and Pb-Pb systems of carbonate rock samples from the Min'yar Formation that overlies the Inzer Formation and characterizes an upper part of the Karatau Group. In this case, the Pb-Pb dating procedure meets some problems owing to epigenetic Pb-Zn sulfides dispersed in the Min'yar rocks (Mirkina *et al.,* 1986; Shirobokova, 1992). The mineralizing fluid was able to considerably decrease U/Pb ratios and to change the Pb isotope composition within a large volume of carbonate deposits, where the initial Pb concentration is extremely low, <1 µg/g (Ovchinnikova *et al.,* 1998a). Accordingly, we had to elucidate influence of secondary Pb-Zn mineralization on the U-Pb and Pb-Pb systems of the Min'yar dolomites, to demonstrate the applicability of U-Pb dating for carbonate rocks subjected to such alteration, and to estimate age of the formation.

STRATIGRAPHIC POSITION, AGE, AND COMPOSITION OF STUDIED SAMPLES

The Karatau Group of siliciclastic-carbonate deposits (3.0-5.5 km thick) is exposed within the Bashkirian meganticlinorium in the western slope of southern Urals. In the regional stratigraphic scheme accepted now, the group is divided into six units (from the base upward): Sil'merdak (1200-3300 m), Katav (200-350 m), Inzer (300-800 m), Min'yar (350-800 m), Uk (160-350 m), and Krivaya Luka (250-300 m) formations. The lower and upper units are siliciclastic, whereas others are composed, predominantly or entirely, of carbonate deposits (Kozlov *et al.,* 1991; Maslov and Krupenin, 1991; Semikhatov *et al.,* 1991; *Unifitsirovannye...,* 1993; Maslov *et al.,* 1998).

Composition, succession, and chronological relationships of almost all formations of the Karatau Group have been established quite a long ago (see *Stratotip rifeya...,* 1983), but the structural and lithostratigraphic interpretation of boundary beds separating the Min'yar and underlying Inzer formations remained ambiguous for a while (see review in Maslov and Krupenin, 1991). In the west of the Bashkirian meganticlinorium (Adzhigardak Ridge), where we studied the Min'yar succession (Fig. 1), the formation in question is situated between the upper Inzer and lower Uk siliciclastic members. The succession that is bounded at the base and crowned at the top by thin limestone members consists mainly of monotonous 350-380 m thick dolomits (Fig. 2) enclosing, within the upper portion, the abundant nodules, lentils, and interlayers of chert (Kozlov *et al.,* 1991).
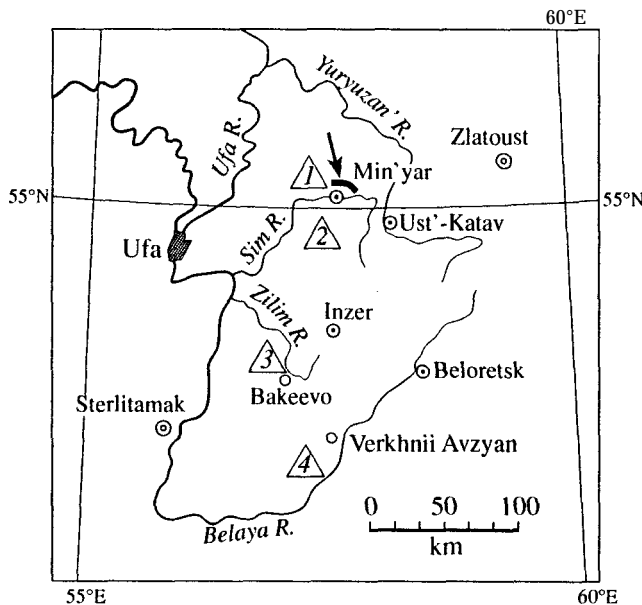
During a rather long period, it was *a priori* accepted that the Karatau Group represents almost completely the stratigraphic range of the Upper Riphean (e.g., Keller and Semikhatov, 1968; *Stratotip rifeya...,* 1982, 1983; Keller *et al.,* 1984; Semikhatov *et al.,* 1991; Koroteev *et al.,* 1997). This opinion was favored by K-Ar dates obtained in the 1960s-1970s for globular glauconites from different levels of the group, although this material was inadequately studied in the mineralogical aspect. These dates depict a regular, decreasing upward succession of age values: 938 Ma for the upper part of the Katav formation, 896-853 Ma for the lower and middle parts of the Inzer Formation, 791-740 Ma for the uppermost member of the latter, 713-680 Ma for the Min'yar Formation, and 658-630 Ma for the basal member of the Uk Formation (Garris, 1977; *Stratotip rifeya...,* 1983 and references therein). The Rb-Sr isochron age measured for the latter is 688 ± 10 Ma (Gorozhanin and Kutyavin, 1986). The upper age limit of the Karatau Group (*Stratotip rifeya...,* 1983; Semikhatov *et al.,* 1991; Koroteev *et al.,* 1997) was inferred from several evidences: K-Ar dates for whole rock samples of gabbro-diabase crosscutting the succession (660-620 Ma); K-Ar dates for glauconites from basal Vendian beds unconformably overlying the group in the Urals and nearby region (625-560 Ma); and from U-Pb dates for zircons from granitoids intruding the presumable analogues of the Karatau Group westward of its distribution area (660 ± 15 Ma), though these dates obtained by A.A. Krasnobaev have never been validated in publications. The estimated lower age limit of the group is based on extrapolation of K-Ar dates for glauconites from the lower Karatau horizons and on occasional K-Ar whole rock dates for gabbro-diabase bodies, which presumably originated before deposition of the latter and yielded, in addition to distinctly rejuvenated results, age values of about 1150-1000 Ma (Garris, 1977).

The listed dates, which seem to be unreliable now in methodical aspect (especially those obtained for the whole rock samples), have been considered off and on as arguments favoring the idea that the Karatau Group represents sufficiently well the succession of rocks ranging in age from 1000 ± 50 to 650 ± 20 Ma. We should mention here, however, that the significance and time range of stratigraphic hiatus obviously separating the Karatau Group from overlying Lower (tillites of the Kurgashlya Formation) or Upper Vendian deposits (clastic rocks of the Asha Group) have never been considered, and erosion marks at the base of the Min'yar and Uk formations (Bekker, 1961, 1988; Raaben, 1975; Kozlov, 1982; Kozlov *et al.,* 1991; Maslov and Krupenin, 1991) were either ignored without comments, or considered as evidencing the synsedimentary growth of local uplifts.

Leaving here the problem of lower age limit of Karatau deposits, we would like to emphasize that paleontological remains from the middle-upper interval of the succession are characteristic of relatively high lev-

Fig. 1. Geographic position of the studied Min'yar section and of the Ivanovsk (7), Srednyaya Kurgashla (2), Zilim (3), and Pravoberezhnoe *(4)* sites of Pb-Zn mineralization in the western slope of southern Urals.

els of the Upper Riphean. The Min'yar Formation encloses remains of *Melanocyrillium* (Maslov *et al.,* 1994), and these vase-shaped protistans appeared in geological records about 850 Ma ago (Knoll, 1996). In addition, stromatolites from the Min'yar and Uk formations (Raaben, 1975) and organic-walled microfossils from the lower Inzer strata (*Stratotip rifeya...*, 1982) are similar to their counterparts occurring in the upper Upper Riphean of Spitsbergen and some other regions (Raaben, 1975; Butterfield *et al., 1994*).

Problems concerning the stratigraphic range and age interpretation of upper subdivisions of the Karatau group showed their unexpected sides in the light of recent chemostratigraphic considerations based on secular variations of carbon (Semikhatov *et al.,* 1995; Podkovyrov *et al.,* 1998) and Sr isotope ratios (Gorokhov *et al.,* 1996a, 1996b; Kuznetsov *et al.,* 1997, 1998a).

First, it was demonstrated that considerable intervals with high $^{13}C_{carb}$ values (from +6 to +8-9‰ PDB), which characterize the successions ranging in age from 850 to 630 Ma in many other regions and are thought to represent an immanent feature of C-isotope variations recorded at that time (Kaufman and Knoll, 1995; Bartley *et al.,* in press), are missing from the Min'yar and Uk successions. In opinion of Podkovyrov, Semikhatov and their colleagues (Podkovyrov *et al.,* 1998), this phenomenon just reflects considerable gaps in the upper Karatau carbonate succession that is conditioned by accumulation of siliciclastic deposits (Krivaya Luka Formation) before the pre-Vendian erosion and by hiatuses in sedimentation at the base of Min'yar and Uk formations, the accumulation time of which was relatively short. For instance, the accumulation of the latter is interpreted as a short-term event that immediately followed the Sturtian glaciation about 700 Ma ago.

Second, C and Sr isotopic characteristics of Karatau carbonates (*op cit.*) suggest that the so-called Shaler event, i.e., a sudden decrease of $^{87}Sr/^{86}Sr$ initial ratios recorded in the synonymous supergroup of Arctic Canada (Asmerom *et al.,* 1991), corresponds in the Urals to the late-Min'yar changes in chemostratigraphic parameters. The Shaler Supergroup appears to be younger than 1100 Ma (the U-Pb age of youngest population of clastic zircons from its base) and older than 723 ± 3 Ma (the U-Pb age of baddeleyite from volcanics discordantly overlying the Supergroup; Heaman and Rainbird, 1990; Heaman *et al.,* 1992; Rainbird *et al.,* 1992). The telecorrelation suggests that this supergroup could be even younger than 802 ± 10 Ma (Rainbird *et al.,* 1996). Accordingly, it seems reasonable to connect the Shaler event with the Rodinia supercontinent breakup that commenced 750-725 Ma ago (Powell *et al.,* 1993; Torsvik *et al.,* 1996). In other words, if all chemostratigraphic considerations are correct, the Min'yar Formation is older than 750-725 Ma, whereas paleontological data cited above show that it is younger than 850 Ma.

