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THE CARBON-ISOTOPIC COMPOSITION OF PROTEROZOIC CARBONATES: RIPHEAN SUCCESSIONS FROM NORTHWESTERN SIBERIA (ANABAR MASSIF, TURUKHANSK UPLIFT)

ANDREW H. KNOLL*, ALAN J. KAUFMAN*, and MIKHAIL A. SEMIKHATOV**

ABSTRACT. Thick carbonate-dominated successions in northwestern Siberia document secular variations in the C-isotopic composition of seawater through Mesoproterozoic and early Neoproterozoic (Early to early Late Riphean) time. Mesoproterozoic dolomites of the Billyakh Group, Anabar Massif, have $\delta^{13}C$ values that fall between 0 and −1.9 permil versus PDB, with values in the upper part of the succession (Yusmastakh Formation) consistently higher than those of the lower (Ust'-Il'ya and Kotuikan formations). Consistent with available biostratigraphic and radiometric data, $\delta^{13}C$ values for Billyakh carbonates compare closely with those characterizing early Mesoproterozoic carbonates (about 1600-1200 Ma) worldwide. In contrast, late Mesoproterozoic to early Neoproterozoic limestones and dolomites in the Turukhansk Uplift exhibit moderate levels of secular variation. Only the lowermost carbonates in the Turukhansk succession (Linok Formation) have $\delta^{13}C$ values that approximate Billyakh values. Higher in the Turukhansk succession, $\delta^{13}C$ values vary from −2.7 to +4.6 permil (with outliers as low as −5.0 permil interpreted as diagentically altered). Again, consistent with paleontological and radiometric data, these values compare well with isotopic values from 1200 to 850 Ma successions elsewhere. Five sections measured in different parts of the Turukhansk basin show nearly identical patterns of variation, confirming that carbonate $\delta^{13}C$ correlates primarily with time and not facies. The Siberian sections illustrate the potential of integrated biostratigraphic and chemostratigraphic data in the intra- and interbasinal correlation of Mesoproterozoic and early Neoproterozoic rocks.

INTRODUCTION

Because of the isotopic fractionation attendant on autotrophic CO_2 fixation and a requirement for isotopic mass balance between carbon entering and leaving the oceans, the isotopic compositions of carbonate C and organic C reflect the instantaneous burial ratio of the two phases (Broecker, 1970; Hayes, 1983). The pattern of secular variation in the $\delta^{13}C$ of marine carbonates is relatively well known for the past 545 my (Ma). The Phanerozoic record shows both broad trends, such as a 6 to 7 permil increase from the Early Cambrian to the Pennsylvanian (Veizer, Holser, and Wilgus, 1980; Popp, Anderson, and Sandberg, 1986), and short-lived excursions, epitomized by a sharp 2 permil drop at the Cretaceous-Tertiary boundary (Zachos and Arthur, 1987). Both long and short term carbon-isotopic events have figured prominently in investigations of Phanerozoic biogeochemical history (Berner 1989; Kump, 1991;

* Botanical Museum, Harvard University, Cambridge, Massachusetts 02138.
** Geological Institute of the Russian Academy of Sciences, Moscow 109017, Russia.

Hayes and others, 1989; Freeman and Hayes, 1992). Their stratigraphic potential has also been recognized, although in general it is overshadowed by biostratigraphy.

Because the Phanerozoic Eon represents only the most recent 12 percent of Earth history, it is important to trace the C-isotopic record backward through Proterozoic and Archean time. Eichmann and Schidlowski (1975; Schidlowski, Eichmann, and Junge, 1975) pioneered studies of the Precambrian record, reporting values for scattered individual samples or groups of samples from numerous successions. Given the difficulties of correlating among sections and relating them to a chronometric time scale, only long term patterns could be recognized. Their principal conclusion (see also Schidlowski, Hayes, and Kaplan, 1983) was that the C-isotopic composition of carbonates varied only within strict limits ($\delta^{13}C = 0 \pm 2$ permil) during the long Archean and Proterozoic eons.

More recently, emphasis has shifted to detailed studies of isotopic variation within individual Proterozoic successions (Tucker, 1986; Magaritz, Holser, and Kirschvink, 1986; Knoll and others, 1986, in press; Aharon, Schidlowski, and Singh, 1987; Fairchild and Spiro, 1987; Derry and others, 1989; Fairchild, Marshall, and Bertrand-Sarfati, 1990; Kaufman and others, 1991; Kaufman, Knoll, and Awramik, 1992; Kaufman, Jacobsen, and Knoll, 1993; Kirschvink and others, 1991; Pokrovsky and Vinogradov, 1991; Pokrovsky and Gertsev, 1993; Narbonne, Kaufman, and Knoll, 1994; Veizer, Clayton, and Hinton, 1992; Veizer and others, 1992; Mirota and Veizer, 1994; Kaufman and Knoll, in press). Samples collected at 1 to 25 m intervals within measured sections provide a record of secular variation on a relatively fine time scale. Indeed, only by building a data base of basinal studies can one hope to identify any but the broadest trends in Precambrian C-isotopic variation.

To date, most reported data for Precambrian successions come from Neoproterozoic (Late Riphean and Vendian; 1000 to about 545 Ma) basins. These have revealed an unanticipated pattern of secular variation having significant biogeochemical and chemostratigraphic implications (Kaufman and Knoll, in press). Beginning about 850 Ma and lasting until about 570 Ma, carbonates were commonly enriched in ^{13}C by 4 to 8 permil. The organic carbon burial rates implied by these data provide a key to understanding the coupled physical and biological events that ushered in the Phanerozoic Eon (Knoll, 1991; Derry, Kaufman, and Jacobsen, 1992; Kaufman, Jacobsen, and Knoll, 1993). The overall pattern of high $\delta^{13}C$ is punctuated by brief excursions to values of 0 to -2 permil, at least some of which correlate lithostratigraphically with Neoproterozoic ice ages. This oscillating isotopic signal provides a chemostratigraphic indicator analogous to that of oxygen isotopes in Pleistocene carbonates, albeit at a far coarser scale of resolution.

The marked secular variation of the later Neoproterozoic Era appears all the more notable in that published data for older Neoproterozoic and Mesoproterozoic rocks do *not* suggest comparable variations.

Most 1600 to 850 Ma old carbonates compiled by Schidlowski, Hayes, and Kaplan (1983) have $\delta^{13}C$ values of 0 ± 2 permil. Grab sample analyses of coeval kerogens indicate a similar monotony, with $\delta^{13}C_{org} = -30 \pm 2$ permil (Des Marais and others, 1992; Strauss and others, 1992).

To a first approximation the emerging stratigraphic picture for the Mesoproterozoic (Lower and Middle Riphean; 1600-1000 Ma) and Neoproterozoic eras is probably accurate: $\delta^{13}C$ varied within relatively narrow limits from 1600 Ma (or earlier) until about 850 Ma ago, when coupled tectonic and biogeochemical changes produced marked variation in the C-isotopic record. However, this picture remains impressionistic, particularly for the Mesoproterozoic, because most available data come from widely scattered samples that have poorly constrained stratigraphic relationships and limited information on diagenesis or depositional environment. The vast volume of Meso- and Neoproterozoic carbonates preserved in Siberia affords an opportunity to expand the available data set using well studied stratigraphic sections. In this paper, we report C-isotopic data for Mesoproterozoic and early Neoproterozoic carbonate successions from six measured sections of two Siberian basins (fig. 1). The Siberian data permit us to test and augment patterns of secular variation proposed previously. They also provide an opportunity to evaluate down-dip isotopic variation within a single Proterozoic basin.

STRATIGRAPHIC SETTING

Samples analyzed in this study were collected by one of us (MAS), P. Yu, Petrov, V. N. Sergeev, and A. F. Veis in key sections of Mesoproterozoic and Neoproterozoic carbonates from the Anabar Massif and Turukhansk Uplift (figs. 1-3). All published descriptions of these successions are in Russian (Semikhatov, 1962; Keller, 1963; Komar, 1966; Zlobin and Golovanov, 1970; Serebryakov, 1975; Semikhatov and Serebryakov, 1983; Kozlov, Votakh, and Alexandrova, 1988). Therefore, because stratigraphic and sedimentological data are critical to our geochemical interpretations, we offer a stratigraphic summary here.

Anabar Massif.—Some 2000 to 2200 m of flat-lying (2°-5°) Riphean strata occur in the Anabar region. The most complete and best studied section is the one we sampled along the Kotuikan River (fig. 2). Here, the light color of organic-walled microfossils, even near the base of the section, indicates that the succession has never been heated above about 70°C (Gorokhov and others, 1991). The Riphean succession begins with the 600 to 640 m thick Mukun Group, which rests on crystalline basement. Mukun strata are predominantly oxidized siliciclastic rocks characterized by cross-bedding, ripple marks, mud cracks, scour surfaces, and channels that indicate flood plain to coastal marine deposition. These rocks are conformably overlain by the predominantly dolomitic Billyakh Group (fig. 2).

