# GLOBAL CLIMATIC AND STABLE ISOTOPIC CORRELATIONS DURING THE EARLY PERMIAN (CISURALIAN) 

A Senior Scholars Thesis<br>by<br>JORDAN NORET

Submitted to the Office of Undergraduate Research
Texas A\&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2009

Major: Geology
Environmental Geoscience

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Approved by:
Research Advisor: Ethan Grossman
Associate Dean for Undergraduate Research: Robert C. Webb

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ABSTRACT<br>Global Climatic and Stable Isotopic Correlations During the Early Permian (Cisuralian). (April 2009)<br>Jordan Noret<br>Department of Geology and Geophysics<br>Texas A\&M University<br>Research Advisor: Dr. Ethan Grossman<br>Department of Geology and Geophysics

The early Permian was an interval when cool, glaciated conditions, similar to those of the present-day, shifted to warm, non-glaciated conditions. As a result, climatological information about this time period is pertinent in studying the causes and effects of global warming. This study presents new oxygen and carbon stable isotopic data $\left(\delta^{18} \mathrm{O}\right.$ and $\delta^{13} \mathrm{C}$, VPDB) from carefully screened, early Permian brachiopod shells from the Ural Mountains. Using cathodoluminescence (CL) microscopy, 24 specimens were determined to be well-preserved and were used for 95 stable isotopic analyses. Interspecimen variability within each time horizon was lower than $0.5 \%$ and intra-specimen variability was lower than $0.2 \%$.

The $\delta^{18} \mathrm{O}$ values of the specimens analyzed average between $-2.2 \%$ and $-2.7 \%$ through the Asselian, Sakmarian, and early Artinskian (297-283 Ma). Values then rapidly increase by $3 \%$ in the late Artinskian and early Kungurian ( $\sim 275 \mathrm{Ma}$ ). The low values before the Kungurian do not suggest glacial conditions and thus disagree with the geological evidence for a glacial maximum during the Asselian. These data also disagree with the early Permian maximum and subsequent decline in $\delta^{18} \mathrm{O}$ suggested from brachiopod shell fragments from the Usolka section in the Urals (Korte et al., 2005. Palaeogeog., Palaeoclim., Palaeoecol. 224, 333-351). However, our data are similar to those obtained from other brachiopods (Grossman et al., 2008. Palaeogeog., Palaeoclim., Palaeoecol. 268, 222-233). The cause of this discrepancy is unknown, but could be a result of differences in regional oceanographic factors, glacial/interglacial conditions, or in source material (i.e. wholly preserved shells versus shell fragments). The ArtinskianKungurian increase in $\delta^{18} \mathrm{O}$ from this study is evidence for the aridification of the epicontinental seas of Laurussia and possibly a return to cooler conditions.

The $\delta^{13} \mathrm{C}$ data from the specimens discussed in this study show a gradual decrease of about $1.5 \%$ from the late Asselian to the Artinskian, followed by a sharp increase of about $1.5 \%$ in the late Artinskian. This $\delta^{13} \mathrm{C}$ increase is not seen in previously published data from Russia or North America. Further work is required before any strong conclusions can be made on global $\delta^{13} \mathrm{C}$ variability during the early Permian.

## DEDICATION

To those who teach, inspire, and set free.

## ACKNOWLEDGMENTS

I would like to thank foremost my advisor, Dr. Ethan Grossman, for giving me the opportunity to participate in primary research as an undergraduate student and for his continual advice and help throughout the duration of this project. Dr. Thomas Yancey lended his paleobiological expertise extensively during this project and Dr. Boris Chuvashov also deserves special acknowledgement for his help in collecting and identifying the specimens used, as well as his expertise in the stratigraphy of the Southern Urals. Beyond the scientific side of this project, acknowledgement is owed to Shane McGary for training me on the laboratory equipment used in preparing the specimens for analysis, to Kai Tao and Josiah Straus for their help with the mass spectrometer work, and Dr. Ray Guillemete for helping me through many of the setbacks and procedural issues that I encountered. Lacey Terrette took measurements of specimen thin-sections which were used to obtain the scales of corresponding images. Lastly, and perhaps most importantly, I am greatly indebted to my mother who read this manuscript many times, giving essential grammatical and editorial advice along the way, and to my wife, Robin, who put up with me throughout this project.