We collected the studied samples of carbonate rocks from the Min'yar Formation stratotype exposed near
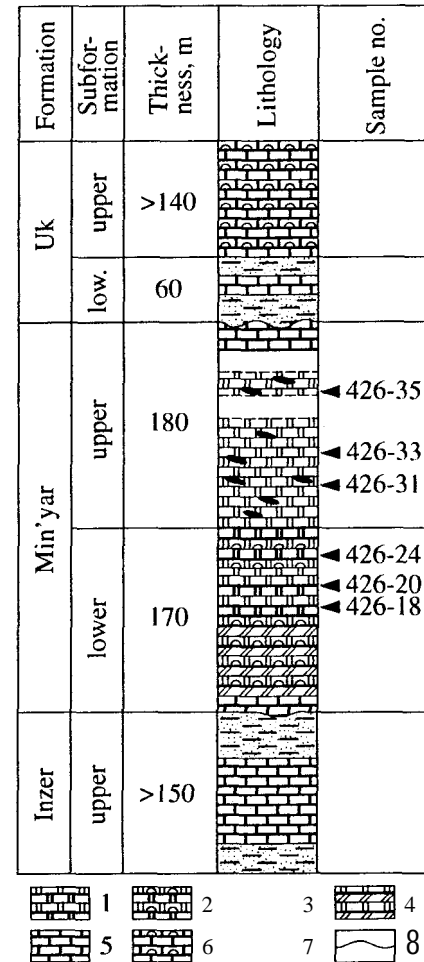

Fig. 2. Lithology and labeled stratigraphic levels of studied samples in the Min'yar Formation section: (1) dolomite; (2) stromatolitic dolomite; (3) limestone; (4) dolomite with cherty inclusions; (5) low-Mg dolomite; (6) stromatolitic limestone; (7) siliciclastic deposits; (8) stratigraphic unconformity.

and inside the synonymous town (Figs. 1 and 2). Dominant here are light gray to pinkish massive or thin-platy stromatolitic and mechanogenic dolomites intercalated with flakestone lentils. In the upper portion of the succession, they enclose abundant nodules and lentils of dark chert, the first occurrence level of which is commonly accepted for the boundary between the lower (200-210 m) and upper (160-190 m) subformations. The basal and topmost members (10-15 m) are composed of limestone; the former incorporates a packet of siliciclastic rocks (1-3 m).

The Min'yar carbonate rocks have the insoluble silicate residue (3% in average) consisting of quartz and less abundant feldspar with a negligible admixture of illite and chlorite (Gareev, 1986). Stromatolitic rock varieties correspond to dolomicrites and dolo(micro)sparites, whereas microsparites and fine-grained sparites are of mechanogenic origin. Small veinlets and inclusions of late crystalline dolomite, abundance of which is irregu-

lar, are characteristic of all rock types. The rocks preserve original bedding structures and clastic texture, though they are noticeably recrystallized according to data of cathodoluminescent analysis. The reddish luminescence visible by analysis varies from weak to moderate, being most intense in the late dolomite segregation. In zonal crystals of that dolomite present in dolosparites, the core and marginal zones differ in the luminescence intensity (Podkovyrov *et al.,* 1998).

In the upper subformation, cherty nodules and lentils are composed of microcrystalline quartz locally associated with chalcedony. Silicified microfossils, some perfectly preserved, are dispersed in these cherty intercalations (Sergeev, 1992). The occurrence of microfossils suggests that cherts of the Min'yar Formation, like many other Upper Precambrian cherts, originated immediately after the postmortal burial of microorganisms in the surface sedimentary layer near the water–sediment interface (Maliva *et al.,* 1989). At the same time, cherty nodules and lentils of the Min'yar Formation locally enclose the dolomicrosparite relicts, and some flakestones distinctly show that silicification predated synsedimentary brecciation of dolomicrosparites. Consequently, the early dolomitization of Min'yar carbonates took place at the initial stage of lithogenesis immediately after accumulation of sediments composed presumably of high-Mg calcite. This does not concerns, however, the late dolomite generation filling veins and local nests in the rocks. This generation is most characteristic of low-Mg dolomites localized in the lower part of the formation, where the rocks experienced the late dedolomitization (Kuznetsov *et al.,* 1998b).

Carbonate sediments of the Min'yar Formation accumulated in a vast marine basin that occupied, in addition to the western slope area of the Urals, also a very wide zone nearby. Structural features of the rocks suggest a transition from relatively deep sedimentation settings at the early Min'yar time to the shallow settings located near the fair weather wave base in the subsequent period (Maslov, 1997).

The Pb-Zn sulfide mineralization in carbonate rocks of the Karatau Group is concentrated mostly in southern and eastern areas of the Bashkirian meganticlinorium, but in the west, where we studied the Min'yar section, it is manifested to a much lesser extent (Mirkina *et al.,* 1986; Shirobokova, 1992). Ore occurrences proper are situated here as far away from the town of Min'yar as 20-30 km (see Fig. 1). In the studied succession, thin (0.2-2.0 mm) veins and segregations of small galena and sphalerite (less abundant) crystals tend to be concentrated in horizons of coarse-grained dolomite, which are localized near the contact of carbonate and siliciclastic deposits.

ANALYTICAL PROCEDURE

Selection of carbonate samples most appropriate for the U-Pb isotope analysis included two consequtive steps. First, we selected visually those 17 of 38 available dolomite samples, which looked homogeneous and affected by secondary recrystallization to a minimum extent. One half of each sample was used for the X-ray, chemical, cathodoluminescent, and isotopic analyses, and another for investigation under petrographic and electron microscopes. Element concentrations in carbonate rock fractions were analyzed by chemical (Ca and Mg) and atomic absorption (Fe and Mn) methods after dissolving weighings of samples in 1 N HCl. We did not use more aggressive acids in order to leave intact the silicate fraction.

Afterward, we selected 6 dolomite samples fitting the following criteria: Mn/Sr <1.5; Fe/Sr < 4.0; Rb/Sr < 0.2; ^{18}O > -5‰ PDB. As is known (Brand and Veizer, 1980, 1981; Veizer, 1983; Banner and Hanson, 1990; Asmerom *et al.,* 1991; Derry *et al.,* 1992; Gorokhov *et al.,* 1995; Gorokhov, 1996; Kuznetsov *et al.,* 1997; and references in these works), the above criteria characterize "best" dolomite samples that suffered to a minimum extent the epigenetic (diagenetic in English literature) alteration by interaction with meteoric waters and are, consequently, most appropriate for further investigation.

Precambrian carbonates usually include non-cogenetic phases with different Sr isotope composition and trace element concentrations. Only one of the phases is of the early diagenetic origin, whereas all others are products of secondary (catagenetic) alterations (Gorokhov *et al.,* 1995; Ovchinnikova *et al.,* 1995, 1998a, 1998b). In order to separate these phases, we treated the powdered samples in 1 N solution of ammonium acetate (NH_4OAc) under the room temperature (Gorokhov *et al.,* 1995; Ovchinnikova *et al.,* 1995). The carbonate residue after this treatment representing the primary rock component is designated here as PCC-1 phase (Fig. 3). It is important that the non-cogenetic carbonate phases of selected samples show the minimum difference, in terms of Rb-Sr systematics, between the measured $^{87}Sr/^{86}Sr$ ratios, and, consequently, the degree of secondary alterations in relevant rocks is at the minimum. The whole rock carbonate fraction used without treatment in NH_4OAc solution is designated as PCC-2 phase. To extract U and Pb from both phases, we dissolved them in 1N HCl under the room temperature. The residue insoluble in HCl represents the ISR phase, and the mixture of concentrated HF and HNO_3 was used to decompose it.

Since carbonate rocks of the Karatau Group are affected by the epigenetic Pb-Zn mineralization, we had to use the additional investigation and treatment methods by analyzing six selected samples. Three of them (426-18, 426-24, and 426-35) have been studied under the scanning electron microscope ABT-55 equipped with microprobe LINK AN-1000. Small

pyrite crystals up to 6 × 12 μm have been detected only in sample 426-24 (Fig. 4). However, it is impossible to guarantee, even after examination under scanning electron microscope, that other samples are free of tiny sulfide crystals less than 6 μm in size that is comparable with the microprobe resolution ability. Accordingly, we used the hard leaching method in order to remove not only possible sulfide microinclusions, but also the carbonate phases formed or recrystallized by the development of Pb-Zn mineralization.

We should emphasize here that application of the Pb-Pb isochron model and differentiated dissolution of carbonate fractions, is a promising approach as only in this case we can obtain a reliable age information analyzing only composition of daughter Pb isotopes without measuring concentrations of parental uranium. It is obvious that dissolution procedure is unable to change the Pb isotope composition bearing geochronological information in any rock phase under analysis. Changes in U/Pb ratios in response to differentiated dissolution are unimportant for the Pb-Pb age calculations.

Reagents commonly used for hard leaching of Precambrian rocks are either 0.1M and 6M solutions of HCl (Whiterhouse and Russell, 1997), or 0.6N and 1.2N solutions of HBr (Babinski et al., 1995). In our study, we used the 0.5N solution of HBr (Vasil'eva et al., 1998) bearing in mind the following criteria: (1) sulfide solubility is higher in HBr than in HCl; (2) final dissolution of carbonate phases in the less concentrated 0.5N HBr is more preferable than in the 6N HCl (or even in 1N HCl), because a chance to extract Pb from siliciclastic admixture decreases; (3) it is a common practice to extract Pb for mass-spectrum analysis filtering the 0.5N bromide solution through the ion-exchange columns, and, having no necessity to convert chloride into bromide, we decrease a possibility of laboratory contamination.

Fractions of carbonate rock sample (PCC-1 or PCC-2) were treated during 30 minutes in 0.5N HBr under the room temperature. The insoluble residue was rinsed three times with water after centrifuging, dried up, and weighted. About 30% of initially weighed portion entered the solution. This dissolved material is designated as L-1 phase (Fig. 3). Carbonate fraction of dry residue after the 30-minute-long leaching was treated once again during 24 hours in 0.5N HBr to be completely dissolved. This fraction is designated as L-2 phase. In all phases, we determined U and Pb concentrations and analyzed the Pb isotope composition. Subjected to the hard leaching are PCC-1 phases of samples 426-18, 426-24, and 426-33, and also PCC-2 phases of samples 426-20, 426-31, and 426-35, that is why indices L-1 and L-2 are supplemented in the table with abbreviations pointing to one or another phase. Likewise, ISR phases residual after carbonate dissolution in different acids (HCl or HBr) are respectively marked in the table. Because of a low Pb concentration in dolomites, the relatively large batches of samples
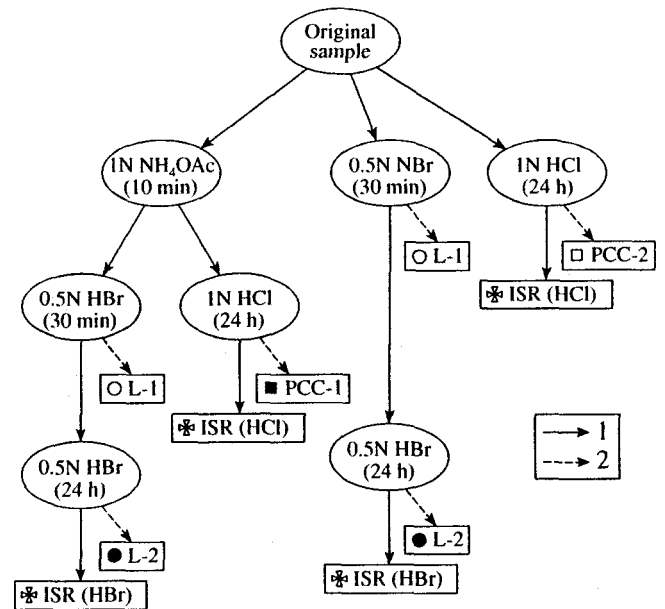

Fig. 3. Scheme of chemical treatment of studied samples and separated insoluble (ISR) and soluble (PCC) phases: (1) insoluble residue after sample treatment in the indicated reagent; (2) soluble phase (centrifugate).