The basal Billyakh Ust'-Il'ya Formation is a thin (55-60 m) succession consisting largely of interbedded planar to hummocky cross-stratified sandstones and shales deposited in a storm-influenced, mid-

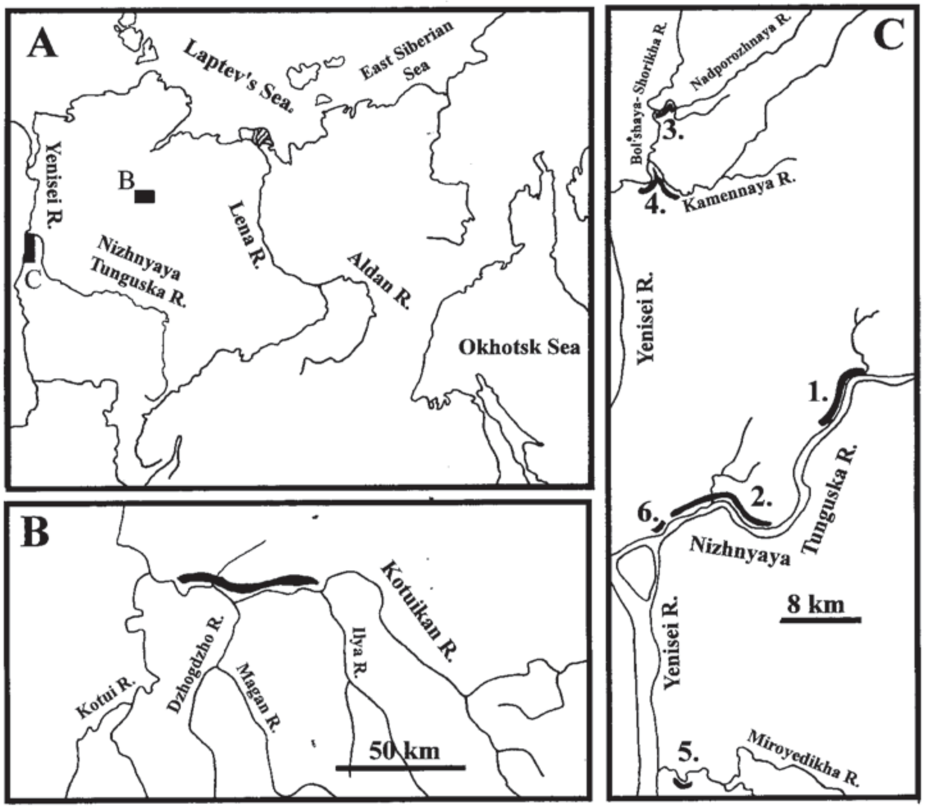

Fig. 1(A) Index map of northern and northwestern Siberia, showing the locations of the regions shown in maps B and C; (B) the western slope of the Anabar Massif with the location of sampled outcrops shown as a solid stripe along the Kotuikan River; (C) the Turukhansk Uplift with locations of sampled outcrops shown as solid stripes: (1) eastern Nizhnyaya Tunguska section, (2) central Nizhnyaya Tunguska section, (3) Nadporozhnaya River section, (4) Kamennaya-Bol'shaya Shorika River sections, (5) Miroyedikha River section, and (6) western Nizhnyaya Tunguska River section.

shelf setting. The shales contain abundant organic-walled microfossils (Veis and Vorobyeva, 1992). Subordinate clastic and stromatolitic dolomites occur in the upper part of the formation. Ust'-Il'ya strata are succeeded by the 450 to 500 m thick Kotuikan Formation. Lower Kotuikan rocks (250-320 m) comprise a mid-shelf accumulation of columnar stromatolitic bioherms bounded both laterally and vertically by inter-reefal shales, flat pebble dolorudites, and rare quartzose and dolomitic sandstones exhibiting hummocky cross-stratification. Inter-reefal shales contain scattered acritarchs and filamentous microfossils (Veis and Vorobyeva, 1992).

The 170 to 190 m thick Upper Kotuikan Member is a peritidal succession of stratiform to domal stromatolites and dolomicrite, with

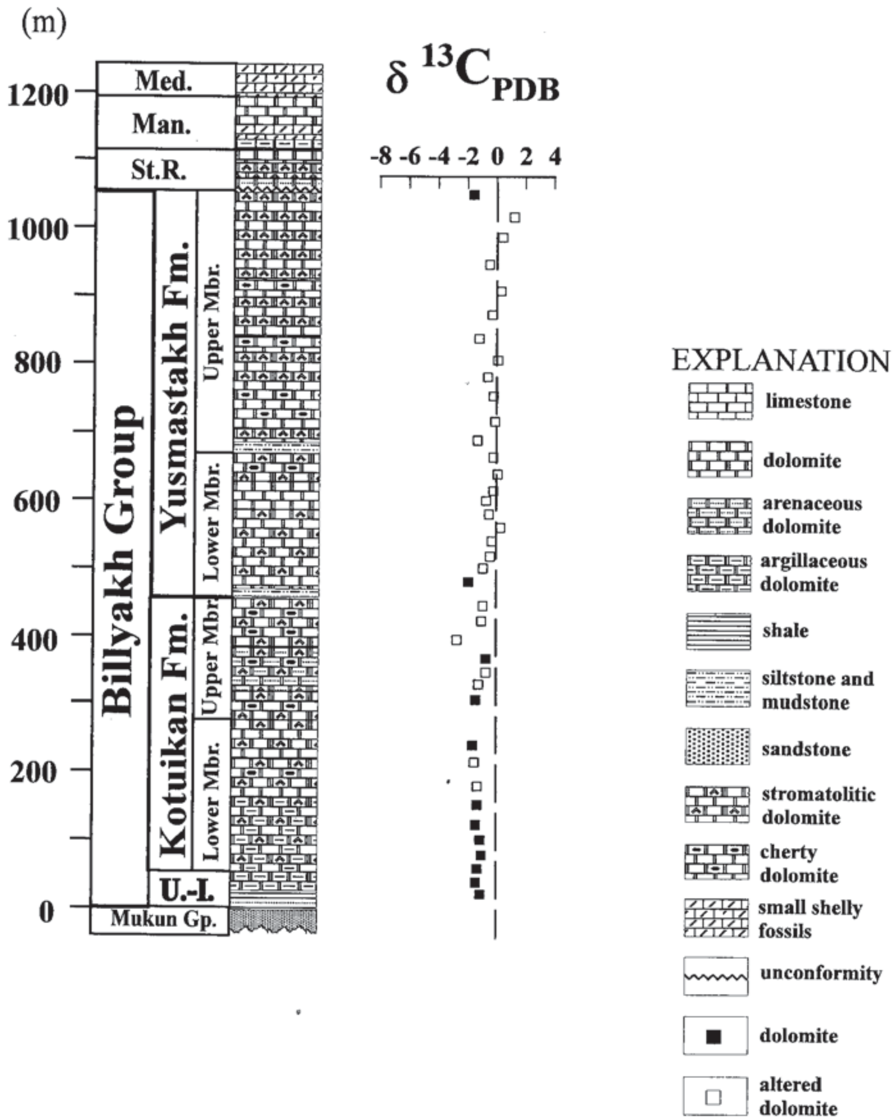

Fig. 2. Stratigraphic column and $\delta^{13}C$ values determined for dolomites in the Riphean Billyakh Group along the Kotuikan River section. U.-I. = Ust'-Il'ya Formation, St. R. = Staraya Rechka Formation, Man. = Manykai Formation, Med. = Medvezhya Formation.

subordinate lenses of microphytolitic, sandy, and intraclastic dolomites. Diverse microfossils in early diagenetic chert nodules corroborate the environmental interpretation (Yakshin, 1991; Sergeev, Knoll, and Grotzinger, 1994).

Disconformably overlying the Kotuikan succession is the Yusmastakh Formation, a 500 to 600 m package of oolites, stratiform to domal (and rare columnar) stromatolites, micrites, and intraclastic dolomites deposited in a peritidal setting. The entire Riphean section is overlain unconformably by late Vendian carbonates of the Staraya Rechka Formation (Khomentovsky, 1990).

