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U-Pb Systematics of Proterozoic Carbonate Rocks: The Inzer Formation of the Upper Riphean Stratotype (Southern Urals)

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Abstract—U-Pb and Pb-Pb isotopic systems were studied in limestones of the Inzer Formation representing the middle part of the Karatau Group of the Urals, whose section is authorized as the Upper Riphean stratotype. Carbonate rock samples selected to study the U-Pb and Pb-Pb systematics are apparently lacking indications of significant secondary alterations. Geochemical criteria applied to select the least altered samples were ratios $Mn/Sr \leq 0.2$, $Fe/Sr \leq 5$, and $Rb/Sr \leq 0.001$, and also the minimum difference between $^{87}Sr/^{86}Sr$ ratios in primary and secondary carbonate phases separated by sample treating in 1 N solution of ammonium acetate (NH_4OAc). Carbonate fractions, some preliminary treated in NH_4OAc to remove secondary carbonate components, were dissolved in 1 N HCl under the room temperature before extracting U and Pb. Samples of the lower Inzer limestones satisfying the above criteria yielded Pb-Pb age value of 836 ± 25 Ma. This value corresponds to the time of early diagenesis in sediments and represents the isotopic date for the Upper Riphean stratotype best substantiated at present in methodical aspects. Diagenetic alterations in the lower Inzer sediments occurred when U and Pb systems in the latter were open under the influence of fluids derived from the underlying deposits of the Katav Formation. The inferred μ value and Pb isotope composition in the fluid are close to these parameters in siliciclastic fractions of the last formation. The parallel study of U-Pb and Pb-Pb systems of carbonate rocks is useful for detecting conditions of diagenesis and for elucidating the composition and possible source of diagenetic fluids.

Key words: isotopic age, U-Pb systematics, carbonate rocks, diagenesis, Upper Proterozoic, Riphean, southern Urals.

INTRODUCTION

Isotopic dates for the Karatau Group of southern Urals, the authorized stratotype of the Upper Riphean, were represented for a long period by K-Ar dates for glauconites poorly studied in mineralogical aspect and for whole-rock samples of gabbro-diabases, which are considered to be pre-Karatavian in age. The dating of glauconites yielded age values decreasing upward from 970–938 Ma in the lower part of the group to 658–600 Ma near its top, whereas dates for gabbro-diabases, except the evidently rejuvenated values, were approaching 1150–1000 Ma (Garris *et al.*, 1964; Garris, 1977; *Stratotip rifeya*, 1983). Later, the Rb-Sr isochron method applied to the Upper Karatau glauconites yielded the age value of 688 ± 10 Ma (Gorozhanin and Kutuyavin, 1986). On the basis of these and other dates for overlying deposits, the time range of the Karatau Group was estimated as ranging either from 1050 ± 50 to 650 ± 50 (680 ± 20) Ma (Garris, 1977; Keller *et al.*, 1977; *Stratotip rifeya*, 1983, and references in these publications), or from 1000 ± 50 to 650 ± 20 Ma (Keller

et al., 1984; Bibikova *et al.*, 1989; Semikhatov *et al.*, 1991). However, these inferences require some verification in the light of recent data on stability of K-Ar and Rb-Sr systems in the above geochronometers.

The current progress in dating the carbonate rocks by using the U-Pb and Pb-Pb methods (for review and references, see Moorbath *et al.*, 1987; Jahn and Cuvelier, 1994; Ovchinnikova *et al.*, 1995b) opens a new possibility for the determination of the isotopic age of the Karatau Group predominantly composed of limestones and dolomites. In this work, we focused our attention on the Inzer Formation constituting a middle part of the group and represented by limestones, whose secondary alterations are very weak.

The practice of using the U-Pb and Pb-Pb methods for dating the carbonate rocks shows that isochron relations between measured values cannot be observed everywhere, and when this is the case, the calculated isotopic age does not always corresponds to the stratigraphic age of the studied samples. The basic reason here is the reorganization of U-Pb and Pb-Pb systems in

carbonates during their postsedimentation history. Accordingly, one of the essential procedures used in this study was a selection of the least altered rock samples appropriate for the U-Pb dating; we used a series of petrographic, geochemical, and isotopic-geochemical criteria to select them.

STRATIGRAPHIC POSITION AND COMPOSITION OF STUDIED SAMPLES

The Karatau Group, which is terminal in the Riphean type section, includes six formations exposed in the western and central areas of the Bashkir anticlinorium of southern Urals, where the total thickness of these deposits is 3.0 to 5.5 km. The lower (Zil'merdak) and upper (Krivaya Luka) formations are siliciclastic in composition, while four other units of the studied section (Katav, Inzer, Min'yar, and Uk formations) are predominantly or completely composed of carbonate deposits (*Stratotip rifeya*, 1983; Keller *et al.*, 1984; Kozlov *et al.*, 1991). The siliciclastic-carbonate Inzer Formation, whose samples have been analyzed in this study, constitutes the middle part of the sequence. Some time ago, lithostratigraphy of this interval, particularly the relations between its carbonate and siliciclastic members, have been variably interpreted (Komar, 1978; Raaben and Komar, 1983; Krylov, 1983; *Stratotip rifeya*, 1983), but now (Kozlov *et al.*, 1991) it is firmly established that in the western part of the anticlinorium, where we collected our samples, carbonates constitute the lower subformation and the middle member in the upper subformation of the Inzer Formation.

Secondary alterations in carbonate rocks of the Inzer Formation usually are insignificant (Kuznetsov *et al.*, 1997; Podkovyrov *et al.*, 1998). Despite this, in the procedure of U-Pb dating, we used only the samples from the lower subformation representing a monotonous limestone sequence, where the rare beds only experienced dolomitization. We excluded from analysis the upper Inzer limestones occurring as a minor member amid sandy to clayey units of the upper subformation, because their Pb system could be contaminated due to the close proximity to siliciclastic rocks.