(600-800 mg) were used for the two-step leaching in HBr. Accordingly, data on PCC-1 and PCC-2, on the one hand, and on their residues L-1 and L-2 are obtained from different sample batches.

The mixed tracer $^{235}U + ^{208}Pb$ was added to aliquots of bromide solutions used to analyze the U and Pb concentrations and the Pb isotope composition. Extraction of U and Pb in bromide forms was performed using the anion-exchange resin Bio-Rad 1×8 in accordance with procedure described by (Manhes et al., 1978). U and Pb isotope compositions were analyzed using mass spectrometer Finnigan MAT-261 in a regime of simultaneous measurements of all isotope ion currents. The measured Pb isotope ratios were corrected for a fractionation factor of 0.13% per atomic mass unit based on recurrent determinations of Pb isotope composition in NBS SRM-982 standard. The procedure blank during the period of measurements is 0.05 ng for U and 0.5 ng for Pb. The computation algorithm by Ludwig (PBDAT) was used to estimate uncertainties and correlation of U-Pb data, and his ISOPLOT program was used to calculate the isochron parameters and MSWD values (Ludwig, 1989, 1990). All inaccuracy values presented in the text and Fig. 6 correspond to two standard deviations (2).

RESULTS

The least altered samples selected to study the U-Pb systematics of the Min'yar Formation characterize its middle strata (Fig. 2) that are situated away from both the basal low-Mg epigenetic dolomites and the recrys-
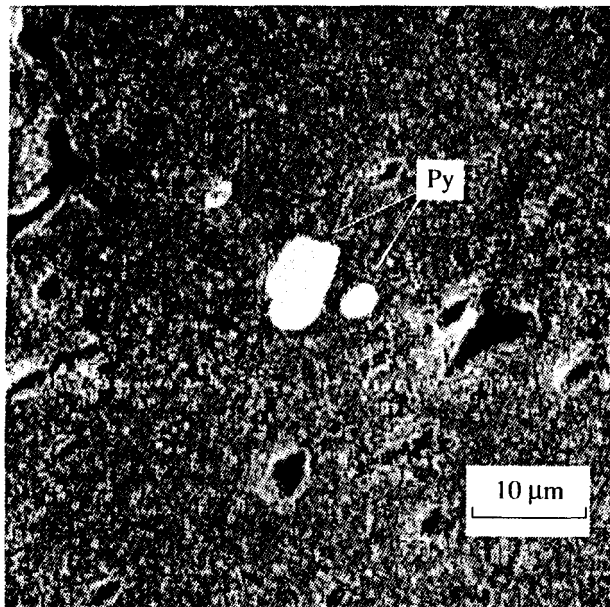
Fig. 4. SEM photograph of pyrite microinclusions (Py) in dolomite sample 426-24 from the Min'yar Formation.

tallized rock varieties crowning the exposed interval of the studied section. As a result of burial and meteoric diagenetic events, dolomites of the last type show elevated values of Mn/Sr (1.4-16.4) and Fe/Sr (4.1-64.5) ratios. As compared to others, the "best" dolomite samples from the middle part of the section mostly consist of pure dolomite (Mg/Ca = 0.606-0.636) and have an insignificant non-carbonate admixture (0.7-2.6%) and micrite relics, but they are almost free of the late, fine- to medium-grained dolomite generation. The Mn, Fe, and Rb contents in these samples are low in contrast to a rather high Sr concentration (Table 1), and consequently, Mn/Sr and Fe/Sr ratios characterizing the relevant rocks are low (0.61-1.53 and 1.46-3.55, respectively). Values of ^{18}O vary in the rocks from -4.0 to -4.8‰ PDB, and difference between $^{87}Sr/^{86}Sr$ ratios measured in PCC-1 and PCC-2 phases (one subjected to and another left without treatment in ammonium acetate) is less than 0.0025. The listed characteristics prove that the studied rocks did not experience a con-

siderable alteration at the burial and meteoric diagenetic stages (Choquette and James, 1987; Barnaby and Read, 1992; Montanez and Read, 1992; Gorokhov *et al.*, 1995; Gorokhov, 1996; Kuznetsov *et al.*, 1998b).

Data on U-Pb systems in different carbonate fractions of the samples studied are shown in Table 2. According to these data, the "delicate" leaching reveals the following characteristics: (1) U and Pb concentrations are higher in the PCC-1 phases of samples 426-20, 426-31, and 426-35, than in their PCC-2 phases, and the former simultaneously have lower values of measured $^{238}U/^{204}Pb$ ratios and less radiogenic Pb isotope composition; (2) in contrast, PCC-1 phases of samples 426-18 and 426-33 show $^{238}U/^{204}Pb$, $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{204}Pb$ ratios that are higher than those in PCC-2 phases; (3) all three isotopic parameters are almost identical (within the limits of analytical error) in PCC-1, PCC-2, and L-I phases of sample 426-24, and only the $^{206}Pb/^{204}Pb$ ratio in L-2 phase is in this case higher by 6% than in others. The established relationships between parameters suggest that leaching in NH_4OAc partially removes the epigenetic carbonate phases (or admixture), where Pb may be relatively more (samples 426-20, 426-31, and 426-35) or less radiogenic (samples 426-18 and 426-33). At the same time, the extraction of secondary carbonate phases from sample 426-24 does not change parameters of its U-Pb isotopic system.

In addition, Table 2 shows that the highest values of $^{238}U/^{204}Pb$, $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{204}Pb$ ratios characterize the L-2 phases of samples 426-18, 426-24, 426-31, and 426-33, which represent residues after leaching in 0.5N HBr. However, in samples 426-20 and 426-33 enriched in radiogenic Pb, the highest values of these parameters are typical of PCC-2 and PCC-1 phases, and this may indicate that carbonate phases of these particular samples are heterogeneous.

Data points corresponding to PCC-1 and PCC-2 phases commonly useable for age determinations produce a linear trend in the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram of Gerling and Houtermans (Fig. 5). The Pb-Pb age calculated using the linear trend of PCC-1 data points is equal to 988 ± 400 Ma, MSWD = 22, and that for PCC-2 phases corresponds to 775 ± 130 Ma,

Table 1. Chemical composition of carbonate rock fraction in dolomite samples from the Min'yar Formation

Sample no.	Insoluble residue, %	Ca, %	Mg, %	Mn, µg/g	Fe, µg/g	Rb, µg/g	Sr, µg/g	Mg/Ca	Mn/Sr	Fe/Sr	^{18}O, ‰ PDB
426-18	1.8	21.7	13.20	44	143	0.12	54.9	0.608	0.80	2.60	-4.0
426-20	2.6	22.1	13.38	101	145	0.14	74.7	0.606	1.35	1.94	-4.3
426-24	0.9	21.8	13.36	51	100	0.15	68.5	0.612	0.74	1.46	-4.8
426-31	1.6	21.6	13.22	68	90	0.49	44.4	0.612	1.53	1.98	-4.6
426-33	0.7	20.9	13.28	63	150	0.18	103	0.636	0.61	1.46	-4.3
426-35	2.2	22.0	13.41	96	240	0.13	67.6	0.609	1.42	3.55	-4.4

Table 2. U-Pb data for different phases of carbonate rocks from the Min'yar Formation

Sample no.	Phase	Pb*, µg/g	U*, µg/g	$^{238}U/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
426-18	PCC-2	0.271	0.126	34.5	28.863	16.401	39.770
	PCC-1	0.227	0.127	43.2	31.537	16.603	40.321
	L-1 (PCC-1)	0.278	0.166	31.1	29.011	16.395	39.612
	L-2 (PCC-1)	0.194	0.176	71.5	33.047	16.710	40.649
426-20	PCK-2	0.244	0.217	80.7	44.479	17.428	42.312
	PCK-1	0.365	0.254	56.3	35.265	16.797	40.749
	L-1 (PCC-2)	0.285	0.197	59.6	40.144	17.073	41.469
	L-2 (PCC-2)	0.306	0.253	69.8	37.907	17.034	41.490
	ISR (HBr)	0.552	1.689	216.1	26.182	16.185	38.439
426-24	PCC-2	1.014	0.160	10.6	22.393	15.993	38.253
	PCC-1	0.939	0.159	11.4	22.592	15.998	38.312
	L-1 (PCC-1)	0.956	0.156	10.9	22.298	15.940	38.240
	L-2 (PCC-1)	0.653	0.282	29.5	23.740	16.066	38.447
426-31	PCC-2	0.366	0.207	43.8	33.631	16.683	38.427
	PCC-1	0.514	0.233	33.3	29.534	16.389	38.180
	L-1 (PCC-2)	0.494	0.226	33.6	29.590	16.377	38.115
	L-2 (PCC-2)	0.338	0.234	54.3	34.803	16.810	38.549
	ISR (HCl)	1.600	3.527	14.8	23.516	16.054	37.188
	ISR (HBr)	2.721	5.486	13.5	23.165	16.081	37.423
426-33	PCK-2	0.272	0.142	40.7	31.003	16.569	41.584
	PCK-1	0.211	0.162	64.3	35.795	16.900	43.554
	L-1 (PCC-1)	0.241	0.242	79.3	31.774	16.584	41.841
	L-2 (PCC-1)	0.227	0.145	52.3	33.926	16.787	42.746
426-35	PCC-2	0.530	0.292	39.5	27.949	16.327	37.632
	PCC-1	0.627	0.326	36.7	26.899	16.253	37.715
	L-1 (PCC-2)	0.778	0.321	28.8	25.883	16.162	37.652
	L-2 (PCC-2)	0.489	0.317	46.9	28.929	16.445	37.599
	ISR (HCl)	2.876	6.057	13.6	20.627	15.838	37.254
	ISR (HBr)	2.845	13.77	31.3	20.605	15.826	37.345

* Concentrations of U and Pb in leachates are calculated relative to the mass difference between PCC-2 phases and residues after leaching.

MSWD = 12. The MSWD values obtained indicate that both calculated ages are unreliable in terms of statistics. In the $^{238}U/^{204}Pb$ – $^{206}Pb/^{204}Pb$ diagram, dispersion of data points is even greater (Fig. 6), and we can definitely state that the U-Pb systems of studied samples have been reset in the course of their geological history.