Depositional ages for the Billyakh Group are constrained by both geochronometric and paleontological data. Glauconites of the Ust'-Il'ya Formation yield ages of 1483 ± 5 Ma (an eight point Rb-Sr isochron) and 1459 ± 10 Ma (mean of seven K-Ar determinations) (Gorokhov and others, 1991). [Single K-Ar analyses of mineralogically unstudied glaucony from the base of the Yusmastakh Formation and from the base of its upper member yielded dates of 1260 and 1170-1070 Ma, respectively (Manuilova, 1968).] An early Mesoproterozoic (Early Riphean = 1600 ± 50 to 1350 ± 20 Ma; Semikhatov and others, 1991) age for the Kotuikan Formation is corroborated by stromatolites (Komar, 1966; Golovanov, 1970; Krylov, 1975; Semikhatov, 1991), as well as microfossils (Sergeev, Knoll, and Grotzinger, 1994). Stromatolites also occur in the Yusmastakh Formation, but most are endemic taxa confined to the North-Siberian stromatolite province (see Semikhatov, 1991, for discussion). Nonetheless, a few Lower Yusmastakh forms have been interpreted as indicating a late Mesoproterozoic (Middle Riphean; 1350 ± 20 to 1000 ± 50 Ma) depositional age. Two Upper Yusmastakh taxa have been regarded as early Neoproterozoic (Upper Riphean; 1000 ± 50 to 650 ± 20 Ma). These belong to form-genera widely distributed in Upper Riphean successions, but the specific forms found in the Upper Yusmastakh are endemic, and their stratigraphic interpretation remains open to debate. In any case, correlation with better dated successions in northeastern Siberia indicates that the Billyakh Group contains no sediments younger than 870 to 850 Ma (Semikhatov and Serebryakov, 1983; Khomentovsky, Shenfil, and Yakshin, 1985).

Turukhansk Uplift.—In the Turukhansk region, unmetamorphosed Riphean rocks occur in three north-south trending, fault-bounded blocks thrust toward the east. Mesoproterozoic and early Neoproterozoic successions form gentle (15°-30°), westward deepening homoclines or an asymmetrical syncline complicated by minor slip faults. Latest Proterozoic (Vendian) and Cambrian rocks lie subhorizontally, separated from older units by an unconformity. The most complete sections of Riphean rocks occur in the central block, in particular along the Nizhnyaya Tunguska River and in the Shorikha River basin. To the east, younger Riphean units have been truncated by pre-Vendian erosion (fig. 2). In the western block, only a small portion of the succession is exposed. Our samples come from two sections in the central and eastern blocks exposed along the Nizhnyaya Tunguska River, two separate partial sections of the central block exposed in the Bol'shaya Shorikha River basin, and a partial section through the uppermost part of the succession along the Miroyedikha River (fig. 3). Two additional samples were collected from an

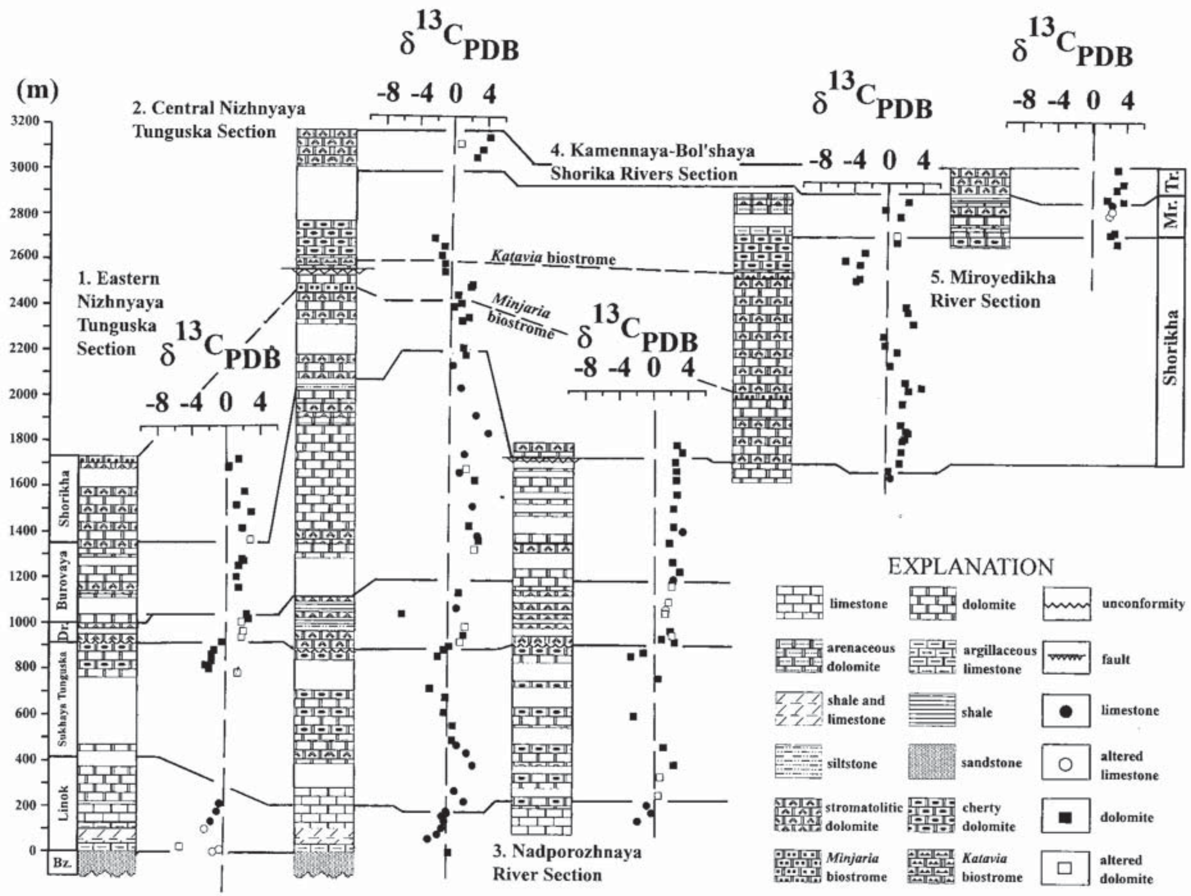

Fig. 3. Stratigraphic columns of Riphean successions in the Turukhansk Uplift, Siberia, showing $\delta^{13}C$ determinations for limestones and dolomites, as well as lithostratigraphic correlations. For the locations of individual sections, see figure 1C. Bz. = Bezymyannyi Formation, Dr. = Derevnya Formation, Mr. = Miroyedikha Formation, Tr. = Turukhansk Formation.

isolated outcrop exposed in the western block along the Nizhnyaya Tunguska River.

The oldest exposed unit is the Bezymyannyi Formation, a 600 to 650 m succession of marine siliciclastic rocks (fig. 3). It is overlain conformably by the 170 to 300 m thick Linök Formation, which contains two units of variegated, platy to hummocky cross-stratified limestone separated by a shaly interval; deposition took place in a shallowing-upward, storm-dominated shelf environment (Petrov, 1993). The overlying Sukhaya Tunguska Formation (500-850 m) consists predominantly of dolomite. Laminated, commonly bituminous micrites containing abundant subaqueous shrinkage cracks typify the lower part of the formation and are interpreted as relatively deep-water deposits. Light-colored dolarenites and dolorudites in the upper Sukhaya Tunguska are peritidal accumulations (Petrov, 1993); they contain abundant chert which preserves diverse microfossils (Mendelson and Schopf, 1982; Golovenok and Belova, 1992).

An erosional surface separates the overlying Derevnya Formation (100-250 m) from Sukhaya Tunguska carbonates. Derevnya lithologies include greenish gray, gray, and buff-weathering dolomites and rare limestones with one or two 20 to 30 m intercalations of sandy and shaly rocks. The carbonates are richly stromatolitic, containing spectacular *Conophyton, Jacutophyton,* and *Baicalia,* usually arranged in cycles (Serebryakov, 1975, 1976). Deposition took place subtidally, episodically below and above wave base.

The overlying Burovaya Formation (350-850 m) is dominated by massively bedded intraclastic or microphytolitic limestones and dolomite. Above this, the lower member of the Shorikha Formation (up to 800 m thick) contains abundant stromatolitic dolomites, as well as subordinate intraclastic and dolomicritic rocks. In the west, these lithologies are interbedded with 30 to 50 m units of hummocky cross-laminated, carbonaceous dolomite, containing scattered chert nodules. Two prominent stromatolitic marker beds anchor lithostratigraphic correlations of this unit: a 15 to 22 m biostrome of *Minjaria uralica* located about one-third of the way up through the member and a 5 to 7 m *Katavia* biostrome near its top (fig. 3). The upper member (160-280 m) consists predominantly of massive, non-stromatolitic dolomites and thick-bedded, in part intraclastic, dolomites containing abundant, fossiliferous chert nodules (Mendelson and Schopf, 1982; Sergeev, 1984).