The studied samples were collected from two sections (Fig. 1). One of them exhibits the entire Inzer succession and is located at the right-hand side of the Sim River in outskirts of town of Min'yar. The lower Inzer Subformation (Podinzer Beds in terminology of Goryainova and Fal'kova, 1933) represents here the 190-m-thick sequence of dark-gray and black, chiefly aphanic limestones with fine horizontal or rare cross-bedded lamination, and interbeds and lenses of carbonate breccias and flakestones. Within the 35-m-thick horizon in the middle part of the sequence, these rocks experienced dolomitization (Fig. 2). Interbeds of clayey limestone analogous to the same rock types in the underlying Katav Formation occur in the basal part of the subformation. Another section is exposed along the highway Ufa-Beloretsk near the settlement of Kul-

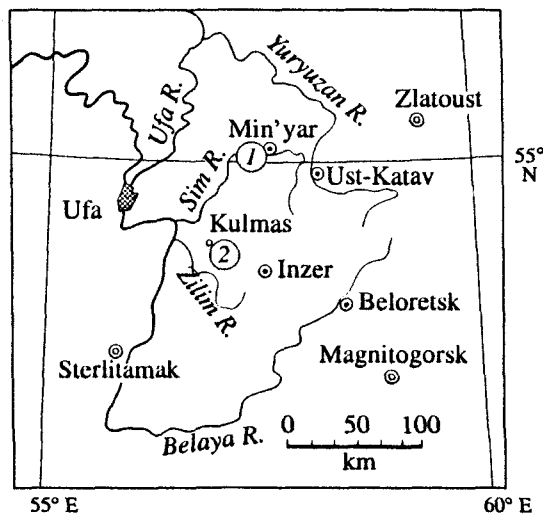


Fig. 1. Geographic map showing the position of the studied Min'yar (1) and Kulmas (2) sections of the Inzer Formation.

mas. This exposure corresponds to the 60-m-thick middle fragment of the lower Inzer Subformation comprising the aforementioned horizon of dolomitic rocks and the limestone member below it. These rocks do not differ in composition and structural features from their counterparts exposed in the Min'yar section.

The recrystallization degree of the lower Inzer carbonates, predominantly represented by micrite and microsparite, is low. In its basal portion, the subformation consists of micritic limestones with thin microsparite lenses and small sparite inclusions. In the upper part, it shows frequently alternating laminae of micrite and microsparite with relict clastic structures and miniature fragments of replaced fibrous calcite. In addition, the fine-grained calcite may form sporadic nests of crystals and occurs as a mineral filling of microfractures in the rock that is characteristic of the Kulmas rather than the Min'yar section. The carbonate fraction of the rocks usually consists of quite pure calcite (Mg content up to 0.35%, Table 1), but in the aforementioned horizon of dolomitic rocks the Mg concentration rises up to 2.5% (Kuznetsov *et al.*, 1997). The low content of residual fraction insoluble in HCl is a characteristic feature of all the rocks. In the studied samples, it is usually 0.2–0.8%; higher values of 1.9 and 4.4% were measured in two cases only (Table 1). The X-ray diffraction data show that the insoluble residue incorporates quartz, less frequent feldspar, and traces of illite. The cathodoluminescent analysis demonstrates that our limestone samples are dominated by nonluminescent calcite, and only rare inclusions of zonal calcite grains of the late generation and their aggregates display the pink to yellow luminescence.

Accumulation of sediments of the lower Inzer Subformation occurred after the paleogeographic rearrangement in the Late Riphean basin of the southern Urals. This event resulted in the following conse-

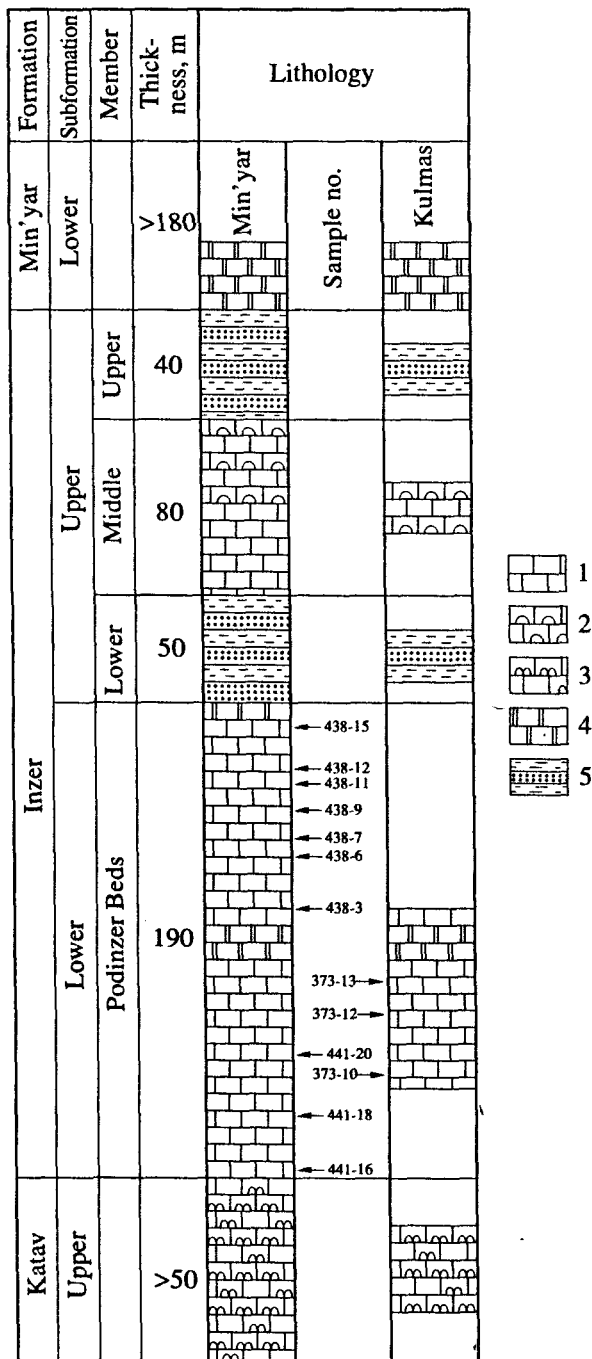


Fig. 2. Lithology and labeled positions of samples in the studied sections: (1) limestones; (2) stromatolitic limestones; (3) clayey limestones; (4) dolomitic limestones and dolomites; (5) siliciclastic deposits.

quences: in reduction of the western provenance, the main source of clastic material during the Zil'merdak-Katav time; in accumulation of thick carbonate and siliciclastic successions in the open-sea settings; and in appearance of the eastern provenance, whose influence on the study region was perceptible only in the late Inzer time (Maslov, 1988). Thus, the studied lower

Inzer deposits of the Min'yar and Kulmas localities accumulated in an open-sea environments outside a zone of active influx of siliciclastic material.