DISCUSSION

According to results obtained, even the "best" Min'yar dolomites that passed the preliminary geochemical test do not fit the isochron model conditions in terms of the U-Pb systematics. The necessary conditions of the model are the uniform composition of primordial Pb and the steady-state equilibrium in the Pb-Pb and U-Pb system of rocks during the whole geo-

logical history of the latter, whereas the established dispersion of data points in Pb-Pb diagrams may be a consequence of the U loss and/or the Pb contamination.

Carbonate rocks that lost uranium under the recent hypergene conditions have been described in a series of publications (e.g., Asmerom and Jacobsen, 1993; Jahn and Cuvellier, 1994; Hoff et al., 1995; Johnes et al., 1995; Ovchinnikova et al., 1995). However, events of this kind were hardly crucial in the history of U-Pb systems in the Min'yar carbonates, as it is evident from the fact that the $^{238}U/^{204}Pb$ ratios and U concentrations measured in different phases of all samples show a poor correlation (see Table 2). At the same time, the studied dolomite samples reveal the following symptomatic characteristics:
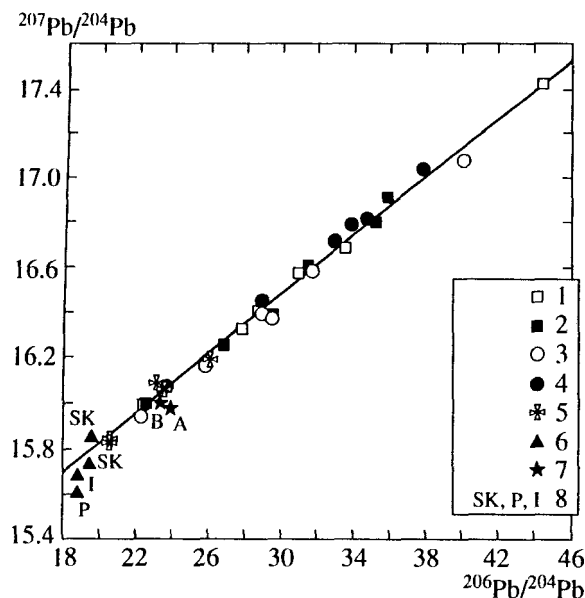
Fig. 5. $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram for different carbonate phases of dolomite samples from the Min'yar Formation and for galena specimens from Pb-Zn mineralization sites: (1-5) carbonate phases PCC-2 (1), PCC-1 (2), L-1 (3), L-2 (4). and ISR (5), see text for explanation; (6) galena from the Srednyaya Kurgashla (SK), Pravoberezhnoe (P), and Ivanovsk (I) sites of ore mineralization (after Mirkina *et at.*, 1986); (7) two calculated isotopic compositions of allogenic Pb.
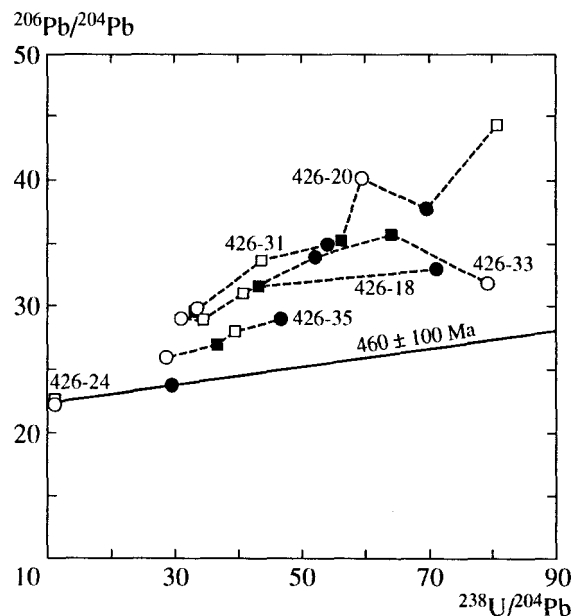
Fig. 6. $^{238}U/^{204}Pb$ – $^{206}Pb/^{204}Pb$ diagram for different carbonate phases of dolomite samples from the Min'yar Formation. Dotted lines connect data points characterizing sample, the number of which is indicated nearby. The U-Pb age of 460 ± 100 Ma is calculated using data on PCC-1, PCC-2, L-1, and L-2 phases of Sample 426-24 (other symbols as in Figs. 3 and 5).

(1) Phases of the same type from various samples and different phases of particular sample show the negative correlation between the Pb content and measured $^{238}U/^{204}Pb$ ratios (Fig. 7*)*.

(2) The highest Pb concentration but lowest $^{238}U/^{204}Pb$ ratio are established in carbonate fractions of one sample (426-24), where pyrite microinclusions have been recognized by examination under the scanning electron microscope.

(3) The Pb isotope composition in PCC and L phases from the last sample is approaching that characterizing phases insoluble in HCl (ISR phases in Table 2 and Fig. 5) and also galena from the Pb-Zn ore deposits of the Bashkirian meganticlinorium (Mirkina *et al.*, 1986).

(4) The laboratory leaching in ammonium acetate that is aimed to remove secondary carbonate phases from samples (Gorokhov *et al.,* 1995; Ovchinnikova *et al.,* 1995) does not result in Pb extraction.

(5) Removing secondary carbonates and decomposing sulfides, the hard leaching in 0.5N HBr noticeably increases Pb concentration in acid leachates (L-1 phases) relative to the residual L-2 phases, which are most depleted in Pb.

All these characteristics suggest that dolomites of the Min'yar succession have been contaminated with Pb at a certain stage of their geological history, and this explains well the data point dispersion in Pb-Pb diagrams (Fig. 5). This allogenic Pb slightly mobile under leaching in NH_4OAc (PCC-1 phases) enters solution much easier under leaching in 0.5N HBr (L-1 phases in Fig. 7). Consequently, dolomite samples from the Min'yar succession yield two types of leads different in isotopic composition and in behavior under leaching. One appears to be fixed in the dolomite crystal lattice (primary carbonate phase), and another one is a component of easily solvable sulfides and, maybe, of epigenetic carbonates that have been formed at the surface of dolomite grains.

The allogenic Pb origin in the Min'yar dolomites can be elucidated by analyzing diagrams of $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$. In these diagrams, all data points for carbonate phases, except for those of Sample 426-20, plot along straight lines (Figs. 8 and 9), which can be considered as mixing lines of primary and allogenic leads. The most radiogenic Pb is typical of phases L-2, whereas the least radiogenic Pb characterizes phases L-1. Since the latter contain, in addition to allogenic Pb, a certain share of Pb from carbonates, isotopic parameters of the allogenic Pb should be searched for along the mixing lines to the left of data points representing phases L-1 (Figs. 8 and 9). These parameters can be estimated using a version of the "isochron family model" that was suggested by Tera (1981) and then successfully used by Neymark and Iskanderova (1987), who calculated isotopic parameters of primary Pb in potassium feldspars from Proterozoic granitoids of Baikal Highland.

As is known, marine sedimentary carbonates lack correlation between $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios characterizing respectively the uranium and thorium decay chains (Jahn and Cuvellier, 1994). Correspondingly, data points for PCC-2 phases in Figs. 8 and 9 reflect variations of Th/U ratios in the mixture of primary carbonate and allogenic Pb. The inclination angles of lines connecting data points of L-1, L-2, PCC-1, and PCC-2 phases in $^{206}Pb/^{204}Pb$ ($^{207}Pb/^{204}Pb$) – $^{208}Pb/^{204}Pb$ diagrams depend on the sample ages and Th/U ratios in their different phases. If, for instance, two samples of identical age with dissimilar Th/U ratios contain allogenic Pb of the same isotopic composition (entering by leaching the phase L-1), the lines connecting phases of each sample must have an intersection point with Pb isotope ratios characterizing the allogenic lead. Data points for Sample 426-20 do not reveal a linear correlation in the $^{206}Pb/^{204}Pb$ – $^{208}Pb/^{204}Pb$ plot, whereas the inclination angles of other correlation lines show that Th/U ratios in the mixture of primary and secondary materials of samples 426-18 and 426-33 are higher than in that of samples 426-31 and 426-35.

An insignificant difference between Pb isotope ratios in various phases of any sample studied is responsible for a high uncertainty of angle coefficients calculated for the mixing lines, and we can outline only an area of their intersection points. Isotopic parameters of intersection points were calculated for two line pairs, one corresponding to samples 426-31 and 426-35, and another to samples 426-33 and 426-18. These points (A and B, respectively) characterizing the isotopic composition of allogenic Pb are shown in Fig. 5. Note also that data point of residual and solvable carbonate phases of Sample 426-24, as well as those of galena, plot close to the area, where all the mixing lines intersect (Figs. 8 and 9).

The origin of sulfide mineralization in the Karatau deposits has been interpreted differently (Mirkina *et al.,* 1986; Shirobokova, 1992; Seravkin *et al.,* 1994). According to one viewpoint, lead involved into mineralization was leached by epigenetic fluids from siliciclastic and carbonate rocks of the Karatau group (Anfimov, 1984; Mirkina *et al.,* 1986), and this idea is compatible with Pb isotopic parameters obtained for galena from the Min'yar Formation and for the residual ISR phases. In Fig. 5, data points for galena samples produce a trend that intersects the errorchron plotted for carbonate phases, and the ISR phases plot close to the intersection point thus being attributable to this errorchron. In addition, data points characterizing the calculated isotopic composition of allogenic Pb also plot close to the above intersection. Thus, it seems possible that Pb-Zn mineralization was accompanied by Pb leaching out of siliciclastic and carbonate rocks composing the upper formations of the Karatau Group. The mineralizing fluid could be also responsible for the partial recrystallization of carbonate components at the
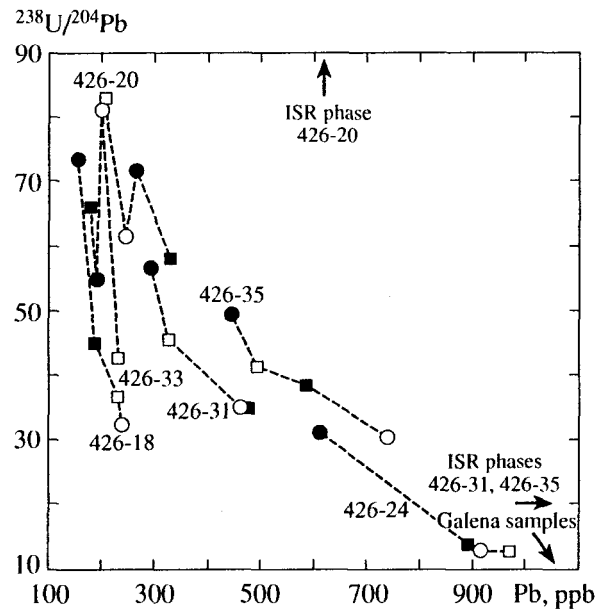

