Multiple $\delta^{13}C$ excursions spanning the Cambrian explosion to the Botomian crisis in Siberia

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ABSTRACT

New high-resolution $\delta^{13}C$ data through the Lower Cambrian of Siberia reveal multiple, positive excursions coincident with phases in the "explosion" of invertebrate phyla (Nemakit-Daldynian to middle Botomian stages). Comparison of the $\delta^{18}O$ and trace element (Mg, Fe, Mn, Sr) chemistry indicate that six new $\delta^{13}C$ cycles are primary rather than diagenetic features, with potential for global correlation. Positive $\delta^{13}C$ excursions up to $+3%$ indicate that fractional organic carbon burial rates were high but variable through the Cambrian explosion. Values for $\delta^{13}C$ dropped sharply from around $+2.2%$ to $-1.6%$ in Botomian time, coincident with mass extinction of the archaeocyathan reef biota. The rapid fluctuation of the $\delta^{13}C$ signal and the temporal coincidence of the pronounced negative shift with the extinction event hint that the $\delta^{13}C$ record may record productivity variations during the Early Cambrian radiation.

INTRODUCTION

The remarkable "explosion" of invertebrate phyla across the Precambrian-Cambrian transition is here calibrated for the first time against a complete $\delta^{13}C$ stratigraphy for the Lower Cambrian of the Siberian platform, northeast Asia. This is the premier region for such studies because reliable isotopic signals can be obtained from well-preserved fossiliferous carbonates in global reference sections with superb biostratigraphic control. Previous papers have reported on latest Proterozoic to early Atdabanian strata, revealing $\delta^{13}C$ cycles Z and I to IV (Fig. 1; Magaritz et al., 1986, 1991; Kirschvink et al., 1991), and their correlation between outcrops on the Aldan and Lena rivers (Kirschvink et al., 1991) and beyond to Uchur, Siberia (Brasier et al., 1993), Prianabar, Siberia (Pokrovsky and Missarzhevsy, 1993), China and Morocco (Kirschvink et al., 1991; Magaritz et al., 1991), and Newfoundland (Brasier et al., 1992). Here we extend the $\delta^{13}C$ data upward to the base of the Middle Cambrian, adding 305 new points from superjacent sections in undeformed, very gently dipping strata along the Lena river: Achchagy Kyyry Taas (AKT), Achchagy Tuoydahk (AT), Labaya (L), and Titary-Elanka (T-E). These span type sections for the Atdabanian, Botomian, and Toyonian stages, correlated by means of published lithological marker beds and biostratigraphy (Rozanov and Sokolov, 1984).

These new $\delta^{13}C$ data reveal a further six $\delta^{13}C$ cycles (V to X, Fig. 1) and a remarkable change in pattern during the middle Botomian. Below we calibrate these data against major geological events in the fossil record of Siberia.

METHODS

Sampled sediments of this succession are mostly shallow-water micrite and microspar carbonates with sparse skeletal fossils (Nikolaeva et al., 1987); their potential for $\delta^{13}C$ stratigraphy is discussed elsewhere (Magaritz et al., 1991; Brasier et al., 1993). Although sparse skeletal carbonate reduces the risk of unwanted vital effects (e.g., Grant, 1992), it lessens the scope for isotopic calibration of micrite against associated and suitable calcitic biominerals. Those of archaeocyathan sponges and corallocorals were studied where available and compared with marine fibrous calcite cement fabrics (Fig. 2, A and B). Rock samples were selected and drilled, and the powder was processed on a VG Isotech PRISM mass spectrometer at Oxford University using standard techniques (e.g., Brasier et al., 1993).

Early diagenetic fibrous cements and archaeocyathan or corallocoral biominerals had $\delta^{13}C$ values close to adjacent micrite-microspar, whereas blocky calcite cements of later diagenetic origin appear negatively displaced (Fig. 2, A and B). This implies that early cements, calcite biominerals, and micrite-microspar record essentially the same $\delta^{13}C$ signature (close to seawater values), whereas later blocky calcites record the input of isotopically lighter carbon derived from degradation of organic matter, and lighter oxygen from warmer pore waters during burial (e.g., Irwin et al., 1977). Although values of $-4.03%$ to $-9.28%$ $\delta^{18}O$ PDB (Pee Dee belemnite) may indicate some later diagenetic modification of micrite and microspar, no clear covariance is seen with $\delta^{13}C$ (Fig. 2C), and other apparently well-preserved Neoproterozoic and Cambrian carbonates yield similar $\delta^{13}C$ values (Hudson and Anderson, 1989; Derry et al., 1992). As a further test, we analyzed the covariance of $\delta^{18}O$ and determined the concentrations in parts per million (ppm) of Mg, Fe, Mn, and Sr at 30 points through the succession, by atomic absorption at Nancy, France. Figure 2D plots these potential dia-

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genetic indicators against $\delta^{18}O$. Pervasive postdepositional alteration should result in correlated changes of the trace element and $\delta^{18}O$ values. The lack of such correlation and the absence of $\delta^{18}O/\delta^{13}C$ covariance (Fig. 2C) suggest that the $\delta^{13}C$ signal on which our study is based is not predominantly caused by diagenetic alteration. We infer that micrite-microspar can provide a good indication of seawater $\delta^{13}C$ through the Tommotian to Toyonian, with potential for global correlation.