## NOMENCLATURE

PL

CL

NL
SMFL

LCBL

HCBL

Ma
thin-section viewed under plane light thin-section viewed under cathodoluminescence light non-luminescent specimen shell margin and fracture luminescence in specimen low contrast banded luminescence in specimen high contrast banded luminescence in specimen megaannum (1 million years ago)

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## CHAPTER I

## INTRODUCTION

The understanding of past climate change is a critical tool for studying current climate. It is crucial in determining the significance of climate trends, how much and how fast the climate has changed in the past, whether human activity has caused past or present-day change, and whether the mitigation of future change is desirable and feasible. Moreover, the conclusions of paleoclimatological studies, particularly those concerning climate conditions similar to those of the present-day, are vital for providing a sound scientific basis for environmental policy decisions.

### 1.1 Significance of the early Permian climate

During the early Permian ( $\sim 300-270 \mathrm{Ma})$, Earth's climate shifted from one similar to the present day to one much warmer, from having abundant glaciers to having few or possibly none. This is evidenced by the widespread distribution of glacial sediments dating to the Carboniferous ( $>300 \mathrm{Ma}$ ) and early Permian, and the subsequent lack thereof soon afterwards until the Cenozoic era, more than 200 million years later (Frakes et al., 1992; Isbell et al., 2003, Fielding et al., 2008). The early Permian is therefore the most recent period in Earth history from which there is ample geologic evidence that an ice-house climate, similar to that of today, shifted to a hot-house climate.
$\overline{\text { This thesis follows }}$ the style of Palaeogeography, Palaeoclimatology, Palaeoecology.

Montañez et al. (2007) synthesized available stable isotope data from this time and used these to estimate atmospheric $p \mathrm{CO}_{2}$. This work further demonstrated that the Permian is a good analogue for the current climate in that their isotopic measurements and model calculations suggest that $\mathrm{CO}_{2}$ concentrations were near present-day levels $(<1000$ ppmV ) during glacial periods, and concentrations during glacial-free periods were similar to those expected in the near future ( $>2000 \mathrm{ppmV}$ ) if fossil fuel resources are totally exhausted (Montañez et al., 2007).

By researching certain climatological and ecological aspects of the early Permian world, scientists will be able to compare a climate change that took place in the absence of human activity with a present-day climate trend, such as the one described by the Intergovernmental Panel on Climate Change (IPCC, 2007). New data, carefully screened for quality, are presented in this study to strengthen the understanding of climate change during the early Permian period.

### 1.2 Stable isotopes as paleoclimate proxies

Stable oxygen $\left({ }^{18} \mathrm{O} /{ }^{16} \mathrm{O}\right)$ and carbon $\left({ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}\right)$ isotopic measurements of well preserved carbonate fossils can be effectively used to study past climate and carbon cycle variability. Isotopic fractionation of oxygen and carbon isotopes occurs during the water cycle, mineral precipitation in seawater, and in biological processes. Some of these
fractionation processes have important global and local effects on $\delta^{18} \mathrm{O}$ and $\delta^{13} \mathrm{C}$ in the ocean-atmosphere system and are critical to consider in stable isotopic studies.

Variation of mean seawater $\delta^{18} \mathrm{O}$ values over million-year time scales is dependent mainly on the volume and distribution of glaciers, but can also be affected by tectonic processes over longer time scales ( $10^{7}$ years) (Shackleton and Opdyke, 1973; Railsback, 1990; Veizer et al., 1999). Higher glacial volume increases seawater $\delta^{18} \mathrm{O}$ because glacial ice is highly depleted in ${ }^{18} \mathrm{O}$. Where marine waters are not well circulated (e.g., epicontinental seas), seawater $\delta^{18} \mathrm{O}$ values can be regionally affected by high evaporation rates, increasing $\delta^{18} \mathrm{O}$, or freshwater input, decreasing $\delta^{18} \mathrm{O}$. Some researchers (e.g., Veizer et al. 1997, 1999; Veizer and Mackenzie, 2004; Wallmann, 2001, 2004) posit that seawater $\delta^{18} \mathrm{O}\left(\delta^{18} \mathrm{O}_{\mathrm{w}}\right)$ values have changed significantly during the Phanerozoic as a result of tectonic processes that drive long-term exchange of lithosphere and hydrosphere components. This hypothesis better accommodates the very low $\delta^{18} \mathrm{O}$ values that have been obtained from early Phanerozoic (Cambrian-Devonian) marine fossils (Veizer et al., 1999). Nonetheless, this long-term trend would not have significant effect over the relatively short span of time considered in this study.