Fig. 7. Plot of $^{238}U/^{204}Pb$ ratios versus Pb concentration in various carbonate phases of indicated dolomite samples ffom the Min'yar Formation (symbols as in Figs. 3 and 5).
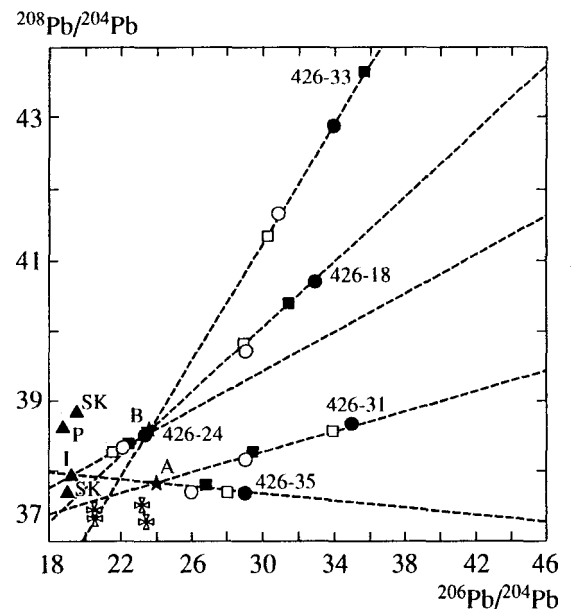

Fig. 8. $^{206}Pb/^{204}Pb$ – $^{208}Pb/^{204}Pb$ diagram for different carbonate phases of indicated dolomite samples from the Min'yar Formation (symbols as in Figs. 3 and 5).

time of precipitation of Pb-Zn sulfides. The highest concentration of trapped Pb is detected in Sample 426-24, where it is 2-4 times higher than in other samples, whereas the $^{238}U/^{204}Pb$ ratio is 3 to 8 times lower. In this connection, we consider data on Sample 426-24 as inappropriate for the Pb-Pb age calculation.

In the diagram of $^{2t16}Pb/^{204}Pb$ versus $1/^{204}Pb$ (Fig. 10), data points of PCC-1, PCC-2, L-1 (leachate after sample
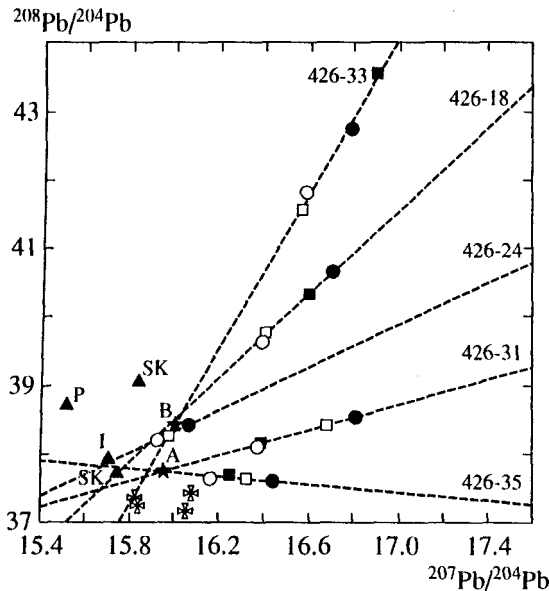
Fig. 9. $^{207}Pb/^{204}Pb$ – $^{208}Pb/^{204}Pb$ diagram for different carbonate phases of indicated dolomite samples from the Min'yar Formation (symbols as in Figs. 3 and 5).

Fig. 10. $1/^{204}Pb$ – $^{206}Pb/^{204}Pb$ diagram for different carbonate phases of indicated dolomite samples from the Min'yar Formation (symbols as in Figs. 3 and 5).

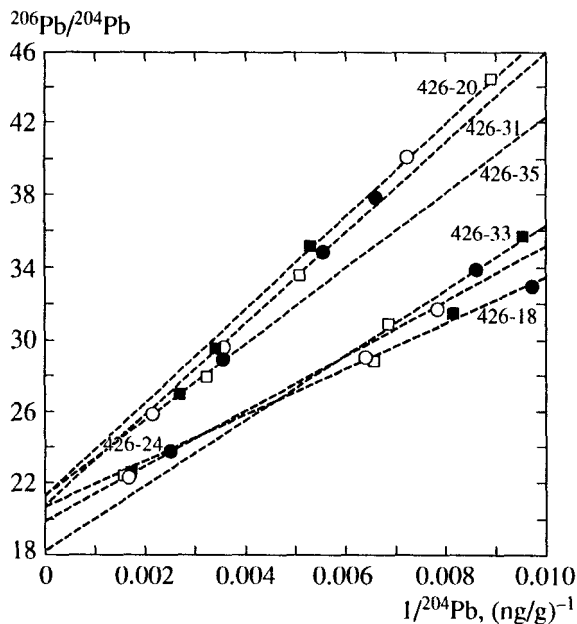treatment in HBr), and residual L-2 phases plot along straight lines. Consequently, we may suspect that each particular sample exemplifies mixing of leads variable in isotopic composition. Note also that one-type phases of all samples do not show any common trend, and this indicates that each sample yields two types of leads, one of the carbonates proper, which consists of primordial and radiogenic components, and another allogenic Pb.

The allogenic Pb of samples 426-33 and 426-18 differs in isotopic composition from that of samples 426-31 and 426-35. Data points A and B characterizing the allogenic lead plot below the Pb-Pb isochron (Fig. 5), close to data points of Sample 426-24, but quite away from those exemplifying PCC-2 phases of all other samples. Hence, we may assume that PCC-2 and L-2 phases of studied samples, except for those of Sample 426-24, have an insignificant concentration of allogenic Pb and can be used for calculating the Pb-Pb age valid in geochronological aspect. For five data points of PCC-2 phases, the calculated value is 780 ±200 Ma, MSWD = 6.

Lead in L-2 phases residual after leaching in 0.5 N HBr should be pretty close in isotopic composition to the lead of primary carbonates, because the general level of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{238}U/^{204}Pb$ ratios is highest exactly in these phases. Age value calculated on the basis of five L-2 phases is 780 ± 110 Ma, MSWD = 1.5, and the last parameter suggests that this date is statistically reliable.

The Pb-Pb isotopic parameters of carbonate rocks bearing Pb-Zn mineralization depend on the time, when mineralizing fluids affected the rocks, and on the degree of secondary recrystallization of carbonates. If sulfides and carbonates are approximately synchronous in origin, then their Pb isotope composition had to be balanced at the early diagenetic stage thus being usable for Pb-Pb dating (Jahn and Cuvellier, 1994; Ovchinnikova *et al.,* 1998a). In this case, the inclination of straight line in the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram is geochronologically meaningful. The case was illustrated by data on the Schmidtsdrift dolomite succession in the Upper Archean Transvaal Supergroup (South Africa), which is bearing the stratiform sulfide mineralization (Jahn *et al.,* 1990). If the mineralization is superimposed on carbonate rocks formed earlier, we have to consider two possibilities: (1) the allogenic Pb source of unknown isotopic composition must confuse correlation of data points for carbonates in the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ plot (Winter and Johnson, 1995); (2) the linear approximation of data points has in this case an ambiguous geochronological meaning. In general, the linear correlation of this type represents the mixing line that could be interpreted sometimes as the "isochron t_1–t_2" which offers a chance to estimate age of initial event (t_1), if we know the age of superimposed process (t_2). Relationships of this kind were suggested for the Lower Proterozoic marbles in the Sjangeli foldbelt (northern Sweden and Norway), which became enriched in radiogenic Pb during the Caledonian events. As a result, the straight line approximating data points of marbles in the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram turned out to be inclined steeper than the Pb-Pb isochron corresponding to formation time t_1 of original carbonate rocks (Romer, 1994). Suggesting that the obtained straight line represents the "isochron t_1-t_2" Romer calculated age t_2 corresponding to recrystallization time of carbonates and demonstrated that the

inferable t_1 value corresponds to the U-Pb age of zircons from basal tonalites of the Sjangeli Complex.

It is unknown how old is the Pb-Zn mineralization in carbonate rocks of the Min'yar Formation. This mineralization of distinct epigenetic origin (Feoktistov *et al.*, 1978; Mirkina *et al.*, 1986; Shirobokova, 1992) seems to be a consequence of concentration of dispersed ore components in response to activation of tectonics and magmatism in the study region. Events of this kind characterize the whole history of the Uralides and pre-Uralides (Ivanov *et al.*, 1986; Puchkov, 1993, 1997; Ivanov, 1998) and have been accompanied from time to time by development of ore mineralization. For instance, the Ordovician deposits in the east of western slope of the Urals, which accumulated on the passive continental margin, enclose the stratiform polymetallic and Ba-polymetallic mineralization related in origin to redistribution of synsedimentary ore components by mineralizing fluids (Shirobokova, 1992; Seravkin *et al.*, 1994).

As is demonstrated above, the correlation between the $^{206}Pb/^{204}Pb$ ratios and Pb concentrations in the studied samples of the Min'yar dolomites characterizes mixing of Pb trapped in carbonates (primordial and radiogenic components) with Pb added to the rocks by epigenetic mineralizing fluids (see Fig. 10). In the $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram, data points characterizing carbonate phases of samples 426-18, 426-31, 426- 33, and 426-35 (except for the L-2 phase of the latter) plot along the almost parallel straight lines (dotted lines in Fig. 11), which run close to data points representing isotopic parameters of hypothetical allogenic Pb (asterisks in Fig. 11) and those measured in galena (triangles in Fig. 11). Like in the case of carbonates from the Sjangeli Complex (Romer, 1994), these mixing lines slope steeper than the Pb-Pb isochrons approximating the PCC-2 or L-2 phases, the first of which yields age value of 780 Ma (see Fig. 10). Slope ratios of mixing lines correspond to age values of 1030-1190 Ma. If the allogenic Pb was leached from carbonate rocks, whose U-Pb systems developed in a closed state from the early diagenesis time (t_1) to the commencement of recrystallization (t_2), the mentioned mixing lines can be considered as "isochrons $t_1=t_2$". Then, assuming one age parameter, e.g., t_2, we may calculate another using the equation:

$$\tan = 1/137.88(\exp {}_5 t_1 - \exp {}_5 t_2)/(\exp {}_8 t_1$$
$$- \exp {}_8 t_2),$$

where ${}_5$ and ${}_8$ are the decay constants of ^{235}U and ^{238}U, respectively.