INVESTIGATION METHODS

To study chemostratigraphy (Kuznetsov *et al.*, 1997; Podkovyrov *et al.*, 1998) and isotopic-geochronological parameters of the Karatau carbonates (this work), we selected homogeneous rock samples lacking signs of secondary recrystallization. Each of them was sawed into two parts, one for the chemical and isotopic analysis, and another for studying petrography and cathodoluminescence.

By chemical analysis, samples were dissolved using 1 N HCl. We used the standard weight method to determine contents of Ca and Mg in the carbonate fraction, and the atomic absorption spectrometry to measure concentrations of Mn and Fe. The isotopic dilution mass spectrometry was used to determine concentrations of Rb and Sr.

Selection of samples intended for investigation of U-Pb systematics was performed in two stages. Initially, we selected those samples of 27 available which were known to have low values of Mn/Sr, Fe/Sr, and Rb/Sr ratios, because one of the factors resetting isotopic systems in carbonates is the mineral interaction with fresh-water fluids that rises concentrations of Mn and Fe in carbonates and also is responsible for their depletion in Sr (Brand and Veizer, 1980; Gorokhov, 1996). It should be stressed that we used strict geochemical criteria indicative of low alteration degree, such as $Mn/Sr \leq 0.2$, $Fe/Sr \leq 5$, and $Rb/Sr \leq 0.001$ (Kuznetsov *et al.*, 1997). Another criterion used to verify the low alteration degree of samples was the $\delta^{18}O$ parameter that ranges in unaltered limestones from -7.5 to -8.5% PDB (Podkovyrov *et al.*, 1998).

During the next step of selection, we took into account that Precambrian limestones and dolomites consist of carbonate phases different in age and geochemical parameters, among which only one phase corresponds to the primary carbonate, whereas another (or others) is related in origin to secondary (catagenetic) stages of the rock alteration (Gorokhov *et al.*, 1995b; Ovchinnikova *et al.*, 1995b). Accordingly, we selected for U-Pb dating only those samples, which were found to display the lowest alteration degree in terms of Rb-Sr systematics (Kuznetsov *et al.*, 1997). In practice, we classified our samples as appropriate when they showed a minimum difference between $^{87}Sr/^{86}Sr$ ratios of the primary and secondary phases.

Some of the samples selected for analysis of U-Pb and Pb-Pb isotopic systems were preliminary treated in 1 N solution of ammonium acetate (NH_4OAc) in order to separate their heterogeneous carbonate phases (Gorokhov *et al.*, 1995b; Ovchinnikova *et al.*, 1995b). The samples were dissolved in 1 N HCl under the room temperature for subsequent extraction of U and Pb.

Table 1. Chemical composition of carbonate fractions in limestones of the lower Inzer Subformation

Sample no.	Insoluble residue, wt %	Ca, %	Mg, %	Mn, µg/g	Fe, µg/g	Rb, µg/g	Sr, µg/g	Ca/Sr	Mn/Sr	Fe/Sr
373-10	0.57	39.3	0.13	18	460	0.11	439	900	0.04	1.1
373-12	0.63	39.5	0.51	14	395	0.09	417	950	0.03	0.9
373-13	4.41	39.1	0.43	11	160	0.12	570	660	0.02	0.3
438-3	0.82	39.1	0.35	23	420	0.07	495	790	0.05	0.8
438-6	0.21	40.0	0.26	19	220	0.07	512	780	0.04	0.4
438-7	0.58	39.6	0.23	18	210	—	—	—	—	—
438-9	0.67	39.9	0.24	21	325	0.04	521	770	0.04	0.6
438-11	0.14	39.8	0.19	18	310	—	—	—	—	—
438-12	0.33	40.0	0.19	21	310	0.07	605	660	0.03	0.5
438-15	0.25	40.0	0.18	22	315	0.21	545	730	0.04	0.6
441-16	1.91	39.2	0.11	75	1735	0.33	486	940	0.15	0.8
441-18	0.77	39.5	0.11	44	420	0.15	411	960	0.11	1.1
441-20	0.54	39.7	0.01	15	330	0.19	423	810	0.04	3.6

Abbreviations used below to designate the analyzed rock fractions are as follows: PCC-1 is for the carbonate residue after the sample treatment with NH_4OAc , and this fraction is assumed to be enriched in the primary carbonate component; PCC-2 is for the whole-rock carbonate material untouched by treatment with NH_4OAc ; and ISR is for the residue insoluble in HCl .

Pb isotope composition and concentrations of U and Pb were analyzed in aliquots using the mixed $^{235}\text{U} + ^{208}\text{Pb}$ tracer. U and Pb were separated from bromide solutions using the ion-exchange technique with Bio-Rad 1 × 8 as described by Manhès *et al.* (1978). U and Pb isotope compositions were analyzed on Finnigan MAT-261 multicollector mass spectrometer using a regime of simultaneous measurement of all isotope ion currents. The measured Pb isotope ratios were corrected for mass fractionation of 0.13% per atomic mass unit calculated from replicate measurements of Pb isotope composition in NBS SRM-982 standard. The procedure blank during the period of our investigation was 0.05 ng for U and 0.5 ng for Pb. Raw U-Pb data were processed using the PBDAT program, and isochron regressions were calculated using the Isoplot v. 2.0 package of Ludwig (1989, 1990). All uncertainty values are quoted in the paper at the 2σ level.

RESULTS

The studied sections with labeled positions of the analyzed samples are illustrated graphically in Fig. 2. Data of chemical analysis are summarized in Table 1, and U-Pb isotopic results for different rock fractions are shown in Table 2.

In the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 3), all data points for PCC-1 and PCC-2 plot along a linear array producing two groups with different ranges of

isotopic ratios. Samples 438-6, 438-9, 438-11, and 438-12 from the upper part of the lower Inzer Subformation (the Min'yar locality) represent the first group and reveal the higher values of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. The second group of data points is displaced toward the origin of the coordinates and corresponds to three samples from the same part of the Min'yar section (438-3, 438-7, and 438-15) and to all samples from lower beds of the above locality (441-16, 441-18, and 441-20) and from the Kulmas section (373-10, 373-12, and 373-13).