Oxygen isotope compositions from well preserved calcite also record paleotemperatures from the time of formation. As a result of thermodynamically-controlled fractionation, $\delta^{18} \mathrm{O}$ values are higher in calcite relative to the seawater in which it was precipitated. The magnitude of this fractionation is dependent on the temperature of the environment.

Epstein et al. (1953) developed an empirical relationship between ambient water temperature and $\delta^{18} \mathrm{O}$ values of precipitated calcite. This relationship was later confirmed by O'Neil et al. (1969) and recast by Hays and Grossman (1991):

$$
\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)=15.7-4.36\left(\delta^{18} \mathrm{O}_{\text {calcite }}-\delta^{18} \mathrm{O}_{\mathrm{w}}\right)+.012\left(\delta^{18} \mathrm{O}_{\text {calcite }}-\delta^{18} \mathrm{O}_{\mathrm{w}}\right)^{2}
$$

where $\delta^{18} \mathrm{O}_{\text {calcite }}$ is the $\delta^{18} \mathrm{O}$ value of the calcite and $\delta^{18} \mathrm{O}_{\mathrm{w}}$ is the value of the seawater. By using this relationship between temperature and $\delta^{18} \mathrm{O}$, data from well-preserved carbonate can ultimately be used to determine the temperature of the ancient marine body in which the carbonate precipitated (Shackleton and Opdyke, 1973; Grossman, 1994). However, an uncertainty in using this method for determining paleotemperatures is that the $\delta^{18} \mathrm{O}$ of ancient seawater $\left(\delta^{18} \mathrm{O}_{\mathrm{w}}\right)$ must be known, and therefore the effect of glacial volume, freshwater input, and evaporation on $\delta^{18} \mathrm{O}_{\mathrm{w}}$ must be estimated.

With regard to carbon isotopes, $\delta^{13} \mathrm{C}$ values record changes in the carbon cycle. These changes are mainly the result of enhanced burials of organic matter, increasing $\delta^{13} \mathrm{C}$ values in the ocean-atmosphere system (Scholle and Arthur, 1980; Schidlowski and Aharon, 1992; Kump and Arthur, 1999). However, the release of ${ }^{13} \mathrm{C}$-depleted volcanic $\mathrm{CO}_{2}$ (Renne et al., 1995) and methane discharges (Dickens et al., 1997) are also possible causes of $\delta^{13} \mathrm{C}$ variability. An important local process that influences regional variation in $\delta^{13} \mathrm{C}$ is the circulation of ${ }^{12} \mathrm{C}$-enriched anoxic bottom-waters of the ocean system (Knoll et al., 1996).

### 1.3 Early Permian $\delta^{18} \mathrm{O}$ and $\delta^{13} \mathrm{C}$ stratigraphy

It has been widely demonstrated that there were three major glacial periods in the late Paleozoic (e.g. Frakes et al., 1992; Isbell et al., 2003, Fielding et al., 2008), the last of which ended in the early Permian (Cisuralian), the time period on which this study focuses. Data from some low paleolatitude (Korte et al., 2005) and high paleolatitude (Korte et al., 2008) brachiopods, give evidence for an Asselian-Artinskian (295-280 Ma) decrease in $\delta^{18} \mathrm{O}$. This is an expected trend for the end of a glacial interval as ${ }^{18} \mathrm{O}$ depleted glacial water is returned to the oceans and is concomitant with the end of the Cisuralian glacial episode. However, some researchers (e.g., Grossman et al., 2008) contend that the conclusions from the low-latitude data require confirmation as the specimens analyzed were small shell fragments and not wholly-preserved shells. In contrast with the trend observed by Korte et al. $(2005,2008)$, data from Grossman et al (2008), including some from the same low latitude sites as Korte et al. (2005), show an Asselian-Artinskian increase in $\delta^{18} \mathrm{O}$. These authors largely attribute the upward trend to regional aridification exacerbated by restricted circulation in the epicontinental seas that covered the specimen localities during this time.