The t_2 value for carbonates of the Min'yar Formation appears to be concordant to the age of epigenetic sulfide mineralization. According to results of leaching experiments, the Pb isotope ratios in all phases of Sample 426-24 contaminated by sulfides are close to the ratios calculated for the allogenic Pb, and it is likely
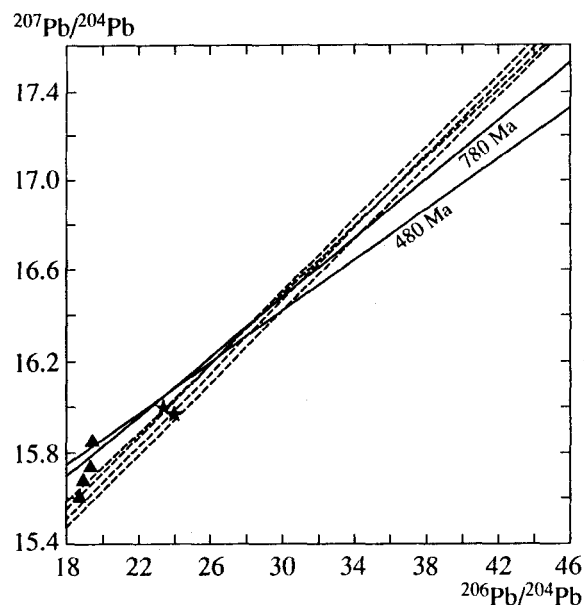

Fig. 11. $^{206}Pb/^{204}Pb$ – $^{207}Pb/^{204}Pb$ diagram for dolomite samples from the Min'yar Formation. Dotted lines correspond to "isochrons $t_1—t_2$" calculated for samples 426-18, 426-31, 426-33, and 426-35 (data points are omitted). Solid lines are isochrons for PCC-2 phases of studied samples (780 Ma) and for carbonate phases of Sample 426-24 (480 Ma). Other symbols correspond to those used in Figs. 3 and 5.

that the Pb-Pb system of this sample was completely reset in the course of Pb-Zn mineralization. As the Pb isotope composition in L-2 phase is more radiogenic than in other carbonate phases of the sample, a certain amount of Pb accumulated here owing to U decay after the time of Pb-Zn mineralization.

The Pb-Pb age calculated on the basis of data points characterizing carbonate phases of Sample 426-24 is equal to 480 ± 100 Ma (see. Fig. 11), and their U-Pb age is estimated to be 460 ± 100 Ma (Fig. 6). Despite a considerable uncertainty of both dates that is related to a narrow variation range of Pb isotopic ratios, one is very close to another, and the average value of 470 ± 80 Ma determines the Early Ordovician age of Pb-Zn mineralization. In the western zone of the Urals, this period corresponded to the initial rifting stage responsible for the crustal shortening in diverging passive margins of the ancient continental masses, whereas in the Uralide zone located eastward of the Main Uralian fault, this was already a time of sea-floor spreading development (Ivanov *et al.*, 1986; Puchkov, 1997; Ivanov, 1998). Geodynamic environments of this kind are commonly thought to be manifestations of the mantle plume activity favorable as well for generation of thermal fluids, which could mobilize ore elements and produce Pb-Zn mineralization in the Karatau Group deposited on the newly formed continental passive margin.

If the U-Pb and Pb-Pb systems of carbonates were reset at the time $t_2 = 470 \pm 80$ Ma, then the t_1 value cal-

culated using the aforementioned equation is 770 ± 200 Ma (an average age value for PCC-2, L-1, and L-2 phases of samples 426-18, 426-31, 426-33, and 426-35). This date is concordant with dates of 780 ± 200 and 780 ± 110 Ma calculated respectively for PCC-2 (carbonates untreated in ammonium acetate) and L-2 phases (residual carbonates after the first-step leaching in 0.5 N HBr).

We should remark here that the model of "isochron $t_1|-t_2$" that was successfully used by interpretation of Pb isotopic data on sulfides and feldspars (Neymark, 1988; Ovchinnikova *et al.,* 1994; Amelin *et al.,* 1998) is correct only then, when it is applied for samples, which are almost free of uranium and radiogenic Pb accumulated after the time t_2. Dolomites of the Min'yar Formation do not fit this requirement, because they accumulated a certain amount of radiogenic Pb after the time of Pb-Zn mineralization. However, the $^{238}U/^{204}Pb$ ratios vary in the studied samples from 10 to 71.5, whereas the radiogenic Pb excess, which accumulated mostly in the L-2 phases, is insignificant. Consequently, the uncertainty in determination of slope ratios for the "isochrons t_1-t_2" is comparable to the determination error for the age t_2. In fact, the slope ratios of these isochrons, which have been calculated on the basis of Pb isotopic data either uncorrected or corrected for the radiogenic Pb accumulation during the last 470 Ma, overlap each other within the limits of uncertainty.

The weighted average age value calculated for dolomites of the Min'yar Formation on the basis of three dates (780 ± 200, 780 ± 110, and 770 ± 200 Ma), which are obtained using different interpretations of Pb-Pb data, corresponds to 780 ± 85 Ma. We consider this value as reliably characterizing the formation age. It is concordant with the formation age limits established on the basis of direct isotopic-geochronological and paleontological data obtained for the Karatau Group, on the one hand, and inferred from the chemostratigraphic telecorrelation of upper horizons of this group.

CONCLUSION

(1) Strict geochemical criteria (Mn/Sr, Fe/Sr, and ^{18}O) and difference between $^{87}Sr/^{86}Sr$ ratios in the secondary and primary carbonate phases were used to select six rock samples of the Min'yar Formation, which seem to be altered to a minimum extent during the events of burial and meteoric diagenesis; they are considered as the "best" samples from our collection in terms of Rb-Sr systematics.

(2) This preliminary procedure does not guarantee, however, the selection of samples, the Pb-Pb isotopic systems of which are intact, because any epigenetic fluid containing Pb is able to lower the U/Pb ratio and to change the Pb isotope composition in a considerable volume of carbonate rocks, where the Pb concentration is extremely low. The epigenetic Pb-Zn mineralization manifested in the Min'yar Formation is the most distinct indication of such fluid activity.

(3) The isotopic data obtained after separation of epigenetic carbonate phases and sulfide microinclusions by means of leaching in the 0.5N solution of HBr were used to calculate a series of Pb-Pb dates for the selected dolomite samples. These are the date of 780 ± 200 Ma for the whole rock samples lacking sulfides, the date of 780 ± 110 Ma for primary carbonate phases residual after leaching in 0.5N HBr, and the date of 470 ± 80 Ma for the acid leachates and residual carbonate fractions of one sample bearing sulfide microinclusions. The last date apparently corresponds to the formation time of Pb-Zn mineralization (t_2). One more date of 770 ± 200 Ma is calculated for the Min'yar dolomites using the "isochron t_1-t_2" model and assuming $t_2 = 470$ Ma.

(4) The weighted average value for three dates obtained by different approaches is 780 ± 85 Ma. The relatively high uncertainty of this value characterizing age of the Min'yar Formation is conditioned by irregular epigenetic alterations in the studied rocks, the U-Pb and Pb-Pb systems of which have been variably modified. Nevertheless, the indicated date is concordant with the direct isotopic-geochronological and paleontological data available for the Karatau Group, and also with the results of chemostratigraphic correlation based on the C- and Sr-isotope records. The date can be considered as reliably characterizing age of the middle part of the Min'yar Formation.

(5) The sample selection method and analytical procedure used in this work opens a perspective for obtaining the stratigraphically significant Pb-Pb isochron age of rocks, the U-Pb and Pb-Pb systems of which were reset in the course of epigenetic sulfide mineralization.

REFERENCES

Amelin, Y.V. and Neymark, L.A., Lead Isotope Geochemistry of Paleoproterozoic Layered Intrusions in the Eastern Baltic Shield: Inferences About Magma Sources and U-Th-Pb Fractionation in the Crust-Mantle System, *Geochim. Cosmochim. Acta,* 1998, vol. 62, no. 3, pp. 493-505.

Anfimov, L.V., The Ore Formation in the Riphean Sedimentary Rocks of the Bashkirian Meganticlinorium, *Geologiya zony sochleneniya Urala i Vostochno-Evropeiskoi platformy* (Geology of the Conjugation Zone of the Urals and East European Platform), Sverdlovsk: Ural. Otd. Akad. Nauk SSSR, 1984, pp. 109-112.

Asmerom, I. and Jacobsen, S.B., The Pb Isotopic Evolution of the Earth: Inferences from River Water Suspended Loads, *Earth Planet. Sci. Lett.*, 1993, vol. 15, no. 1/4, pp. 245-256.

Asmerom, Y., Jacobsen, S.B., Knoll, A.H., *et al.*, Strontium Isotopic Variation of Neoproterozoic Seawater: Implications for Crustal Evolution, *Geochim. Cosmochim. Acta,* 1991, vol. 55, no. 10, pp. 2883-2894.

Babinski, M., Chemale, F.J., and Van Schmus, W.R., The Pb/Pb Age of the Minas Supergroup Carbonate Rocks, Quadrilatero Ferrifero, Brazil, *Precambrian Res.,* 1995, vol. 72, no. 3/4, pp. 235-245.

Banner, J.K. and Hanson, G.N., Calculation of Simultaneous Isotopic and Trace Element Variation during Water-Rock Interaction with Applications to Carbonate Diagenesis, *Geochim. Cosmochim. Acta,* 1990, vol. 54, no. 11, pp. 3123-3137.

Barnaby, R.J. and Read, J.F., Dolomitization of a Carbonate Platform during Late Burial: Lower to Middle Cambrian Shady Dolomite, Virginia Appalachians, *J. Sediment. Petrol.,* 1992, vol. 62, no. 6, pp. 1023-1043.

Bartley, J.K., Semikhatov, M.A., Kaufman, A.J., *et al.,* Global Events across the Mesoproterozoic-Neoproterozoic Boundary: C and Sr Isotopic Evidence from Siberia, *Precambrian Res.* (in press).

Bekker, Yu.R., Age and Succession of Deposits of the Karatau Group of the Southern Urals, *Izv. Akad. Nauk SSSR,* Ser. Geol., 1961, no. 9, pp. 49-60.

Bekker, Yu.R., *Mollasy dokembriya* (The Precambrian Molasses), Leningrad: Nedra, 1988.

Brand, U. and Veizer, J., Chemical Diagenesis of a Multicomponent Carbonate System. – I. Trace Elements, *J. Sed. Petrol.,* 1980, vol. 50, no. 4, pp. 1219-1236.

Brand, U. and Veizer, J., Chemical Diagenesis of a Multicomponent Carbonate System – II. Stable Isotopes, *J. Sed. Petrol.,* 1981, vol. 51, no. 3, pp. 987-997.

Butterfield, N.J., Knoll, A.H., and Sweet, K., Paleobiology of the Neoproterozoic Svanbergfjellet Formation, Spitsbergen, *Fossils and Strata,* 1994, no. 34, p. 84.

Choquette, P.W. and James, N.P., Diagenesis in Limestones – 3. The Deep Burial Environment, *Geosci. Canada,* 1987, vol. 14, no. 1, pp. 3-35.