The combination of all PCC-1 and PCC-2 data points ($n = 19$) defines the Pb-Pb errorchron corresponding to a date of 891 ± 46 Ma with the MSWD value of 21.9. Omission of five data points most obviously deviating from the regression line (PCC-1 and PCC-2 phases of samples 438-9 and 441-16, and PCC-2 phase of Sample 438-3) reduces the date to 836 ± 25 Ma (MSWD = 3.9, $n = 14$). The low MSWD value allows us to consider the last date as statistically reliable. Within the admissible error, this date is concordant with the Pb-Pb age value for the lower Inzer Subformation calculated on the basis of a lesser group of samples (848 ± 48 Ma according to Ovchinnikova *et al.*, 1995a). The result is also well compatible with the succession of K-Ar dates on glauconites from the middle horizons of the Karatau Group: 938 Ma for the upper part of the Katav Formation underlying the Inzer beds; 896–853 Ma for the lower–middle interval of the Inzer Formation; 791–683 Ma for the upper member of this formation; and 740–680 Ma for deposits of the overlying Min'yar Formation (Garris, 1977; *Stratotirifeya*, 1983).

The U-Pb age values calculated on the basis of selected 14 data points turn out to be much older, as compared to the Pb-Pb date, and characterized by much

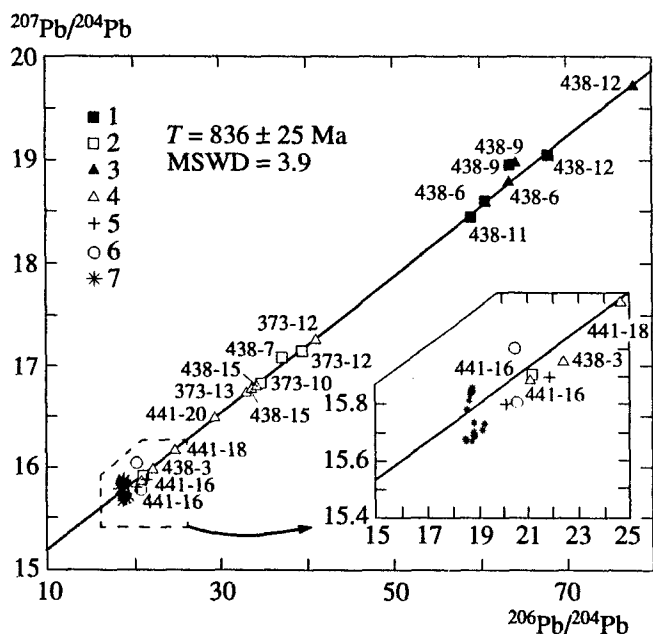


Fig. 3. $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for carbonate rocks from the Inzer and Katav formations: (1–5) data points for the Inzer Formation indicating PCC-I phases of the first (1) and second (2) groups, PCC-2 phases of the first (3) and second (4) groups, and (5) ISR phases of the studied samples; (6–7) data points for the Katav Formation indicating ISR (6) and carbonate (7) phases of limestones (abbreviations are explained in the text).

higher uncertainties and MSWD magnitudes: $T(^{206}\text{Pb}/^{238}\text{U}) = 1160 \pm 150 \text{ Ma}$ with the MSWD value of 7110 and $T(^{207}\text{Pb}/^{235}\text{U}) = 1060 \pm 50 \text{ Ma}$ with the MSWD value of 219. This remark concerns in full measure to U–Pb dates calculated for the second group of samples from the Inzer Formation (Figs. 4, 5). The high magnitude of uncertainties and MSWD indicates a distortion of U–Pb isotopic systems in the studied limestones, especially in the second group of our samples.

The overstated U–Pb ages may be a consequence of the U loss from, and/or Pb introduction into the isotopic system. The migration ability of U under conditions of hypergenesis is well known (Asmerson and Jacobsen, 1993; Jahn and Cuvellier, 1994; Hoff *et al.*, 1995; Jones *et al.*, 1995; Ovchinnikova *et al.*, 1995b), whereas the principal possibility of low-radiogenic Pb introduction into limestones of the lower Inzer Subformation is discussed below. Taking into account all these factors, we consider the U–Pb age values calculated for the whole set of samples as meaningless in the geological aspect and exclude them from the subsequent geochronological considerations. As for the U–Pb ages calculated separately for the first group of our samples (see Figs. 4, 5), they are concordant within the error limits to the Pb–Pb date calculated for the whole group of the analyzed samples. However, the age uncertainty and MSWD estimated for the last group are also high, and these U–Pb dates are excluded from consideration as well.

DISCUSSION

U–Pb systematics of carbonate rocks. Geochemical parameters of the studied Inzer limestones show that their samples attributed to the second group are more rich in U and Pb, as compared to the first sample group, and they are also characterized by the less radiogenic Pb isotope composition and by low measured values of $\mu = ^{238}\text{U}/^{204}\text{Pb}$ (Table 2). This situation may be either a consequence of initial geochemical variations in sedimentation environments, or a result of postdepositional disturbances in U–Pb systems of our samples that is the more likely case.

Difference in U–Pb systematics between both groups of carbonates is well evident in $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{238}\text{U}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{235}\text{U}/^{204}\text{Pb}$ diagrams (Figs. 4, 5). Whereas data points of the second sample group plot along a single trend together with ISR phases of Inzer limestone and with all studied phases of the Katav rocks, those of the first group plot a little above this trend. In addition, MSWD value characterizing the data point dispersion relative to the regression line is much higher for the second group, than for the first one. This suggests that in one rock group the disturbance of U–Pb systems was more significant than in another.

In terms of U–Pb systematics, $\mu_1 = ^{238}\text{U}/^{204}\text{Pb}$ is a decisive parameter of environment (geochemical reservoir), under which the carbonate sediments were accumulated or recrystallized. This parameter is usually calculated in accordance with the one-stage model of Pb evolution. The model suggests that radiogenic Pb isotopes reside in a closed system with a definite μ_1 value at the time ($T = 4.55 \text{ Ga}$) of the Earth formation (Tatsumoto *et al.*, 1973). In the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, the Pb growth curves corresponding to different μ_1 values take their origin from one point characterizing the isotopic composition of primordial Pb of the Earth. Hypothetical data points of the growth curves illustrating the Pb isotope composition in systems with different μ_1 values at the time t plot along a single line (the so-called primary isochron) connecting these points with the point of primordial Pb (whose age is T). Intersection of the primary isochron, whose age is t , and the secondary one, which is plotted on the basis of experimental Pb–Pb data and also corresponds to the age t , defines the model μ_1 value. Such an intersection point belongs to a particular Pb growth curve, and its μ_1 value is characteristic of both this curve and environments of rock formation (Faure, 1986).