The overlying Miroyedikha Formation is developed only in the westernmost part of the region; it is composed of a 160 to 200 m package of variegated inner shelf dolomites, limestones, and shales. The shales contain exceptionally well preserved microfossils (German, 1990). Miroyedikha beds rest conformably on the Shorikha Formation and are overlain, in turn, by the youngest unit of the Riphean package, the Turukhansk Formation—up to 180 m predominantly of red stromatolitic dolomites with subordinate intraclastic beds.

Radiometric dates on Turukhansk rocks are limited. A recent 11-point Pb-Pb isochron for carbonates from the middle Sukhaya Tunguska Formation yields an age of 1017 ± 91 Ma (Ovchinnikova and others, in press). K-Ar determinations on globular glaucony from the Bezymyannyi (830-910 Ma), Derevnya (800-860 Ma), and Burovaya (830-895 Ma) formations are all considered to reflect resetting of the K-Ar clock about 850 to 900 Ma ago (see Ivanovskaya and others, 1973, for review and bibliography). Stromatolites, acritarchs, and a striking lithostratigraphic similarity permit the correlation of the Turukhansk succession with better dated strata in the Uchuro-Maya region and Yenesei Ridge (Semikhatov, 1962, 1991; Semikhatov and Serebryakov, 1983; Khomentovsky, Shenfil, and Yakshin, 1985; Veis, 1988; Jankauskas, 1989). Uchuro-Maya units correlative with upper Turukhansk strata have yielded ages of 950 to 840 Ma (K-Ar on glauconite), and granites that cut correlative successions in the Yenesei Ridge have reported U-Pb ages of about 830 Ma. Glauconites in correlatives of lower Turukhansk strata in both the Uchuro-Maya and Yenesei regions have yielded K-Ar dates of 1100 to 1150 Ma (Kazakov and Knorre, 1973; Semikhatov and Serebryakov, 1983). Thus, paleontological and geochronometric data suggest a late Mesoproterozoic to early Neoproterozoic (late Middle Riphean to early Late Riphean) age for Turukhansk deposition. In particular, the Pb-Pb date for the Sukhaya Tunguska Formation and the first appearance of Neoproterozoic acritarchs (Semikhatov, 1991) in Derevnya shales suggest that the Mesoproterozoic/Neoproterozoic boundary should be placed at or near the base of the Derevnya Formation.

ANALYTICAL PROCEDURES

Powders of whole-rock samples of dolomites and limestones ($n = 187$) were used for elemental and isotopic analyses. Aliquots of these powders were weighed (typically < 20 mg) and leached in ultraclean 0.5 M acetic acid to avoid the dissolution of clastic components noted to occur with the use of dilute solution of HCl. After leaching, solutions were decanted and diluted to 100 ml in 2 percent HNO_3; residues were dried and weighed to determine percent dissolution. Major and trace element analyses were performed on a VG $PQ2^+$ plasma source mass spectrometer. Gravimetrically determined standards were analyzed in order to develop response calibration curves, and a 100 ppb ^{115}In spike was added for normalization. Accuracy of elemental abundances determined by this technique are better than ± 5 percent compared to isotope dilution techniques for the same elements. Limestones were reacted on line with concentrated H_3PO_4 ($\rho > 1.89$ g/ml) in the auto-sample magazine of a VG PRISM gas isotope ratio mass spectrometer for the determination of C- and O-isotopic compositions. Since a longer reaction time is necessary for the quantitative digestion of dolomites, CO_2 in these samples was exsolved using off-line techniques under identical conditions and was subsequently isolated by cryogenic distillation. Fractionation factors used for the calculation of ^{18}O abundances of calcites and dolomites based on analyses of

CO_2 prepared at 90°C were 1.00798 and 1.00895, respectively. Accuracy of these isotopic techniques as determined by multiple determinations ($n > 25$) of calcite and dolomite standards is ± 0.1 permil for C and ± 0.3 permil for O (Getty and Selverstone, 1994).

Polished thin and thick sections were prepared from an additional 34 samples. These were examined using optical petrography and cathodoluminescence; microsamples were drilled from petrographic phases thought to represent the least-altered portions of the carbonates (compare Kaufman and others, 1991).

EVALUATION OF DIAGENESIS

Ancient carbonates commonly retain near primary C-isotopic compositions (Marshall 1992); however, diagenesis can alter $\delta^{13}C$ values (Veizer, 1983; Fairchild, Marshall, and Bertrand-Sarfati, 1990; Kaufman, Knoll, and Awramik, 1992; Marshall, 1992). Therefore, if an isotopic determination is to be regarded as meaningful, the sample must be screened for evidence of diagenetic alteration.

Several screens are possible. Commonly, carbonate rocks contain a number of petrographically distinct phases. Non-luminescent (under cathodoluminescence) micrite or microspar is often regarded as a best bet for retention of isotopic ratios, although this is not invariably the case (Marshall, 1992). Fine-grained stromatolites, ooids, and syndepositional marine cements are also preferred candidates for isotopic analysis. We obtained petrographically-defined microsamples for 34 samples. The remainder of the samples were received as crushed powders. Whole-rock samples of Proterozoic carbonates commonly have isotopic compositions that approximate least-altered petrographic microsamples (Fairchild and Spiro, 1987; Burdett, Grotzinger, and Arthur, 1990; Kaufman and others, 1991); nonetheless, in the absence of petrographic data, geochemical screening is necessary.

Oxygen isotope ratios provide a sensitive indication of diagenetic alteration. Diagenesis commonly drives $\delta^{18}O$ toward more negative values; thus, the effects of diagenesis on C-isotopic ratios can often be recognized in $\delta^{13}C/\delta^{18}O$ cross-plots (Hudson, 1977). Fairchild, Marshall, and Bertrand-Sarfati (1990) have even advocated the use of such cross-plots to reconstruct depositional signals from altered sample suites. Figure 4 shows the relationships between C- and O-isotopic ratios within individual formations. In the Derevnya Formation (and other units not illustrated), there is little change in $\delta^{13}C$ with decreasing $\delta^{18}O$, but C-O cross-plots of Linok samples from the Nizhnyaya Tunguska River (and Burovaya samples from the Bol'shaya Shorikha basin) show a correlation between $\delta^{18}O$ and $\delta^{13}C$ that suggests alteration of C-isotopic ratios in samples characterized by very negative $\delta^{18}O$.

Brand and Veizer (1980) found that Mn/Sr provides a sensitive indicator of diagenetic alteration in carbonates. Derry, Kaufman, and Jacobsen (1992) suggested that Sr-isotopic values are suspect when $Mn/Sr > 2$. We have determined Mn/Sr ratios for all samples (table 1);

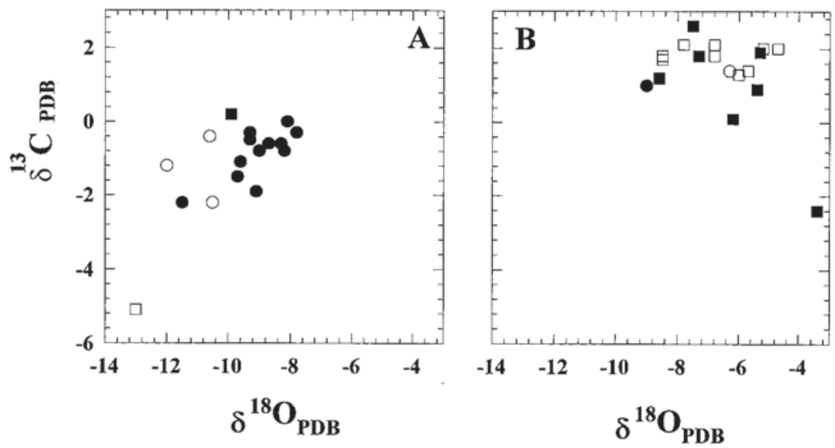

Fig. 4. Crossplots of $\delta^{13}C$ versus $\delta^{18}O$ for the: (A) Linok Formation and (B) Derevnya Formation. The symbols are the same as those used in figure 3. See text for discussion.

C-isotopic ratios appear to be little-altered in samples having Mn/Sr < 10. However, very high Mn/Sr (>10) correlates with anomalous $\delta^{13}C$ values, suggesting diagenetic alteration.