Derry, L.A., Kaufman, A.J., and Jacobsen, S.B., Sedimentary Cycling and Environmental Change in the Late Proterozoic: Evidence from Stable and Radiogenic Isotopes, *Geochim. Cosmochim. Acta,* 1992, vol. 56, no. 3, pp. 1317-1329.

Feoktistov, V.P., Mirkina, S.L., Bekker, Yu.L., and Lyakhnitskii, Yu.S., Isotopic Composition of Ore Leads from Polymetallic Deposits in the Western Slope of the Urals, *Dokl. Akad. Nauk SSSR,* 1978, vol. 238, no. 5, pp. 1214-1217.

Gareev, É.Z., Geochemistry and Formation Conditions of the Min'yar Formation of the Southern Urals, *Stratigrafiya, litologiya i geokhimiya verkhnego dokembriya Yuzhnogo Urala i Priural'ya* (Upper Precambrian Stratigraphy, Lithology, and Geochemistry of the Southern Urals and Adjacent Region), Ufa: Bashkir. Filial Akad. Nauk SSSR, 1986, pp. 50-58.

Garris, M.A., *Etapy magmatizma i metamoifizma* v *doyurskoi istorii Urala i Priural'ya* (Stages of Magmatism and Metamorphism in the Pre-Jurassic History of the Urals and Adjacent Region), Moscow: Nauka, 1977.

Gorokhov, I.M., Diagenesis of Carbonate Sediments: Behavior of Trace Elements and Strontium Isotopes, *Litologiya i paleogeografiya* (Lithology and Paleogeography), Verba, Yu.L., Ed., St. Petersburg: St. Petersb. Gos. Univ., 1996, issue 4, pp. 141-164.

Gorokhov, I.M., Melnikov, N.N., Turchenko, T.L., *et al.,* Two Illite Generations in An Upper Riphean Shale: the Rb-Sr Isotope Evidence, *EUG 8, Strasbourg, France, Abstracts Supplement no. 1 to Terra Nova,* 1995, vol. 7, pp. 330-331.

Gorokhov, I.M., Semikhatov, M.A., Baskakov, A.V, *et al.,* Sr Isotopic Composition in Riphean, Vendian, and Lower Cambrian Carbonates from Siberia, *Stratigr. Geol. Korrelyatsiya,* 1995, vol. 3, no. 1, pp. 3-33.

Gorokhov, I.M., Semikhatov, M.A., Kuznetsov, A.B., and Melnikov, N.N., Improved Reference Curve of Late Proterozoic Seawater $^{87}Sr/^{86}Sr$, *Proceedings of the 4th Int. Symp. on the Geochemistiy of the Earth's Sutface, Yorkshire, England, Theme 5. Land – Atmosphere – Hydrosphere Interactions,* Leeds: 1996a, pp. 714-717.

Gorokhov, I.M., Semikhatov, M.A., Ovchinnikova, G.V., *et al.,* Lead and Strontium Isotopes in Ancient Carbonates from the Urals and Siberia: Evolution of Seawater $^{87}Sr/^{86}Sr$ over the Late Proterozoic, *6th V.M. Goldchmidt Conference, Heidelberg, Germany. J. Conf Abs.,* 1996b, vol. 1, no. 1, p. 207.

Gorozhanin, V.M. and Kutyavin, É.P., Rb-Sr Dating of Glauconite from the Uk Formation, *Dokembrii i paleozoi Yuzhnogo Urala. Ufa* (The Precambrian and Paleozoic of the Southern Urals), Bashkir. Nauch. Tsentr Akad. Nauk SSSR, 1986, pp. 60-63.

Heaman, L.M. and Rainbird, R.H., A Baddeleyite Study of Franklin Igneous Events, Canada, *Geo. Assoc. Can. Mineral. Assoc. Canada Prog.,* 1990, vol. 15, no. A55.

Heaman, L.M., LeCheminsnt, A.N., and Rainbird, R.H., Nature and Timing of Franklin Igneous Events, Canada: Implications for a Late Proterozoic Mantle Plume and Breakup of Laurentia, *Earth Planet. Sci. Lett.,* 1992, vol. 109, no. 2, pp. 117-131.

Hoff, J.A., Jemerson, J., and Hanson, J.N., Application of Pb Isotopes to the Absolute Timing of Regional Exposure Events in Carbonate Rocks: an Example from U-rich Dolostones from the Wahoo Formation (Pensylvanian), Prude Bay, Alaska, *J. Sed. Res.,* 1995, vol. 65, no. 1, pp. 225-233.

Ivanov, K.S., *Osnovnye cherty geologicheskoi istorii (1.6-0.2 mlrd, let) i stroenie Urala* (Main Features of Geological History 1.6-0.2 Ga ago and Structure of the Urals), Yekaterinburg: Inst. Geol. Geokhim. Ural. Otd. Ross. Akad. Nauk, 1998.

Ivanov, S.N., Puchkov, V.N., Ivanov, K.S., *et al., Formirovanie zemnoi koty Urala* (Formation of the Earth's Crust in the Urals), Moscow: Nauka, 1986.

Jahn, B.-M. and Cuvellier, H., Pb-Pb and U-Pb Geochronology of Carbonate Rocks: an Assessment, *Chem. Geol. (Isotope Geosci. Sect.),* 1994, vol. 115, no. 1/2, pp. 125-151.

Jahn, B.-M. and Simonson, B.M., Carbonate Pb-Pb Ages of the Wittenoom Formation and Carawine Dolomite, Hamersley Basin, Western Australia (with Implications for Their

Correlation with the Transvaal Dolomite of South Africa), *Precambrian Res.,* 1995, vol. 72, no. 3/4, pp. 247-261.

Jahn, B.-M., Bertrand-Sarfati, J., Morin, N., and Mace, J., Direct Dating of Stromatolitic Carbonates from the Schmidtsdrif (Transvaal Dolomite), South Africa, with Implication on the Age of the Ventersdorp Supergroup, *Geology,* 1990, vol. 18, no. 12, pp. 1211-1214.

Johnes, C.E., Halliday, A.N., and Lohmann, K.C., The Impact of Diagenesis on High-Precision U-Pb Dating of Ancient Carbonates: an Example from the Late Permian of New Mexico, *Earth Planet. Sci. Lett.,* 1995, vol. 134, no. 3/4, pp. 409-423.

Kaufman, A.J. and Knoll, A.H., Neoproterozoic Variations in the C-Isotopic Composition of Seawater: Stratigraphic and Biogeochemical Implications, *Precambrian Res.,* 1995, vol. 73, no. 1/4, pp. 27-49.

Keller, B.M. and Semikhatov, M.A., Riphean Reference Sections in Continents, *Itogi Nauki Tekh., Ser. Geol. Stratigr., Paleontol.* (Achievements of Science and Technology, Ser. Geol. Stratigr. Paleontol.), Moscow: Vses. Inst. Nauchno-Techich. Inform., 1968, pp. 5-108.

Keller, B.M., Semikhatov, M.A., and Chumakov, N.M., Type Sections of the Upper Erathem of the Proterozoic, *Geologiya dokembriya, 27-oi Mezhdunar. geol. kongress. Sektsiya S-05. Doklady* (The Precambrian Geology, 27th Int. Geol. Congr. Section 05. Reports), Moscow: Nauka, 1984, vol. 5, pp. 56-76.

Knoll, A.H., Archean and Proterozoic Paleontology, *Palynology, Principles and Applications, Am. Assoc. Stratigr., Palinologists Foundation,* 1996, vol. 1, pp. 51-80.

Koroteev, V.A., Krasnobaev, A.A., and Necheukhin, V.M., Upper Proterozoic Geochronology and Geodynamics of the Northern Eurasia, *Rifei Severnoi Evrazii. Geologiya. Obshchie problemy stratigrafii* (The Riphean of Northern Eurasia: Geology and General Problems of Stratigraphy), Yekaterinburg: Ural. Old. Ross. Akad. Nauk, 1997, pp. 28-36.

Kozlov, V.I., *Verkhnii rifei i vend Yuzhnogo Urala* (The Upper Riphean and Vendian of the Southern Urals), Moscow: Nauka, 1982.

Kozlov, V.I., Krasnobaev, A.A., Kozlova, E.V., *et al., Stratigrafiya rifeya v stratotipicheskom razreze Yuzhnogo Urala* (The Riphean Stratigraphy in the Stratotype Section of the Southern Urals), Ufa: Bashkir. Nauch. Tsentr Ural. Otd. Akad. Nauk SSSR, 1991.

Kuznetsov, A.B., Gorokhov, I.M., Mel'nikov, N.N., *et al.,* Dolomitization of the Upper Riphean Carbonates of the Min'yar Formation, Karatau Group, Southern Urals, *Osadochnye formatsii dokembriya i ikh rudonosnost'. Tez. dokl.* (Precambrian Sedimentary Formations and Their Ore-Bearing Potential. Abstracts of Papers), St. Petersburg: Inst. Geol. Geokhronol. Dokembriya Ross. Akad. Nauk, 1998b, p. 31.

Kuznetsov, A.B., Gorokhov, I.M., Semikhatov, M.A., *et al.,* Sr Isotope Composition in Limestones of the Inzer Formation of the Upper Riphean Stratotype, Southern Urals, *Dokl. Akad. Nauk,* 1997, vol. 353, no. 2, pp. 249-254.

Kuznetsov, A.B., Gorokhov, I.M., Semikhatov, M.A., *et al.,* The $^{87}Sr/^{86}Sr$ Ratio in Sea Water at the End of the Late Riphean: Limestones of the Uk Formation, Southern Urals, *Osadochnye fonnatsii dokembriya i ikh rudonosnost'. Tez. dokl.* (Sedimentary Formations of the Precambrian and Their Ore-bearing Potentials. Abstracts of Papers), St. Petersburg: Inst.

Geol. Geokhronol. Dokembriya, Ross. Akad. Nauk, 1998a, pp. 31-32.

Ludwig, K.R., PBDAT for MS-DOS. A Computer Program for IBM-PC Compatibles for Processing Row Pb-U-Th Isotope Data. Version 1.06, US Geol. Surv. Open File Rep. 88-542, 1989.

Ludwig, K.R., Isoplot for MS-DOS. A Plotting and Regression Program for Radiogenic Isotope Data for IBM-PC Compatible Program Computers. Version 2.00, *US Geol. Survey, Open File Rep. 88-557,* 1990.

Maliva, R.G., Knoll, A.H., and Seiver, R., Secular Change in Chert Distribution: a Reflection of Evolving Biological Participation in the Silica Cycle, *Palaios,* 1989, vol. 4, no. 5, pp. 519-532.