Jahn and Cuvellier (1994) demonstrated that the mean μ_1 value calculated in accordance with the one-stage model for carbonates of a wide stratigraphic range (from 2.6 to 0.18 Ga old) is equal to 8.4 ± 0.4 , i.e., it is several orders of magnitude lower than in recent marine carbonates (>50000). Our limestones are not an exception, because the model μ_1 value calculated for the lower Inzer Subformation is equal to 8.4. This striking uniformity of μ_1 values calculated for carbonates highly variable in age indicate that their U–Pb sys-

Table 2. Element concentrations and U-Pb isotopic ratios measured in different rock fractions of the Inzer limestones

Sample no.	Rock fraction	Pb, $\mu\text{g/g}$	U, $\mu\text{g/g}$	μ	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
441-16	PCK-2	1.009	0.247	16.20	21.088	15.887	38.294
441-16	PCK-1	0.971	—	—	21.172	15.907	38.369
441-16	HPO	6.810	3.59	33.99	20.137	15.805	37.697
441-18	PCK-2	—	—	—	24.664	16.164	37.781
441-20	PCK-2	—	—	—	29.397	16.481	37.393
438-3	PCK-2	0.377	0.124	22.09	22.395	15.956	38.165
438-6	PCK-2	0.154	0.346	234.2	63.504	18.808	37.521
438-6	PCK-1	0.167	0.350	213.2	60.694	18.599	37.535
438-7	PCK-1	—	—	—	37.164	17.070	38.765
438-9	PCK-2	0.202	0.488	256.8	64.230	18.982	39.140
438-9	PCK-1	0.209	0.488	247.0	63.493	18.965	39.197
438-11	PCK-1	0.200	0.394	197.4	58.923	18.456	38.146
438-12	PCK-2	0.158	0.435	325.1	77.800	19.732	38.570
438-12	PCK-1	0.177	0.423	261.5	68.162	19.058	38.415
438-15	PCK-2	0.583	0.542	71.49	33.376	16.748	37.892
438-15	PCK-1	0.516	0.628	94.74	34.313	16.809	37.925
373-10	PCK-2	0.639	0.779	96.17	34.092	18.814	39.520
373-12	PCK-2	0.419	0.744	151.5	41.113	17.271	39.514
373-12	PCK-1	0.415	—	—	39.539	17.151	39.330
373-13	PCK-2	0.624	0.586	72.67	32.902	16.714	38.992
373-13	HPO	16.50	5.73	22.76	21.851	15.905	37.099

tems were reset at the similar stages of lithogenesis in response to the Pb introduction and, possibly, to the U loss. Accordingly, the U-Pb and Pb-Pb isotopic dates for carbonates, which did not suffer catagenetic and metamorphic alteration, reflect the age of this process. The known experience of dating shows that in the case of nonmetamorphosed marine carbonates their U-Pb systems were reset in the course of early diagenesis, when carbonate minerals incorporated the mixed leads consisting of fractions derived from sediments themselves and introduced by diagenetic fluids (Haglund *et al.*, 1969; Russell *et al.*, 1994; Jahn and Cuvellier, 1994; Ovchinnikova *et al.*, 1995b; Johnes *et al.*, 1995; Jahn and Simonson, 1995).

The calculated $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ age is correct only then, when the U-Pb systems in a series of studied samples either remained closed since the moment of early diagenesis, or episodically opened at the very beginning of the rock history and/or in the recent time. It is likely that these systems of the Inzer carbonates opened two times. However, such an opening in the course of the early diagenesis (the initial stage of the rock history) and the U loss during the recent hypergenesis do not discredit the correctness of the Pb-Pb dating.

Naturally, a case of mixing the materials with different Pb isotope composition could also produce a straight regression line in the $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. In this case however, we should expect the same correlation between data points in the $^{208}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates. For the Inzer car-

bonates, the last assumption is invalid, and the mixing model seems to be hardly appropriate to the occasion. Therefore, we may consider the straight line in Fig. 3 as an isochron, whose inclination angle is meaningful in the geochronological aspect.

Thus, the Pb-Pb age value of 836 ± 25 Ma calculated on the basis of 14 data points apparently corresponds to the time of early diagenesis of carbonate sediments of the lower Inzer Subformation. This inference is supported by Rb-Sr isochron age values of 805–835 Ma measured for the fine-grained mineral fractions of the Inzer shales and corresponding to a later geological event of burial diagenesis (Ovchinnikova *et al.*, 1995a; Gorokhov *et al.*, 1995a).

Source of diagenetic fluids. Comparing the U-Pb systematics of the lower Inzer carbonates and underlying limestones of the Katav Formation (unpublished data of Ovchinnikova and Vasil'eva), we may get an insight into the essence of postsedimentation geochemical processes in the studied part of the Karatau Group. As one can see in $^{238}\text{U}/^{204}\text{Pb}$ -U and $^{238}\text{U}/^{204}\text{Pb}$ -Pb diagrams (Figs. 6, 7), in the carbonate phase of the Inzer samples have higher μ values and are enriched in U, but significantly depleted in Pb (2–10 times of magnitude) as compared to the carbonate phase of the Katav limestones. This is especially characteristic of the first group of the Inzer carbonates, while data points of the second group plot closer to siliciclastic phases of the studied rock samples from both formations. As one would expect, U and Pb concentrations in the last

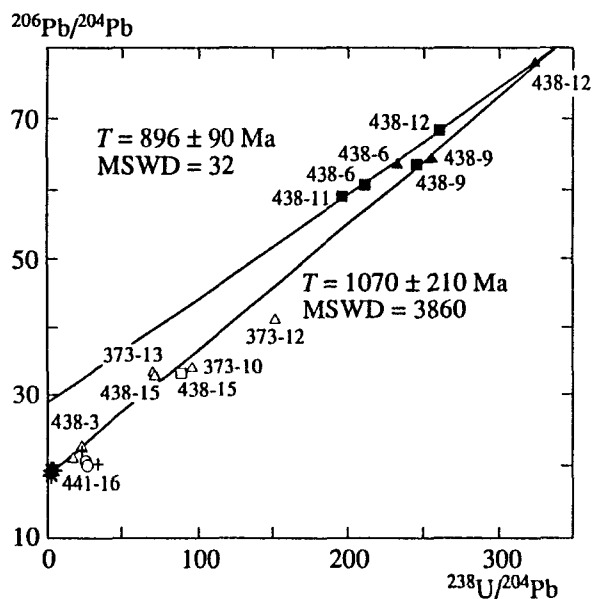


Fig. 4. $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{238}\text{U}/^{204}\text{Pb}$ diagram for carbonate rocks from the Inzer Formation (symbols as in Fig. 3).