A final method of evaluating carbonate C-isotopic ratios is to determine $\delta^{13}C$ for organic carbon (TOC) in the same samples. In a study of Neoproterozoic samples from Spitsbergen, Knoll and others (1986) found that stratigraphic trends for carbonate carbon and organic carbon covaried smoothly with a $\Delta\delta$ of 28 to 30 permil, an unlikely circumstance if either phase were altered appreciably. The 28 to 30 permil value is empirically determined; nonetheless, continuing analyses suggest that $\Delta\delta$'s of 28 to 30 permil characterize many unaltered Neoproterozoic carbonates (Kaufman, Knoll, and Awramik, 1992). Substantially higher or lower $\Delta\delta$ values may result from the alteration of either carbonate or organic C-isotopic ratios.

In the Siberian samples, dolomites commonly have moderately elevated Mn/Sr, reflecting both loss of Sr and uptake of Mn during dolomitization (which, on petrological evidence, appears to have occurred predominantly during very early diagenesis; see also Fairchild, Knoll, and Swett, 1991). In contrast, limestones tend to have low Mn/Sr. Oxygen isotopes ratios show just the opposite trend, with limestones exhibiting more negative $\delta^{18}O$. In part, this may reflect equilibrium fractionation between dolomite and calcite established during early diagenesis, but several observation favor an alternative, or at least additional explanation. Petrographic evidence for later diagenetic neomorphism of limestones, the common stratigraphic segregation of limestones and dolomites, and the occurrence in some formation's of between-mineral O-isotopic differences that exceed equilibrial fractionation at near-

TABLE 1

Elemental and isotopic compositions of Riphean carbonates, Anabar Massif and Turukhansk Uplift, northern and northwestern Siberia

sample	fm[1]	section[2]	height[3]	lithology[4]	Mn/Sr	Mg/Ca	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C_{TOC}$ (‰,PDB)
A-1	US	AMS	36	dol	36.07	0.586	-1.1	-7.3	
A-6	"	"	55	dol	16.91	0.580	-1.4	-5.9	
A-5	KO	"	75	dol	14.05	0.590	-1.3	-7.8	
A-2	"	"	83						
A-3	"	"	96	dol	16.63	0.586	-1.0	-7.5	
A-4	"	"	120	dol	11.63	0.599	-1.1	-6.0	
A-7	"	"	143	dol	28.46	0.586	-1.4	-5.6	
A-8	"	"	174	dol	14.45	0.601	-1.3	-7.3	-29.4
A-9	"	"	203	dol	8.98	n.d.	-1.3	-7.3	-29.1
A-10	"	"	239	dol	6.69	0.604	-1.5	-6.4	
A-11	"	"	265	dol	25.22	0.589	-1.6	-6.2	
A-12	"	"	335	dol	12.10	0.599	-1.4	-3.8	
A-13	"	"	359	dol	4.24	0.588	-1.2	-6.6	
A-14	"	"	377	dol	6.48	0.604	-0.7	-7.0	
A-15	"	"	398	dol	14.36	0.612	-0.7	-8.9	
A-16	"	"	426	dol	7.60	0.629	-2.7	-7.6	-30.5
A-17	"	"	455	dol	4.38	0.607	-1.0	-7.0	-28.4
A-18	"	"	478	dol	4.82	0.619	-0.9	-6.0	
A-19	YU	"	515	dol	12.60	0.594	-1.9	-6.8	
A-20	"	"	536	dol	9.34	0.617	-0.9	-6.8	
A-21	"	"	554	dol	4.83	0.604	-0.4	-7.0	
A-22	"	"	577	dol	6.31	0.607	-0.3	-7.3	
A-23	"	"	598	dol	3.98	0.607	0.3	-6.0	
A-24	"	"	619	dol	3.35	0.617	-0.5	-6.0	
A-25	"	"	640	dol	5.88	0.601	-0.7	-8.1	
A-26	"	"	655	dol	2.17	0.622	-0.2	-6.4	
A-27	"	"	681	dol	7.12	0.601	0.1	-6.8	
A-28	"	"	707	dol	2.76	0.600	-0.2	-6.5	

A-29	"	"	733	dol	9.71	0.618	-1.3	-6.0	-28.4
A-30	"	"	762	dol	2.01	0.597	-0.1	-4.7	
A-31	"	"	801	dol	2.51	0.597	-0.2	-5.2	
A-32	"	"	829	dol	1.22	0.597	-0.6	-5.2	
A-33	"	"	855	dol	4.21	0.610	0.1	-5.4	-29.0
A-34	"	"	889	dol	3.14	0.604	-1.2	-7.6	
A-35	"	"	926	dol	2.03	0.613	-0.3	-6.3	
A-36	"	"	962	dol	3.63	0.609	0.3	-5.8	
A-37	"	"	1004	dol	2.40	0.602	-0.5	-7.2	
A-38	"	"	1045	dol	6.82	0.615	0.4	-9.5	
A-39	"	"	1076	dol	3.37	0.592	1.2	-8.4	-28.0
A-40	"	"	1110	dol	12.02	0.592	-1.6	-8.2	
T-2	LK	ENTS	23	dol/lms	27.85	0.286	-1.2	-11.0	
T-3	"	"	33	dol/lms	10.08	0.107	-0.4	-10.6	
T-4	"	"	44	dol	20.13	0.564	-5.1	-13.0	-30.0
T-5	"	"	121	dol/lms	19.67	0.260	-2.2	-9.5	-30.5
T-6	"	"	154	dol/lms	1.48	0.137	-1.5	-9.7	
T-7	"	"	197	lms	0.77	0.077	-0.8	-9.0	
T-8	"	"	231	lms	1.28	0.006	-0.5	-9.3	
T-27	"	CNTS	10	lms/dol	n.d.	0.344	0.2	-9.9	
T-28	"	"	67	lms	4.77	0.085	-2.2	-11.5	
T-29	"	"	87	lms	1.75	0.066	-1.1	-9.6	
T-30	"	"	115	lms	0.69	0.003	-0.6	-8.3	
T-31	"	"	146	lms	0.83	0.010	-0.3	-7.8	
T-32	"	"	167	lms	2.35	0.003	-0.6	-8.7	
T-33	"	"	180	lms	0.81	0.050	0.0	-8.1	
T-75	"	NRS	95	dol/lms	4.86	0.156	-1.9	-9.1	-30.6
T-76	"	"	133	lms	0.88	0.050	-0.3	-9.3	
T-77	"	"	167	lms	1.65	0.001	-0.8	-8.2	

TABLE 1
(continued)

sample	fm[1]	section[2]	height[3]	lithology[4]	Mn/Sr	Mg/Ca	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C_{TOC}$ (‰,PDB)
T-9	ST	ENTS	792	dol	16.79	0.560	1.4	-6.0	
T-10	"	"	808	dol	0.78	0.542	-2.0	-4.0	
T-11	"	"	823	dol	1.10	0.523	-2.4	-6.1	
T-12	"	"	841	dol	0.92	0.608	-1.7	-5.3	
T-13	"	"	869	dol	0.70	0.609	-1.7	-6.0	
T-14	"	"	887	dol	0.46	0.582	-1.4	-4.4	
T-15	"	"	921	lms/dol	6.46	0.463	-0.5	-7.5	
T-34	"	CNTS	190	lms	0.84	0.077	-0.1	-7.0	
T-35	"	"	231	lms	0.07	0.085	2.0	-7.1	
T-36	"	"	277	lms	1.81	0.031	0.9	-6.5	
T-37	"	"	387	lms	0.05	0.029	3.0	-8.9	
T-38	"	"	441	lms	0.09	0.009	2.3	-9.8	
T-39	"	"	474	lms	0.19	0.013	1.1	-9.2	
T-41	"	"	497	dol	0.83	0.598	0.5	-6.7	
T-40	"	"	559	dol	1.18	0.556	0.6	-5.9	
T-42	"	"	615	dol	0.53	0.598	-0.4	-5.4	
T-43	"	"	680	dol	0.74	0.559	-0.3	-3.5	
T-44	"	"	718	dol	0.44	0.539	-2.1	-5.4	
T-45	"	"	856	dol	0.87	0.507	-1.2	-6.6	
T-46	"	"	885	dol	3.64	0.587	-0.5	-5.1	
T-78	"	NRS	213	dol	n.d.	0.581	0.3	-8.6	
T-79	"	"	297	dol	18.57	0.627	0.7	-6.8	
T-80	"	"	351	dol	3.62	0.619	2.3	-10.1	
T-81	"	"	433	dol	0.38	0.505	1.1	-5.6	
T-82	"	"	574	dol	0.52	0.595	-2.4	-4.1	
T-83	"	"	746	dol	1.53	0.604	0.5	-5.6	
T-84	"	"	847	dol	0.77	0.564	-2.7	-4.5	
T-85	"	"	862	dol	1.98	0.602	-1.2	-5.4	