**ISOTOPES AND BIOEVENTS**

The Proterozoic-Cambrian (Pz-C) boundary has recently been defined in Newfoundland at the first appearance of an assemblage of trace fossils with branching forms including *Phycodes pedum* (Landing et al., 1988). The position of the Pz-C boundary in Siberia is uncertain, as definitive correlations with the type section have not yet been firmly established. Cambrian trace fossils are known below the Tommotian, in the Nemakit-Daldynian Stage of Olenek, north Siberia (Fedonkin, 1993) at a level herein correlated with level B (Fig. 1; M. Fedonkin, 1993, oral commun.). This is above the first appearance of small shelly fossil assemblages with *Anabarites trisulcatus*.
joined at about levels B and B' by a more west Prianabar region of northern Siberia (Fig. 1, level A; Pokrovsky and Missarzhevsky, 1993) and the Uchur region of east Siberia (Fig. 1, level A'; Brasier et al., 1993). Note that negative \( \delta^{13}C \) values characterize the latest Proterozoic (Strauss et al., 1992); they become more positive toward the boundary interval (levels A to B) and culminate in a positive excursion (cycle Z).

In the Uchur region, this early biota is joined at about levels B and B' by a more diverse assemblage of small shelly fossils, including the first cap-shaped shells (mollusk sclerites?) and snails (Brasier et al., 1993). This *Purrella* fauna spans a major \( \delta^{13}C \) excursion (cycle I) now traced on a global scale (Kirschvink et al., 1991). A greater increase in invertebrate diversity occurs at levels C to D near the base of the Tommotian, where the earliest Brachiopoda and archaeocyathan sponges appear (Rozanov, 1992) at the top of \( \delta^{13}C \) cycle I.

The first trilobites are found at level F, followed by a radiation of other arthropods (bradoriids and phyllocarids, levels G to H), during the positive \( \delta^{13}C \) excursion of cycle IV, correlated into Morocco (Kirschvink et al., 1991) and Newfoundland (Brasier et al., 1992). Major innovations in archaeocyathan architecture also took place then, but their peak of innovation and diversity occurred between levels L and N (Debrenne, 1991) during the positive \( \delta^{13}C \) excursion of cycle VII (Fig. 1), which can be traced into southwest Mongolia (our unpublished data) and Comley, England (Brasier et al., 1992). Echinodermata also radiated at this time.

Turnover in shallow-shelf trilobites (levels M and N) was followed by a rapid decline in archaeocyathan sponge diversity (levels O and P) leading to mass extinction of numerous clades by late Toyonian time (see Fig. 1; Zhuravlev, 1986; Debrenne, 1991; Signor, 1992). Our isotopic data reveal a major offset near level O, followed by a prolonged negative interval that broadly coincides with this biotic crisis (Fig. 1). Limited data from upper Botomian-Toyonian carbonates in Labrador (Grant, 1992), the Great Basin, United States (Brasier, 1993), and northwest Scotland (M. D. Brasier, unpublished) also yield negative values. Closer sample spacing is still needed to characterize the *L. grandis* Zone, but positive values are known from elsewhere at this level in Siberia (Galimov, 1968) and Australia (Donnelly et al., 1988).

**DISCUSSION**

Multiple spikes occur throughout an interval of mainly high \( \delta^{13}C \), coincident with explosive evolutionary events (Fig. 1, levels A to N). Such positive excursions imply
creases in the fraction of carbon buried as organic matter. The duration of these intervals appears too long to be explained by oceanic overturn or increased upwelling (cf. Kump, 1991); they may have been caused by increased rates of sedimentation (e.g., Derry et al., 1992), raised primary productivity, and/or marine anoxia (Brasier, 1992).

Oxygen thus liberated would normally be balanced by oxidation of sulfides (Veizer et al., 1980), but heavy $^{34}$S values from early Cambrian sulfates and sulfides (e.g., Claypool et al., 1986; Hayes et al., 1992) suggest that oxygen may have been released to the atmosphere during intervals of carbon burial. More $^{34}$S data, and more paleobiological studies, are needed to test this and the connection between oxygen, the first invertebrates, and the Cambrian explosion (e.g., Derry et al., 1992; Hayes et al., 1992; Kasting et al., 1992).

The sharp drop in values in middle to late Botomian time suggests a significant decrease in the fraction of carbon buried as organic matter. It is also possible that this shift reflects a decrease in primary productivity related to the extinction event, as at the K-T boundary (cf. Magaritz, 1989). A clue to the cause of these isotopic variations may be provided by the newly calibrated Early Cambrian time scale. Bowring et al. (1993) have shown that the Tommotian to Botomian interval was ~10 Ma, which would imply that these $^{81}$C cycles averaged between 1 and 2 Ma. Together with the coincidence between the Botomian extinction event and a negative shift, the short time scale suggests that variations in primary productivity could have caused shifts in carbon burial. If so, the $^{81}$C record during this key interval may reflect flurries of biological activity in the rapidly changing Cambrian oceans.

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