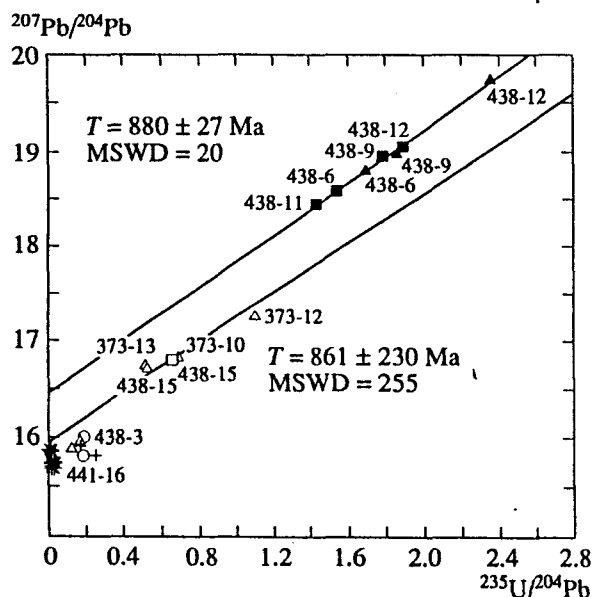


Fig. 5. $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{235}\text{U}/^{204}\text{Pb}$ diagram for carbonate rocks from the Inzer Formation (symbols as in Fig. 3).

phases are much higher than in carbonates, but their measured μ values are lower.

A significant exchange of Pb isotopes between carbonate and noncarbonate phases (siliciclastic material including) is shown to be a feature of diagenesis and metamorphism (Moorbath *et al.*, 1987; Farquhar *et al.*, 1994; Jahn and Cuvellier, 1994; Babinski *et al.*, 1995; Ovchinnikova *et al.*, 1995b). Consequently, one may assume that a high content of siliciclastic (mostly clayey) fraction in the Katav limestones (14.4% in

average according to data published by Kuznetsov *et al.* (1995a), was the main factor responsible for enrichment of diagenetic fluids in U and Pb, and for a lower $^{238}\text{U}/^{204}\text{Pb}$ ratio in the fluids as compared to carbonate sediments. This resulted not only in a radical disturbance of Rb-Sr and U-Pb systems of the Katav limestones whose PCC-1 phases were enriched in Pb and radiogenic ^{87}Sr (Kuznetsov *et al.*, 1995b), but also in a partial growth of low-radiogenic Pb content in the overlying Inzer carbonates (especially in the second group of our samples). This assumption appears to be supported by the relative stratigraphic position of samples attributed to the first and second groups (Fig. 2), and by data implying that during the compaction of sediments, fluids predominantly migrate in the vertical direction (Choquette and James, 1987). Nevertheless, among samples whose data points highly deviate from the isochron regression line (Fig. 3), two (438-3 and 438-9) are located in the upper horizons of the subformation, and only one (441-16) is collected from its lower part. This situation may indicate that local factors contributed as well to changes in U-Pb systems of the studied samples.

The early diagenetic disturbance of U-Pb systems of the studied Inzer carbonates are responsible for a significant dispersion of data points relative to the regression lines in Figures 4 and 5. Consequently, the intersection points between these lines and axes of ordinates, i.e., the initial Pb isotope composition, can be defined with a considerable uncertainty. As we calculated at the confidence level of 95%, $(^{206}\text{Pb}/^{204}\text{Pb})_0$ and $(^{207}\text{Pb}/^{204}\text{Pb})_0$ ratios range within 25.5–32.2 and 16.3–16.5, respectively, for the first group of samples, and within 16.6–23.6 and 15.6–16.1, for the second one. Despite the high uncertainty, the calculated ranges suggest that the initial Pb isotope composition was somewhat different in the first and second group of carbonates, though they do not prove this directly. Nevertheless, the Pb-Pb age values calculated separately for each group are concordant within the error limits with the age value estimated on the basis of all data points. Consequently, a difference in the initial composition of Pb isotopes, if possible at all, was not greater than the analytical error.

At the same time, both groups of carbonates are clearly different in their ranges of ^{208}Pb and ^{206}Pb content (Fig. 8). In the studied limestones, any correlation between isotopic ratios of ^{206}Pb , the decay product of ^{238}U , and ^{208}Pb , the decay product of ^{232}Th , is lacking, and this is a consequence of the extremely low (approaching zero) value of $^{232}\text{Th}/^{238}\text{U}$ ratio in the sea water and recent carbonate sediments. Dispersion of data points in this diagram reflects the variable $^{208}\text{Pb}/^{206}\text{Pb}$ ratios in the diagenetic fluid whose isotopic composition was controlled by Pb derived from the siliciclastic ISR phase of the Katav limestones. A separate position of data point areas illustrating the ^{208}Pb distribution in siliciclastic ISR phases of the Katav limestones, on the one hand, and of the Inzer limestones, on the other (Fig. 8), sug-

gest a primary difference in composition of siliciclastic material in both formations. In their $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, the Inzer carbonate phases of the second group of our samples (sample series 373 and some samples from series 441) are more similar to ISR phases of the Katav limestones (Fig. 8), and this similarity favors the assumption that silicate components of the latter affected the chemical and isotopic composition of diagenetic fluids responsible for the distortion of Pb-Pb systems in the Inzer carbonates.

Considering the aforementioned geochemical factors, we may understand why data points of three studied samples (PCC-1 and PCC-2 phases of samples 438-9 and 441-16, and PCC-2 phase of sample 438-3) significantly deviate from the linear regression line shown in $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 3).

In the $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{238}\text{U}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{235}\text{U}/^{204}\text{Pb}$ diagrams (Figs. 4, 5), data points of both carbonate phases from samples 438-3 and 441-16 plot close to data points of ISR phases and thus demonstrate that carbonates have been contaminated with Pb derived from the silicate fractions. This conclusion well accords with a high content of siliciclastic material, Fe, and Mn in Sample 441-16 (Table 1), and also with its stratigraphic position directly above the thick Katav carbonate succession containing a considerable admixture of fine clayey material enriched in Fe (Gareev, 1982).

Sample 438-3 was collected in the upper part of the lower Inzer Subformation above a horizon of dolomitic limestone that separates the sample series 441 and 438 (see Fig. 2). As this sample, when compared to many others, is enriched in ISR and Fe and shows a higher Fe/Sr ratio (Table 1), we may suspect that in this case the U-Pb system was also distorted because of the isotopic exchange between siliciclastic and carbonate fractions of the rock. However, Sample 373-13 shows a higher ISR content than Sample 438-3 (4.41 versus 0.82%), but the data point of the former plots on the isochron line. This controversial situation may reflect some peculiar features of ISR phases of these samples.