T-16	DV	ENTS	944	dol	14.64	0.565	1.8	-6.8	
T-17	"	"	969	dol	21.96	0.574	2.0	-4.7	
T-18	"	"	1008	dol	17.81	0.584	1.8	-8.5	
T-19	"	"	1021	dol	3.71	0.602	2.6	-7.5	
T-47	"	CNTS	900	dol	5.32	0.579	0.1	-6.2	
T-48	"	"	918	dol	15.45	0.511	1.4	-5.7	
T-49	"	"	949	dol	6.33	0.572	1.8	-7.3	
T-50	"	"	985	dol	12.92	0.556	2.0	-5.2	
T-51	"	"	1041	dol	6.24	0.551	-2.4	-3.4	
T-52	"	"	1064	lms	4.04	0.023	1.0	-9.0	
T-53	"	"	1133	dol	6.64	0.572	1.2	-8.6	
T-87	"	NRS	922	dol	6.50	0.600	2.4	-9.2	
T-90	"	"	923	dol	8.27	0.577	0.9	-5.4	
T-91	"	"	938	dol	22.06	0.570	2.1	-7.8	
T-88	"	"	959	dol	7.16	0.558	1.9	-5.3	
T-89	"	"	1038	dol	13.10	0.500	1.3	-6.0	
T-92	"	"	1054	dol/lms	8.88	0.204	1.4	-6.3	
T-93	"	"	1090	dol	11.92	0.595	1.7	-8.5	
T-94	"	"	1159	dol	21.52	0.589	2.1	-6.8	-28.4
T-20	BU	ENTS	1041	dol	2.42	0.601	2.4	-7.8	
T-22	"	"	1154	dol	1.29	0.585	1.4	-6.0	
T-21	"	"	1200	dol	2.86	0.578	1.1	-9.0	
T-23	"	"	1249	dol	1.80	0.577	1.4	-6.4	
T-24	"	"	1269	dol	2.11	0.567	2.0	-6.7	
T-25	"	"	1279	dol	2.70	0.541	1.8	-6.6	
T-54	"	CNTS	1321	lms/dol	3.80	0.488	3.0	-10.7	
T-55	"	"	1359	lms/dol	0.42	0.311	3.5	-5.1	
T-56	"	"	1377	dol/lms	0.25	0.201	3.4	-5.4	
T-57	"	"	1421	dol	3.80	0.610	2.4	-11.3	
T-58	"	"	1505	lms	0.09	0.019	2.8	-6.2	
T-59	"	"	1618	dol	0.51	0.510	3.0	-7.1	

TABLE 1
(continued)

sample	fm[1]	section[2]	height[3]	lithology[4]	Mn/Sr	Mg/Ca	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C_{TOC}$ (‰,PDB)
T-60	BU	CNTS	1649	lms	2.06	0.089	1.2	-8.7	
T-61	"	"	1667	dol	9.38	0.616	2.0	-10.2	
T-62	"	"	1728	lms	0.08	0.016	1.8	-8.9	
T-63	"	"	1820	lms	0.05	0.017	4.6	-7.8	-28.2
T-64	"	"	1897	lms	0.04	0.005	3.1	-6.4	-26.9
T-65	"	"	2015	lms	3.14	0.018	1.3	-9.5	
T-66	"	"	2113	lms	2.27	0.022	0.3	-8.2	
T-67	"	"	2159	dol	4.80	0.519	1.8	-8.9	
T-95	"	NRS	1177	lms	0.79	0.052	2.2	-5.5	
T-96	"	"	1190	lms	1.21	0.053	2.3	-6.2	
T-97	"	"	1226	dol	8.22	0.578	3.0	-8.7	-28.3
T-98	"	"	1269	dol	6.23	0.592	2.2	-8.2	
T-99	"	"	1356	dol	3.62	0.590	1.8	-9.9	
T-101	"	"	1405	lms	0.10	0.012	3.4	-6.2	-29.5
T-100	"	"	1428	dol	1.69	0.598	2.3	-4.7	
T-102	"	"	1510	dol	6.33	0.603	2.3	-8.8	
T-103	"	"	1574	dol	5.10	0.598	2.7	-8.0	
T-104	"	"	1641	dol	2.25	0.583	2.6	-7.0	
T-105	"	"	1682	dol	1.12	0.593	2.6	-6.9	
T-107	"	"	1723	dol	2.00	0.601	2.5	-7.3	
T-109	"	K-BSRS	1703	lms	9.16	0.044	0.5	-11.0	
T-150	SH	ENTS	1360	dol*	10.37	0.576	2.7	-5.4	
T-151	"	"	1410	dol*	3.39	0.578	1.9	-7.8	
T-152	"	"	1460	dol*					
T-153	"	"	1480	dol*	3.02	0.508	2.9	-6.2	
T-154	"	"	1510	dol*	1.46	0.571	1.2	-5.2	
T-155	"	"	1570	dol*	2.20	0.568	2.1	-5.9	
T-156	"	"	1675	dol*	2.05	0.577	0.2	-6.7	
T-26	"	"	1680	dol	3.82	0.528	0.3	-6.2	
T-157	"	"	1710	dol*	1.29	0.582	1.4	-5.3	

T-68	"	CNTS	2192	dol	1.31	0.542	1.5	-7.4	
T-69	"	"	2310	dol	0.90	0.603	1.3	-6.3	
T-158	"	"	2325	dol*	1.20	0.570	2.1	-4.8	
T-159	"	"	2370	dol*	0.67	0.567	0.3	-6.2	
T-70	"	"	2385	dol	1.48	0.611	1.2	-6.1	
T-160	"	"	2420	dol*	0.76	0.564	1.7	-5.4	
T-161	"	"	2455	dol*	1.13	0.569	2.4	-4.1	
T-162	"	"	2465	dol*	0.53	0.563	2.5	-4.5	
T-163	"	"	2520	dol*	3.01	0.577	-0.8	-4.9	
T-164	"	"	2555	dol*	2.95	0.572	-0.8	-4.1	
T-165	"	"	2590	dol*	1.08	0.576	-1.2	-5.2	
T-166	"	"	2630	dol*	1.56	0.569	-0.9	-4.4	
T-167	"	"	2665	dol*	1.30	0.577	-2.1	-4.9	
T-106	"	NRS	1767	dol	1.28	0.602	3.3	-7.6	
T-108	"	"	1800	dol	2.94	0.606	2.7	-8.0	
T-110	"	K-BSRS	1736	dol	9.37	0.606	0.2	-7.2	
T-111	"	"	1769	dol	2.90	0.610	1.5	-9.9	
T-112	"	"	1820	dol	3.77	0.608	1.7	-8.8	
T-113	"	"	1867	dol	4.31	0.622	1.8	-7.4	
T-114	"	"	1877	dol	5.71	0.595	2.1	-6.2	
T-117	"	"	1905	dol	3.81	0.584	2.5	-6.8	
T-115	"	"	1912	dol	6.42	0.597	2.2	-6.7	-29.8
T-116	"	"	1941	dol	6.60	0.597	1.6	-5.7	
T-118	"	"	2036	dol	2.37	0.619	1.8	-6.9	
T-119	"	"	2095	dol	4.10	0.634	2.5	-7.0	
T-122	"	"	2108	dol	2.74	0.597	4.0	-6.3	-28.9
T-120	"	"	2131	dol	1.96	0.614	2.1	-7.1	-27.0
T-123	"	"	2205	dol	4.35	0.609	0.3	-5.5	
T-121	"	"	2267	dol	2.16	0.624	1.1	-6.5	

TABLE 1
(continued)

sample	fm[1]	section[2]	height[3]	lithology[4]	Mn/Sr	Mg/Ca	$\delta^{13}C$ (‰, PDB)	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C_{TOC}$ (‰,PDB)
T-124	SH	K-BSRS	2297	dol	2.99	0.631	-0.3	-6.6	
T-125	"	"	2338	dol	2.22	0.588	-0.5	-6.8	-28.0
T-128	"	"	2395	dol	2.54	0.609	3.0	-5.2	
T-127	"	"	2446	dol	2.03	0.617	2.3	-5.4	
T-126	"	"	2472	dol	2.51	0.597	2.1	-7.7	
T-129	"	"	2590	dol	3.07	0.592	-3.8	-5.9	-30.8
T-130	"	"	2600	dol	3.15	0.632	-3.3	-5.6	-30.4
T-131	"	"	2664	dol	2.60	0.607	-3.3	-4.2	-28.6
T-132	"	"	2682	dol	2.37	0.593	-5.0	-4.3	
T-133	"	"	2718	dol	6.12	0.614	-2.7	-6.5	
T-134	"	"	2764	dol	4.43	0.622	1.0	-4.8	
T-173	"	MRS	2675	dol*	3.46	0.597	3.0	-1.7	
T-135	MR	K-BSRS	2795	dol	11.26	0.625	1.0	-4.8	
T-136	"	"	2879	dol	3.43	0.564	1.4	-4.3	
T-137	"	"	2913	dol	1.44	0.616	-0.4	-3.9	-30.8
T-138	"	"	2949	dol	n.d.	0.591	2.3	-5.2	-30.5
T-174	"	MRS	2715	dol*	7.15	0.571	2.2	-3.6	
T-175	"	"	2725	dol*	7.42	0.571	2.7	-4.8	
T-177	"	"	2800	lms*	32.12	0.046	2.1	-6.1	
T-178	"	"	2820	lms*	42.90	0.026	2.4	-10.6	
T-179	"	"	2850	lms*	3.51	0.024	2.4	-5.6	