Manhes, G., Minster, J.E., and Allegre, C.J., Comparative Uranium-Thorium-Lead and Rubidium-Strontium Study of the Severin Amphoterite: Consequences for Early Solar System Chronology, *Earth Planet. Sci. Lett.,* 1978, vol. 39, no. 1, pp. 14-24.

Maslov, A.V., *Osadochnye assotsiatsii rifeya stratotipicheskoi mestnosti* (Riphean SedimentaryAssociations in the Stratotype Area), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1997.

Maslov, A.V. and Krupenin, M.T., *Razrezy rifeya Bashkirskogo megantiklinoriya (zapadnyi sklon Yuzhnogo Urala)* (Riphean Sections of the Bashkirian Meganticlinorium, Western Slope of the Urals), Sverdlovsk: Ural. Otd. Akad. Nauk SSSR, 1991.

Maslov, A.V., Gareev, É.Z., and Krupenin, M.T., *Osadochnye posledovatel'nosti rifeya tipovoi mestnosti* (Sedimentary Successions of the Riphean in the Type Area). Ufa: GP "Print", 1998.

Maslov, A.V., Abduazimova, Z.M., Karsten, L.A., and Puchkov, V.N., First Findings of *Melanocerillum* in the Riphean Reference Sections of the Southern Urals, *Sostoyanie, problemy i zadachi geologicheskogo kartirovaniya oblastei razvitiya dokembriya na territorii Rossii* (All-Russia Conference: State, Problems, and Objectives of Geological Mapping in the Regions of Precambrian Strata in Russia. Abstracts), St. Petersburg: Vseross. Geol. Inst., 1994, p. 90.

Mirkina, S.L., Lyakhnitskii, Yu.S., Neymark, L.A., and Shirobokova, T.L, Sulfur and Lead Isotopes in Ore Manifestations of Bashkirian Anticlinorium, *Znachenie izotopnykh issledovanii dlya povysheniya ejjfektivnosti i kachestva geologo-poiskovykh rabot* (Significance of Isotope Studies for Efficiency and Quality of Geological Prospecting Works), Mirkina, S.L. and Zagruzina, I.A., Eds., Leningrad: Nedra, 1986, pp. 14-26.

Montañez, I.P. and Read, J.R., Fluid-Rock Interaction History during Stabilization of Early Dolomites, Upper Knox Group (Lower Ordovician), US Appalachians, *J. Sed. Petrol.,* 1992, vol. 62, no. 5, pp. 753-778.

Moorbath, S., Taylor, R.N., Orpen, J.L., *et al.,* First Direct Radiometric Dating of Archean Stromatolite Limestone, *Nature,* 1987, vol. 326, no. 6116, pp. 865-867.

Neymark, L.A., Ore Lead Isotopes and Some Problems of the Ore Genesis, *Izotopnaya geokhimiya protsessa rudoobrazovaniya* (Isotope Geochemistry of the Ore Formation), Moscow: Nauka, 1988, pp. 99-117.

Neymark, L.A. and Iskanderova, A.D., Study on Lead Isotope Composition in Potassium Feldspars using the "Divergent Isochron" Method (Evidence from the Proterozoic Granitoids of

the Baikal Mountains), *Geokhronologiya i geokhimiya izotopov* (Isotopic Geochronology and Geochemistry), Leningrad: Nauka, 1987, pp. 128-151.

Ovchinnikova, G.V., Matrenichev, V.A., Levchenkov, O.A., *et al.,* U-Pb and Pb-Pb Isotope Study of Volcanics front the Khautavaara Greenstone Structure, Central Karelia, *Petrologiya,* 1994, vol. 2, no. 3, pp. 266-281.

Ovchinnikova, G.V., Semikhatov, M.A., Gorokhov, I.M., *et al.,* U-Pb Systematics of Precambrian Carbonates: the Riphean Sukhaya Tunguska Formation of the Turukhansk Uplift of Siberia, *Litol. Polezn. Iskop.,* 1995, no. 5, pp. 525-536.

Ovchinnikova, G.V., Vasil'eva, I.M., Semikhatov, M.A., *et al.,* Pb-Pb Dating of Dolomites from the Min'yar Formation of the Upper Riphean Slratotype, *Osadochnye formatsii dokembriya i ikh rudonosnost'* (Precambrian Sedimentary Formations and Their Ore-Bearing Potential, Abstracts of Papers), St. Petersburg: Inst. Geol. Geokhronol. Dokembriya Ross. Akad. Nauk, 1998a, pp. 50-51.

Ovchinnikova, G.V., Vasil'eva, I.M., Semikhatov, M.A., *et al.,* U-Pb Syslematics of Proterozoic Carbonate Rocks: the Inzer Formation of the Upper Riphean Slratotype (Southern Urals), *Stratigr. Geol. Korrelyatsiya,* 1998b, vol. 6, no. 4, pp. 20-31.

Podkovyrov, V.N., Semikhatov, M.A., Kuznetsov, A.B., *et al.,* Carbonate Carbon Isotopic Composition in the Upper Riphean Slratotype, the Karatau Group, Southern Urals, *Stratigr. Geol. Korrelyatsiya,* 1998, vol. 6, no. 4, pp. 3-19.

Powell, C., Mc, A., Li, Z.X., McElhinny₁ M.W., *et al.,* Paleomagnetic Constraints on Timing of the Neoproterozoic Break-Up of Rodinia and Cambrian Formation of Gondwana, *Geology,* 1993, vol. 21, no. 10, pp. 889-982.

Puchkov, V.N., Paleooceanic Structures of the Urals, *Geotektonika,* 1993, no. 3, pp. 18-33.

Puchkov, V.N., Tectonics of the Urals (Recent Considerations), *Geotektonika,* 1997, no. 4, pp. 42-61.

Raaben, M.E., *Verkhnii rifei kak edinitsa obshchei stratigraficheskoi shkaly* (Upper Riphean As a Unit of the General Stratigraphic Scale), Moscow: Nauka, 1975.

Rainbird, R.H., Heaman, L.M., and Young, G.M., Sampling Laurentia: Detrital Zircon Geochronology Offers Evidence for an Extensive Neoproterozoic River System Origination from the Grenville Orogen, *Geology,* 1992, vol. 20, no. 3, pp. 351-354.

Rainbird, R.H., Jefferson, G.W., and Young, G.M.,The Early Neoproterozoic Sedimentary Succession of Northwestern Laurentia: Correlations and Paleogeographic Significance, *Geol. Soc. Am. Bull.,* 1996, vol. 108, pp. 454-470.

Romer, R.L., Deformation-Related Paleozoic Radiogenic Lead and Strontium Additions in Proterozoic Marbles from the Romback-Sjangeli Basement Culmination., Scandinavian Caledonides, *GFF,* 1994, vol. 116, no. 1, pp. 23-29.

Russell, J., Chadwick, B., Krishna Rao, B., and Vasudiv, V.N., Whole-Rock Pb-Pb Isotopic Ages of Late Archean Limestones, Karnataka, India, *Precambrian Res.,* 1996, vol. 78, no. 4, pp. 261-272.

Semikhatov, M.A., Shurkin, K.A., Aksenov, E.M., *et al.,* New Stratigraphic Scale of the Precambrian in the Soviet Union, *Izv. Akad. Nauk SSSR, Ser. Geol.,* 1991, no. 4, pp. 3-13.

Semikhatov, M.A., Podkovyrov, V.N., Vinogradov, D.P., *et al.,* Carbon Isotope Composition in Riphean Carbonates: the Type Upper Riphean Succession, the South Urals *Precambrian of Europe: Stratigraphy, Structure, Evolution and Mineralization, MAEGS-9. Abstracts* St. Petersburg: IPGG, 1995, p. 101.

Seravkin, I.B., Znamenskii, A.M., Kosarev, A.M,, *et al.,* *Vulkanogennaya metallogeniya Yuzhnogo Urala* (Voleanogenic Metallogeny of the Southern Urals), Moscow: Nauka, 1994.

Sergeev, V.N., *Okremnennye mikrofossili dokembriya i kembriya Urala i Srednei Azii* (Precambrian Silicificd Microfossils from the Urals and Central Asia), Moscow: Nauka, 1992.

Shirobokova, T.I., *Stratiformnye, poliinetallicheskie i baritovye orudeneniya Urala* (Stratiform Polymetallic and Barite Mineralization in the Urals), Sverdlovsk: Ural. Otd. Akad. Nauk SSSR, 1992.

Stratotip rifeya. Paleontologiya. Paleomagnetizm (The Riphean Slratotype: Paleontology and Paleomagnetism), Keller, B.M. Ed., Moscow: Nauka, 1982.

Stratotip rifeya. Stratigrafiya. Geokhmnologiya (The Riphean Stratotype: Stratigraphy and Geochronology), Keller, B.M. and Chumakov, N.M., Eds., Moscow: Nauka, 1983.

Tera, F., Aspects of Isochronism in Pb-Isotope Systematics: Application to Planetary Evolution, *Geochim. Cosmochim. Acta,* 1981, vol. 45, no. 9, pp. 1439-1449.

Torsvik, T.H., Smethurst, M.A., Meert, J.G., *et al.,* Continental Break-Up and Collision in the Paleoproterozoic and Paleozoic – a Tale of Baltica and Laurentia, *Earth Sci. Rev.,* 1996, vol. 4, no 2, pp. 229-258.

Unifitsirovannye regional'nye stratigraficheskie skhemy Urala (Unified Regional Stratigraphic Schemes of the Urals), Yekaterinburg: Ural Otd. Ross. Akad. Nauk, 1993.

Vasil'eva, I.M., Ovchinnikova, G.V., Gorokhov, I.M., *et al.,* Procedure of Separating (Concentrating) Primary and Secondary Carbonates for the Pb-Pb Geochronology, *Osadochnye formatsii dokembriya i ikh rudonosnost'* (Sedimentary Formations of the Precambrian and Their Ore-Bearing Potential, Abstracts of Papers), St. Petersburg: Inst. Geol. Geokhronol. Dokembriya Ross. Akad. Nauk, 1998, pp. 8-9.

Veizer, J., Chemical Diagenesis of Carbonates: Theory and Application, *Stable Isotopes in Sedimentary Geology, SEPM Short Course,* Tulsa: SEPM, 1983, pp. 31-100.

Winter, B.L. and Johnson, C.M., U-Pb Dating of a Carbonate Subaerial Exposure Event, *Earth Planet. Sci. Lett.,* 1995, vol. 131, no. 1/2, pp. 177-187.

Winterhouse, M.J. and Russell, J., Isotopic Systematics of Precambrian Marbles from the Lewisian Complex of Northwest Scotland: Implications for Pb-Pb Dating of Metamorphosed Carbonates, *Chem. Geol. (Isotop. Geosci. Sect.),* 1997, vol. 136, no. 3/4, pp. 295-307.