PCC-1 and PCC-2 phases of Sample 438-9 plot significantly above the Pb-Pb isochron (Fig. 3), and this may be a consequence of several factors: (1) the sample may be older than others; (2) Pb isotope composition in diagenetic fluid could be unusual; (3) there was the U loss from the system, or the ^{238}U decay chain was disturbed in response to Rn loss; (4) the initial Pb isotope composition in this carbonate phase was different as compared to that in others.

We can easily exclude the first factor, because the sample under consideration is one in a series collected from the continuous stratigraphic succession of deposits (Fig. 2). The second factor also appears to be unrealistic. The carbonate fraction of Sample 438-9 exhibits higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than all studied ISR phases, and this eliminates a possibility of contamination with Pb derived from the silicate compo-

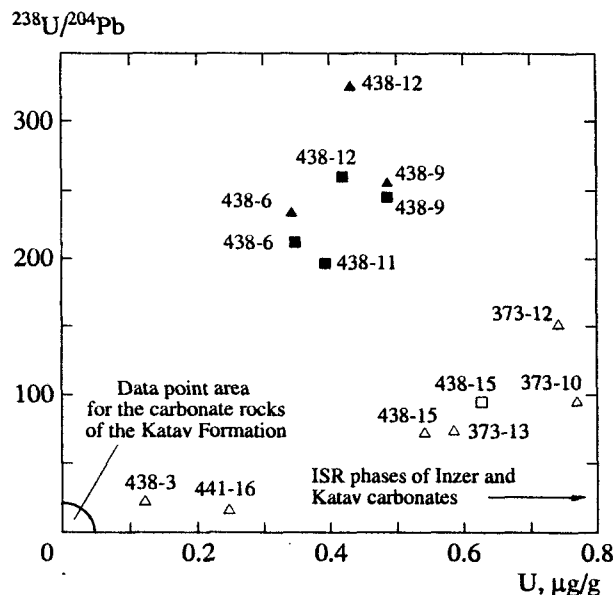


Fig. 6. $^{238}\text{U}/^{204}\text{Pb}$ ratios and U concentrations in the first and second group of the Inzer carbonates (symbols as in Fig. 3).

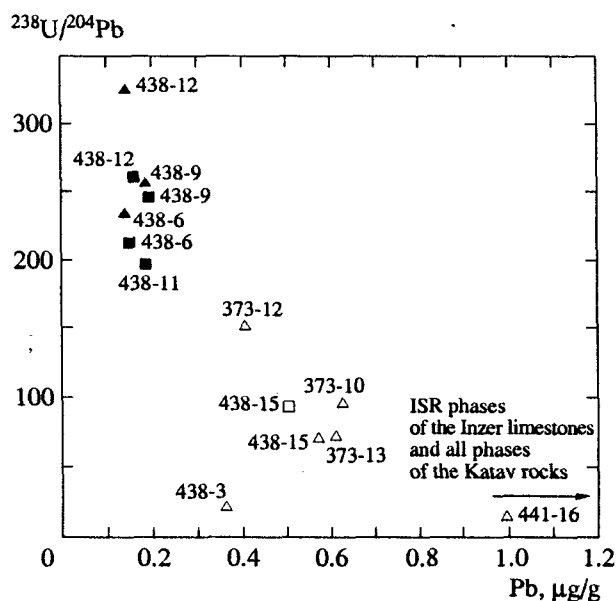


Fig. 7. $^{238}\text{U}/^{204}\text{Pb}$ ratios and Pb concentrations in the first and second group of the Inzer carbonates (symbols as in Fig. 3).

nents. In addition, low concentrations of Mn and Fe in the sample together with low Mn/Sr and Fe/Sr ratios exclude a chance that some exotic Pb entered the system with meteoric waters.

In contrast, the third and fourth factors appear to be quite real. Displacement of data points upward from the isochron (and accordingly, the greater Pb-Pb age) may result from both the U loss from the rock (Moorbath and Taylor, 1985), and the degassing of ^{222}Rn , an intermediate decay product of ^{238}U . The half-life of ^{222}Rn is

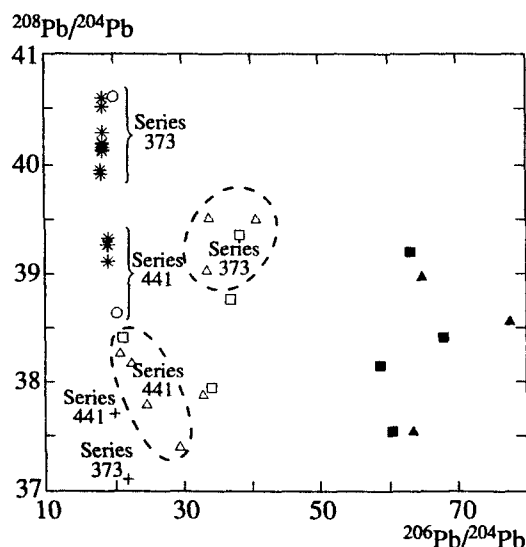


Fig. 8. $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for carbonates from the Inzer Formation (symbols as in Fig. 3).

several orders of magnitude greater than this parameter of ^{219}Rn , one of isotopes in the decay chain of ^{235}U (3.82 days versus 3.92 seconds), and hence the potential diffusion loss is much higher for the former, than for the latter. After a considerable period of time, this factor may and must significantly increase isotopic ratios of ^{207}Pb and ^{206}Pb , the final decay products of ^{235}U and ^{238}U . Disturbance of U-Pb systems in response to diffusion loss of ^{222}Rn was revealed in the course of investigation of the uranium ores (Ludwig *et al.*, 1981; Holliger *et al.*, 1989) and Proterozoic carbonates (Jahn and Cuvellier, 1994). In such a case, the Pb-Pb age turns out to be overstated, whereas the age value calculated on the basis of $^{206}\text{Pb}/^{238}\text{U}$ ratio is understated. In contrast, the ^{235}U - ^{207}Pb system in the same sample retains a quasi-closed state, because the diffusion loss of ^{219}Rn is neglectfully small. Distribution of data points corresponding in Figs. 5 and 6 to PCC-1 and PCC-2 phases of Sample 438-9 is consistent with these considerations.