Trends in carbon sequestration have also been used to investigate the record of climate change. Although $\delta^{13} \mathrm{C}$ data from carbonate fossils are sparse and vary widely, Grossman et al. (2008) observed that each of the three late Paleozoic glacial events described by Isbell et al. (2003) and Fielding et al. (2008) occurred nearly concurrently with or after a rise in $\delta^{13} \mathrm{C}$. This suggests that these glacial events were in some way
related to carbon sequestration. However, inconsistencies that exist in the available data from Korte et al. (2005) and Grossman et al. (2008) (i.e., differences between Uralian and North American data) points to the difficulties in resolving a global signal for carbon system perturbations.

### 1.4 Significance of this study

In this study, I present new $\delta^{18} \mathrm{O}$ and $\delta^{13} \mathrm{C}$ data from 30 carefully screened brachiopod shells to strengthen the present understanding of the climate during the early Permian. My data are especially interesting in that the specimens used are similar in locality and age as those used by Korte et al. (2005), but wholly-preserved brachiopod shells were micro-sampled ( $<150 \mu \mathrm{~g}$ powders) for analysis instead of macro-sampled shell fragments (150-450 $\mu \mathrm{g}$ "splinters" and 1-3 mg aliquots) (Korte et al., 2005).

## CHAPTER II

## SPECIMENS AND METHODS

### 2.1 Specimens and specimen localities

Many marine organisms such as foraminifera, brachiopods, and bivalves precipitate accretionary hard parts such as shells that are made of calcium carbonate $\left(\mathrm{CaCO}_{3}\right)$ which can then be analyzed for stable oxygen and carbon isotopes. Fossil brachiopods have been shown to be especially useful for stable oxygen and carbon isotopic research (Compston, 1960). Most importantly, the thick secondary layer of contemporary brachiopod shells has been shown to precipitate at or near oxygen isotopic equilibrium with coeval seawater (e.g. Parkinson et al., 2005) and oxygen isotope data from fossil brachiopods show minimal variability between co-occurring taxa (Grossman et al., 1991; Lee and Wan, 2000). Secondly, the calcitic mineralogy, low magnesium content, and dense microstructures of the shells give them a superior resistance to diagenetic alteration (Compston, 1960; Lowenstam, 1961; Popp et al., 1986). Thick shells can be especially resistant, so that studies of seasonal variation are even possible (Mii and Grossman, 1994). For these reasons, carbon and oxygen stable isotope data from chemically-pristine brachiopod shells can be used to construct reliable stable isotope stratigraphies for sediments as old as Paleozoic.

The specimens used in this study were collected from early Permian exposures in the Southern Urals near the Russian cities of Kungur, Krasnoufimsk, and Sterlitimak
(Figure 1). This field work was conducted by Dr. Thomas Yancey, a professor of geology at Texas A\&M University, USA, with the help of Dr. Boris Chuvashov, a geologist with the Urals Branch of the Russian Academy of Sciences. Specimens collected were assigned to stratigraphic "horizons", roughly the Russian equivalent to U.S. formations, based on the stratigraphy established by Russian stratigraphers (e.g. Chuvashov and Nairn [1993], Chuvashov and Chernykh [2000], and Chuvashov et al. [2002]). These stratigraphic horizons are primarily based on faunal zones (foraminifers, ammonoids, and conodonts) described by Chuvashov et al. (2002).

Originally, 45 brachiopod shells were selected for this study. However, 14 were excluded from analysis because they were poorly preserved or were too thin for proper isotopic analysis. This left 31 specimens: eight from the late Asselian, four from the early Sakmarian, one from the early Artinskian, two from the middle Artinskian, 11 from the late Artinskian, and five from the early Kungurian. The genera include Chaoiella, Kalitvella, Purdonella, and Stenoscisma. See Figure 2 for an overview of these 31 specimens and Appendix C for detailed information on all of the specimens selected for this study.