T-169	TR	CNTS	3020	dol*	3.03	0.549	2.7	-4.4	
T-72	"	"	3040	dol	1.82	0.597	n.d.	n.d.	
T-170	"	"	3055	dol*	2.11	0.568	3.4	-4.2	
T-171	"	"	3080	dol*	12.04	0.537	0.8	-4.3	
T-172	"	"	3110	dol*	5.90	0.566	4.2	-4.2	
T-180	"	MRS	2865	dol*	8.55	0.583	3.7	-5.2	
T-181	"	"	2875	dol*	6.30	0.571	1.8	-5.6	
T-182	"	"	2920	dol*	6.66	0.572	2.9	-7.8	
T-183	"	"	2945	dol*	2.87	0.557	3.7	-4.4	
T-184	"	"	3010	dol*	5.01	0.569	3.0	-6.0	
T-73[5]		WNTS		dol/lms	0.51	0.108	4.1	-7.3	-27.8
T-74[5]		"		dol	7.39	0.589	3.4	-4.9	-28.3

[1]fm = formation: LK = Linok, ST = Sukhaya Tunguska, DV = Derevnya, BU = Burovaya, SH = Shorikha, MR = Miroyedikha, TR = Turukhansk, US = Ust'-Il'ya, KO = Kotuikan, YU = Yusmastakh.

[2]section: AMS = Anabar Massif section, ENTS = eastern Nizhnaya Tunguska River section, CNTS = central Nizhnaya Tunguska River section, NDS = Nadporozhnaya River section, K-BSRS = Kamennaya-Bol'shaya Shorika River section, MRS = Miroyedikha River section, WNTS = Western Nizhnyaya Tunguska River section.

[3]height: Anabar Massif sample heights measured above the base of the Ust'-Il'ya Formation, Turukhansk Uplift sample heights measured above the base of the Linok Formation.

[4]lithology: lms = limestone, dol = dolomite, dol/lms = dolomitic limestone, lms/dol = calcareous dolomite, astericks (*) indicate microsamples.

[5]Samples T-73 and T-74 were collected in the Western Nizhnyaya Tunguska River section from the so-called Rechka and Durnoi Mys formations, respectively; these "formations" correlate with the middle interval of the central Nizhnyaya Tunguska section exposed in a separate tectonic block (Komar and Serebryakov, 1968; Serebryakov, 1975).

surface temperatures collectively suggest that dolomites were stabilized isotopically during early diagenesis, while limestones remained vulnerable to ground water oxygen exchange until stabilization by neomorphism or recrystallization at depth. Except in cases of unusually strong ^{18}O depletion and/or anomalously high Mn/Sr, there is little evidence that C-isotopic ratios were affected by these processes. As shown in figure 2, broad stratigraphic trends are defined by samples with $\delta^{18}O > -10$ and Mn/Sr < 10. In the following discussion, we rely principally on these samples.

RESULTS AND DISCUSSION

The Anabar Massif.—In a previous survey of Billyakh dolomites, Pokrovsky and Vinogradov (1991) found that $\delta^{13}C$ values fell consistently between 0 and -1.8 permil, with a few modestly positive values (up to $+1.2$ permil) in the upper Yusmastakh Formation. Our analyses are concordant (table 1; fig. 2). $\delta^{18}O$ values are > -10 permil, and while Mn/Sr varies from 1.2 to 14.4, there is no correlation between $\delta^{13}C$ and Mn/Sr. Therefore, we believe that $\delta^{13}C$ values are little altered. Ust'-Il'ya and lower Kotuikan carbonates tend to be slightly depleted in ^{13}C relative to upper Kotuikan and Yusmastakh samples ($\bar{x}$ and $s_{\bar{x}} = -1.3 \pm 0.2$ permil and -0.4 ± 0.6 permil, respectively). While this difference might record subtle secular variation in the isotopic composition of the ocean, it may alternatively reflect minor but consistent differences in the isotopic composition of water masses bathing the mid-shelf and peritidal zones.

Billyakh data support the conclusion that carbonates younger than about 850 Ma are not represented in the Anabar section; the unusually positive $\delta^{13}C_{carb}$ values (>5 permil) seen in later Neoproterozoic carbonates is nowhere in evidence in our Anabar suite. Thick units characterized by mildly negative $\delta^{13}C$ values occur in a number of 1600 to 1200 Ma successions, including the Carswell Formation, Saskatchewan (Abell and others, 1989); the McArthur Group, Australia (Veizer and Hoefs, 1976; Veizer, Clayton, and Hinton, 1992); the Bungle Bungle Dolomite, Australia (Schidlowski, Hayes, and Kaplan, 1983); the Bangemall Group, Australia (Buick, Des Marais, and Knoll, in press); the Jixian Group, China (Zhou and Zhang, 1991), and the Debengda Formation, northern Siberia (Sergeev, Knoll, and Grotzinger, 1994); with consistent but single sample analyses coming from the Sibley Group, Canada, and the Vempalle Formation, India (Schidlowski, Eichman, and Junge, 1975). Data for organic C generally corroborate this picture (Liu and others, 1991; Strauss and others, 1992). Thus, available isotopic data broadly support depositional ages inferred for the Billyakh Group. As noted above, stromatolites in the Yusmastakh Formation have been interpreted as indicating a younger (perhaps 1350-900 Ma) range of ages for this part of the Billyakh succession. $\delta^{13}C$ values of $+2$ to $+3$ in some 1200 to 900 Ma rocks might be interpreted as ruling out the younger part of this range (Beeunas and Knauth, 1987; Fairchild, Knoll, and Swett, 1990; Butterfield, Knoll, and Swett, 1990), but the limited amount of geochronometrically constrained C-isotopic data for upper Mesoproterozoic and lower Neoproterozoic rocks leaves considerable uncertainty about isotopic coverage for this interval. As discussed below, C-isotopic data do rule out more than a limited stratigraphic overlap between Yusmastakh carbonates and the more securely dated late Mesoproterozoic and early Neoproterozoic strata of the Turukhansk region.

Turukhansk Uplift.—Turukhansk samples are interesting from at least two points of view. First, they permit us to compare similar stratigraphic horizons in sections representing different parts of the basin. If C-isotopic chemostratigraphy is to have any validity, stratigraphic trends should not be a strong function of facies. Second, Turukhansk analyses permit an evaluation of the goodness of fit among paleontological, geochronometric, and chemostratigraphic age estimates for successions that span the Mesoproterozoic/Neoproterozoic (Middle Riphean/Late Riphean) boundary.

Linok Formation.—This formation was sampled in three sections along the Nizhnyaya Tunguska and Nadporozhnaya rivers. O-isotopic ratios and Mn/Sr values indicate variable alteration, and the most negative $\delta^{13}C$ values (for example, T-4 = −5.1 permil) may also be altered. The "best" samples, as judged by our geochemical criteria, define a trend from about −2 permil in the lower part of the section to about 0 permil in its upper part. This trend is consistent among all three sections.

Sukhaya Tunguska Formation.—Essentially all samples in this formation have relatively low Mn/Sr and high $\delta^{18}O$; therefore, all qualify as little altered. Three sections were sampled, although only the upper part of the formation is represented in our collections from the eastern Nizhnyaya Tunguska River section. In its lower part, Sukhaya Tunguska $\delta^{13}C$ values continue the trend begun in the underlying Linok Formation, with values increasing from near 0 to as high as +3 permil. In the upper Sukhaya Tunguska Formation, $\delta^{13}C$ values decrease to values as low as −2.4 to −2.7 permil, before returning to about −0.5 permil at the top of the unit. Once again, the stratigraphic trend is consistent across all sections.