The last opportunity that Sample 438-9 is unusual with respect to the initial Pb isotope composition cannot be disregarded as well. Because of a short residence time of Pb in the sea water (≈ 50 years), isotopic ratios of this element in a sea basin could vary in space and with time depending on the Pb isotope composition in the continental runoff. From this viewpoint, our Sample 438-9 may correspond, though not necessarily, to the stratigraphic level of carbonates incorporating the more radiogenic, and consequently the older initial Pb.

Comparison of the behavior of U-Pb and Rb-Sr systems in carbonates of the lower Inzer Subformation. The sample series used to analyze the Rb-Sr systematics (Kuznetsov *et al.*, 1997) includes 11 samples considered in this work along with one sample from the horizon of dolomitic limestones in the middle part of the subformation, and Sample 441-15 from its basal

portion in the Min'yar section. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for PCC-1 phases of samples from the Min'yar section are within the range of 0.70525–0.70538, i.e., they are lower than any values previously published for coeval deposits. The last named fact and aforementioned strict criteria used to select the least altered samples allow us to consider the above range as adequately characterizing the Sr isotope composition in the sea water of the middle Late Riphean time. In other words, the primary carbonate phases of these samples attained first an isotopic equilibrium with the sea-water Sr, and afterward their Rb-Sr systems stood closed at the stage of early diagenesis and during the subsequent geological history. Only two samples from the base of the Min'yar section (441-15 and 441-16) represent an exception, since they show higher values of Fe/Sr, Rb/Sr, Mn/Sr, and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and this is interpreted as a result of influence of fluids derived from the underlying clayey carbonates of the Katav Formation (Kuznetsov *et al.*, 1997).

The lower Inzer carbonates of the Kulmas section differ from coeval rocks of the Min'yar sequence in having greater magnitudes of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, although they also satisfy all the criteria used to select the least altered samples. This disturbance of their Rb-Sr isotopic systems was interpreted as a result of secondary alterations, which were not reflected in the geochemical parameters but still were manifested in a higher recrystallization degree of the rocks (Kuznetsov *et al.*, 1997).

Thus, the initial Rb-Sr signature is generally preserved in the analyzed Inzer carbonates of the Min'yar section, whereas it is changed in the rocks of the Kulmas locality. At the same time, the U-Pb systems of limestones from both localities turned out to be open at the early diagenetic stage. This is evident from μ_1 values characteristic of all samples and from enrichment of carbonates of the second group in the common Pb derived from the silicate components of the underlying Katav deposits. Analyzing the behavior of U-Pb and Rb-Sr isotopic systems in the Inzer limestones, we may divide the studied samples into three categories, each corresponding to a particular state of stability of the above systems.

The first category is classed with samples collected from the upper part of the Min'yar section, whose PCC-1 phases are enriched in radiogenic Pb and show lower values of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (the first of groups considered above). The Rb-Sr systems of these samples stood closed after the sedimentation stage, whereas the U-Pb systems experienced transformations at the early diagenetic stage ($\mu_1 = 8.4$) and evolved under the quasi-closed conditions afterward.

The second category is represented by several limestone samples (438-3, 438-7, and 438-15) from the lower and, partly, from the upper parts of the Min'yar section, which preserve the initial Rb-Sr signature, but are enriched in U and Pb. The Pb isotope composition

in these samples is less radiogenic, and measured μ values are lower than in carbonates of the first category.

In both cases, the behavior of U-Pb and Rb-Sr systems appears to be understandable, if we accept the above conclusion that the composition of diagenetic fluids in the Inzer sediments was formed under the influence of the underlying clayey limestones of the Katav Formation. The Pb content in the latter is 2–10 times higher than in the Inzer carbonates, whereas the Sr concentration is 4–5 times lower (Anfimov *et al.*, 1987; Kuznetsov *et al.*, 1997). It is quite likely that the Rb/Sr ratio in the diagenetic fluid, which migrated into the Inzer deposits, was close in average to its value in the whole-rock samples of the Katav limestones. This fluid with high Pb and low Sr concentrations significantly transformed the U-Pb systems in a large volume of the Inzer deposits, and to a lesser extent affected their Rb-Sr systems. The latter were noticeably transformed only in the lowermost beds of the subformation (samples 441-15 and 441-16). In this connection, we should remember that the PCC-1 phase of the last sample plots clearly away from the Pb-Pb isochron in Fig. 3.

Finally, all samples from the Kulmas section represent the third category. Like in the second category, these samples reveal the lowered $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, the rather high concentrations of U and Pb, and low measured values of μ , but they display a somewhat higher range of the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. As we believe, the postdiagenetic recrystallization that transformed the Rb-Sr systems of the rocks (Kuznetsov *et al.*, 1997) occurred soon after the early diagenesis. Otherwise, the samples from the Kulmas section would not plot at the same isochron together with other samples of the Inzer limestones. Unfortunately, any reliable geological information about the recrystallization time of the Kulmas carbonate deposits is unknown.

Thus, the degree of diagenetic transformations in U-Pb and Rb-Sr systems of the Inzer carbonates was dependent on the isotopic composition and concentrations of Pb and Sr in these deposits and diagenetic fluids. All the factors are obviously variable and may differently influence the migration ability of components of both isotopic systems under particular conditions of diagenesis. The comparative analysis of U-Pb and Rb-Sr systematics is a useful approach, if the objective is to understand the geochemical features of lithogenesis in the history of marine carbonates.

CONCLUSION

(1) The isochron Pb-Pb age of the lower Inzer Subformation is calculated as equal to 836 ± 25 Ma on the basis of 14 data points of the limestone samples collected near the town of Min'yar and at the Kulmas locality. This value corresponds to the time of the early diagenetic stage in sediments; it currently represents

the most reliable isotopic date for the Upper Riphean type section—the Karatau Group of the southern Urals.

(2) Deposits of the subformation experienced the diagenetic alteration under influence of fluids that distorted their initial U-Pb systems. The fluids migrated from the underlying deposits of the Katav Formation and were close in the μ value and Pb isotope composition to the siliciclastic fraction of these deposits. Based on the comparative analysis of U-Pb systematics of the Inzer and Katav limestones, this inference is well compatible with the stratigraphic position of samples whose U-Pb systems have been disturbed to a different extent.

(3) The considered data on U-Pb and Rb-Sr systems in carbonate deposits show that these systems are variably resistant against various postsedimentary alterations. They elucidate conditions of the rock diagenesis, and also the likely source and composition of diagenetic fluids.

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