## Specimen paleogeography

According to Blakey (2008) and Scotese (2008), the study area was at a latitude of $\sim 30^{\circ}$ north during the early Permian. Laurussia was converging with the Kazakhstanian and Siberian plates - producing the Ural orogeny and shoaling the Russian Platform Seaway


Figure 1. Specimen localities in the Southern Urals of Russia.

|  | LEGEND | Specimen ID | Latitude, Longitude |
| :---: | :---: | :---: | :---: |
| $\square$ | Russia | SQ17 | $56^{\circ} 52.1{ }^{\prime} \mathrm{N}, 57^{\circ} 25.0^{\prime} \mathrm{E}$ |
| $\square$ | Kazakhstan | KQ8 | $57^{\circ} 23^{\prime} \mathrm{N}, 57^{\circ} 05.9^{\prime} \mathrm{E}$ |
|  | Ka | KQ1 | $57^{\circ} 23^{\prime} \mathrm{N}, 57^{\circ} 05.9^{\prime} \mathrm{E}$ |
| W | specimen locality | AY2 | $55^{\circ} \mathbf{2 2}$ ' $\mathrm{N}, 57^{\circ} 59{ }^{\prime} \mathrm{E}$ |
| 0 | city or town | CQ | $56^{\circ} \mathbf{4 8 . 1}{ }^{\prime} \mathrm{N}, 57^{\circ} \mathbf{4 3 . 7}{ }^{\prime} \mathrm{E}$ |
|  | river (width not | AS4 | $56^{\circ} 30.3{ }^{\prime} \mathrm{N}, 57^{\circ} 41.9^{\prime} \mathrm{E}$ |
|  | to scale) | AA1 | $53^{\circ} 33.9$ ' , 56 ${ }^{\circ} 04.4{ }^{\prime} \mathrm{E}$ |
| ------ | Meridians/Parallels | ST1 | $53^{\circ} 44.3{ }^{\prime} \mathrm{N}, 56^{\circ} 06.1^{\prime} \mathrm{E}$ |
|  |  | KY | $53^{\circ} \mathbf{4 4 . 3}{ }^{\prime} \mathrm{N}, 56^{\circ} 06.1^{\prime} \mathrm{E}$ |
|  |  | BT1 | $53^{\circ} 33.2^{\prime} \mathrm{N}, 56^{\circ} 05.9^{\prime} \mathrm{E}$ |


| Stage | Horizon (Formation) | Locality* | Depositional Environment | Taxon | Specimen ID | Age\# |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Saraninian (Lower Saraninian Member) | Nizhneizginsk | argillaceous micrite / interreef muds | Kalitvella sp. | SQ17b | 274.8 |
|  |  |  |  |  | SQ17a | 274.8 |
|  |  | Chikali quarry, <br> Kungur city | biomicrite / small 'reef' and bedded limestone | Stensocsisma mutabilis | KQ8-2 | 274.5 |
|  |  |  |  |  | KQ8-1 | 274.5 |
|  |  |  |  | Chaoiella | KQ1-1 | 275 |
|  | Sarginskian | Mechetlino village | gravelly shell concentrates and poorly sorted argillaceous sands / debris flow into flysch basin (non-reef) | Stenoscisma mutabilis | AY2-6 | 275.7 |
|  |  |  |  | Kalitvella sp. | AY2-4b | 275.7 |
|  |  |  |  |  | AY2-4a | 275.7 |
|  |  |  |  |  | AY2-3 | 275.7 |
|  |  |  |  | Chaoiella | AY2-2 | 275.7 |
|  |  | Lebayshye quarry, Chatlik village | biomicrite \& biosparite / small reef with abundant fossils |  | CQ3-1 | 276 |
|  |  |  |  | Stenoscisma mutabilis | CQ15-1 | 276.3 |
|  |  |  |  | Kalitvella sp. | CQ12-2 | 276.3 |
|  |  |  |  |  | CQ12-1 | 276.3 |
|  |  |  |  | Chaoiella | CQ13-2 | 276.5 |
|  |  |  |  |  | CQ13-1 | 276.5 |
|  | Irginskian | Sarana village | argillaceous micrite with shells / bedded limestone | Chaoiella | AS4-6 | 278.6 |
|  |  |  |  | Stenoscisma mutabilis | AS4-3 | 278.6 |
|  | Burzevskian | Maly tau shikhan, Sterlitamak | biomicrite \& biosparite / reef massif with abundant fossils (bioherm) | Kalitvella sp. | AA1-1 | 283 |
|  | Tastubskian | Yurak tau shikhan, Sterlitamak | biomicrite \& biosparite / reef massif with abundant fossils (bioherm) | Purdonella nikitini | ST1-2 | 293 |
|  |  |  |  |  | ST1-1 | 293 |
|  |  |  |  | Kalitvella sololovi | KY-2 | 293 |
|  |  |  |  |  | KY-1 | 293 |
|  | Shikhanskian | Tra tau shikhan, Sterlitamak | biomicrite \& biosparite / reef massif with abundant fossils (bioherm) | Stenoscisma mutabilis | BT1-6 | 296 |
|  |  |  |  |  | BT1-5 | 296 |
|  |  |  |  | Chaoiella | BT1-4 | 296 |
|  |  |  |  |  | BT1-3 | 296 |
|  |  |  |  | Purdonella nikitini | BT1-2 | 296 |
|  |  |  |  |  | BT1-1 | 296 |
|  |  |  |  | Kalitvella sololovi | BT1-K2 | 296 |
|  |  |  |  |  | BT1-K1 | 296 |