Derevnya Formation.—Derevnya samples display relatively high $\delta^{18}O$ and Mn/Sr values. With the exceptions of sample T-47 at the base of the western Nizhnyaya Tunguska River section ($\delta^{13}C$ = 0.1 permil) and T-51 in the middle of the same section ($\delta^{13}C$ = −2.4 permil, probably altered by the diagenetic remineralization of organic matter), Derevnya dolomites in all sections have $\delta^{13}C$ values of +1 to +2.5 permil). The sharp break between Derevnya and underlying Sukhaya Tunguska values highlights the erosional discontinuity between these units.

Burovaya Formation.—Nearly all Burovaya samples show low Mn/Sr and relative depletion in ^{18}O. The central Nizhnyaya Tunguska and Nadporozhnaya River sections exhibit two successive trends from more (+3 to +4.6 permil) to less positive (+1 to +2 permil) $\delta^{13}C$ values. In the eastern Nizhnyaya Tunguska River section, only the basal and middle portions of the formation were sampled, but C-isotopic compositions from these strata permit correlation with the other sections. One of the strongest discrepancies among sections in the entire data set occurs near the top of the Burovaya Formation. $\delta^{13}C$ values recorded in the uppermost part of the central Nizhnyaya Tunguska River section do not match those determined along the Nadporozhnaya River. One possible explanation for the mismatch is variation in C-isotopic composition among water masses at the time of Burovaya deposition; however, data from other Turukhansk horizons and elsewhere suggest that this is unlikely (for discussion, see Kaufman and Knoll, in press). More likely, correlatives of uppermost Burovaya carbonates in the central Nizhnyaya Tunguska River section are faulted out along the Nadporozhnaya River. The contact between the Burovaya and overlying Shorikha formations is not exposed along the Nadporozhnaya River, and the thicknesses of both Burovaya deposits and Shorikha strata beneath the prominent *Minjaria* biomarker bed higher in that unit are significantly smaller in this section than in other measured sections (fig. 3).

Shorikha Formation.—All Shorikha samples are dolomitic, have moderate Mn/Sr, and are relatively enriched in ^{18}O. In the well-sampled type section along the Kamennaya and Shorikha rivers, $\delta^{13}C$ values in the lower member increase from near 0 at the base of the formation to +4.0 permil slightly above the *Minjaria uralica* marker bed. A thin unit above this peak records an excursion to slightly negative values, above which there is a second increase to +3 permil.[1] The *Katavia* biostrome and associated beds near the top of the lower member and most of the upper member are characterized by strongly negative $\delta^{13}C$ values (as light as −5 permil), but $\Delta\delta$ values of 25 to 27 permil suggest that isotopically light carbon was added diagenetically to carbonates whose depositional $\delta^{13}C$ was around 0 to −1 permil. A single sample near the top of the upper member has a $\delta^{13}C$ value of +1 permil, marking the beginning of a positive shift that continues into younger formations.

Comparison of the type section with the other well sampled Shorikha section (central Nizhnyaya Tunguska River) reveals a second discrepancy between localities. In the central Nizhyaya Tunguska section, $\delta^{13}C$ values for the lower member exhibit a moderate positive trend that peaks just above the *Minjaria uralica* biostromes, followed by a sharp drop to slightly negative values—just as in the type section. Stratigraphically higher units, however, show differences in isotopic pattern (fig. 3). Younger Shorikha beds in the central Nizhnyaya Tunguska River section are exposed on the opposite bank from those of the lower part. The section has generally been regarded as continuous, but as the thickness of Shorikha strata between the two marker beds is several times smaller in this section than in its equivalent in the type area (fig. 3), this would require condensed sedimentation, for which there is no evidence. The

[1] Within this interval of the exposed type section, there is a thin breccia zone which indicates minor slip faulting. There is no duplication of strata above and below this zone. Possibly, some strata have been faulted out locally, but the thickness of missing section, if any, would appear to be small.

upper of the two distinct negative to positive C-isotopic excursions evident in the type section is not seen along the central Nizhnyaya Tunguska River, suggesting, instead, that part of the lower Shorikha member is faulted out in this locality. A marked shift in dip angle from 20° to 28° to about 60° lends further support to this interpretation. Above the level of the *Katavia* biostrome, upper Shorikha cherty dolomites of the central Nizhnyaya Tunguska River section yield $\delta^{13}C$ values that mostly center around -1 permil, as predicted on the basis of $\Delta\delta$ in the type section.

Miroyedikha and Turukhansk formations.—Only a few samples were analyzed for the relatively thin and discontinuously outcropping Miroyedikha and Turukhansk formations. These samples have moderate $\delta^{18}O$ and low to unusually high Mn/Sr. "Best" limestones and dolomites in the Miroyedikha Formation exhibit $\delta^{13}C$ values of $+1.1$ to $+2.7$ permil; given the high proportion of poorly exposed shales in this formation, intersectional correlations are approximate, at best. Turukhansk samples tend to be more positive, with values as high as $+4.2$ permil.

Summary of Turukhansk data.—C-isotopic data from Turukhansk carbonates corroborate other data indicating that these rocks were deposited more than 850 but less than about 1250 Ma ago. Linok carbonates have mildly negative $\delta^{13}C$'s like those of the Billyakh Group in the Anabar Uplift, and it is possible that the Linok and Upper Yusmastakh successions overlap in time. Higher Turukhansk units, on the other hand, show levels of C-isotopic variation that preclude correlation with Anabar formations. $\delta^{13}C$ values for the Sukhaya Tunguska Formation show smooth stratigraphic variation from a high near $+3$ permil in the lower part of the succession to moderately negative values (-1 to -2.7 permil near its top); sections in different parts of the basin show the same stratigraphic pattern. Carbonates above the sub-Derevnya erosional surface are predominantly mildly positive ($+1$ to $+3$ permil, with a maximum of $+4.6$ permil).

As noted above, biostratigraphic and limited radiometric data suggest a depositional age range of about 850 to 1200 Ma. The isotopic data are consistent with this estimate; similar values have been reported for the Kurnool System, India (Schidlowski and others, 1975); the Roan Group and Kundelungu "Series," Africa (Schidlowski, Eichman, and Junge, 1975); the Mescal Limestone, Arizona (Beeunas and Knauth, 1985); and the probably related Thule Group, lower Bylot Supergroup, and Hunting Formation of northwestern Greenland and Arctic Canada (Hayes and others, unpublished data). The strongly positive $\delta^{13}C$ values determined for Shorikha and overlying strata suggest that these rocks may be correlative, at least in part, with the Veteranen Group, Spitsbergen (Knoll and others, 1986) and the lower Shaler Group, Arctic Canada (Asmerom and others, 1991), which document the early part of the later Neoproterozoic positive $\delta^{13}C$ interval, about 850 to 800 Ma ago. Paleontological data are consistent with such a correlation, and it can be tested more rigorously using Sr-isotopic chemostratigraphy.

The concordance of isotopic data from different Turukhansk sections further underscores the applicability of isotopic chemostratigraphy to problems of *intrabasinal* correlations. This was first demonstrated by Knoll and others (1986), who showed that C-isotopic data could be used to correlate the thick Neoproterozoic successions of Svalbard and central East Greenland (see also Kirschvink and others, 1991, and Narbonne, Kaufman, and Knoll, 1994, for more recent examples). The Turukhansk data allow us to identify two previously unrecognized breaks in local sections of the Burovaya and Shorikha formations.

CONCLUSIONS

Anabar and Turukhansk samples add to a growing array of data that collectively enable us to extend the carbonate carbon isotope curve backward more than 1000 Ma before Phanerozoic Eon. Our new determinations corroborate and extend earlier data suggesting that $\delta^{13}C$ varied only within narrow limits during the interval about 1600 to 1200 Ma. Secular variation is greater for uppermost Mesoproterozoic and lower Neoproterozoic successions but does not approach the magnitude of variation documented in upper Neoproterozoic (<850 Ma) rocks. Nonetheless, isotopic data can facilitate both intra- and interbasinal correlations of Mesoproterozoic and older Neoproterozoic sedimentary rocks. Facies and geographic variation within a single basin is small relative to observed secular variations and, therefore, does not constitute a significant impediment to chemostratigraphic correlation.

The Turukhansk succession, in particular, permits interdigitation of C-isotopic (this paper) and Sr-isotopic (Gorokhov and others, in press) data with biostratigraphic information from stromatolites and acritarchs. Thus, it will figure prominently in attempts to characterize the Mesoproterozoic/Neoproterozoic transition chronostratigraphically.

Perhaps most significant, the Siberian data underscore the distinctive carbon isotopic excursions of the later Neoproterozoic and early Paleoproterozoic (Karhu, 1993, and references therein). The beginning and the end of the Proterozoic Eon are emerging as unique periods of biogeochemical, tectonic, and climatic change that are as different from intervening Proterozoic intervals as they are from the Phanerozoic.

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