[^0]that connected the Paleo-Tethys and Boreal oceans (Figure 3). The study area was located in this seaway, with most of the brachiopod specimens coming from the shelf margin on the west side of the Preuralian foredeep, an area characterized by shallow, nutrient-rich water, large reef systems, and bioherms (Chuvashov and Nairn, 1993). These reefs and bioherms first began to grow in the Asselian and mark the geographic transition zone between shallow seas covering the eastern margins of the Russian craton and the deeper seas of the Preuralian foredeep (Chuvashov and Nairn, 1993). Many of the specimens chosen for this study were collected from Tra tau shikhan, Yurak tau shikhan, and Maly tau shikhan, which are examples of these large bioherms (Figure 4). Most of the specimen lithologies are dominated by biomicrites, biosparites, or argillaceous micrites, suggestive of a reef environment. The five AY specimens were taken from gravelly shell concentrates and poorly sorted argillaceous sands indicative of deposition by a debris flow that originated on the east margin of the Preuralian foredeep.



Figure 4. Photo of Yurak Tau shikhan (background) near Sterlitamak, Russia; courtesy of Ethan L. Grossman. This is an example of the immense bioherms (shikhans) from which the Asselian, Sakmarian, and early Artinskian specimens used in this study were collected.

### 2.2 Methods

First, brachiopod specimens were obtained and identified to genus and species, if possible. Specimens were embedded in epoxy and cut longitudinally in preparation for making thin sections. The plane of thin section was determined to take advantage of the thickest part of each shell when sampling the resulting billets. To acquire isotopic data most representative of original shell chemistry, I used a slightly modified version of the "TAMU" method described by Grossman (1994) and Mii et al. $(1999,2001)$ for checking specimen preservation. This method is itself a modification of the method first used by Popp et al. (1986) who used cathodoluminescence (CL) microscopy to determine manganese $(\mathrm{Mn})$ content of thick-sectioned shells, as increasing Mn content causes brighter luminescence. Increased Mn content is indicative of post-deposition
alteration and is thus used as an indicator for diagenetic influence (Popp et al., 1986; Grossman, 1994). This technique was extended in the TAMU method by going a step further and producing and photographing thin sections under plane-polarized light (PL) and CL. Shells that are characterized as luminescent under CL or as opaque, dark, or cloudy under PL were avoided for isotopic analysis. This CL microscopy technique was demonstrated by Bruckschen et al. (1999), as discussed by Grossman et al. (2008), to be more effective at reducing the contamination by secondary calcite than the "Ruhr" method used by Veizer et al. (1999), Bruckschen et al. (1999), and Korte et al. (2005, 2008).

Specifically, I used a TECHNOSYN Model 8200 MK II cathodoluminescence stage to obtain PL and CL photographs of my specimens. The physical preservation of each was checked using the PL photographs. Each shell that displayed a prismatic or fibrous microstructure was characterized as "preserved" and the rest as "not preserved". The degree of luminescence in each specimen was characterized using a slightly modified version of the scheme used in the TAMU method. Shells that were dominantly nonluminescent were labeled as "non-luminescent" (NL; Figure 5A). Shells that only displayed luminescence along shell margins and fractures were labeled as "shell margin and fracture luminescent" (SMFL; Figure 5B). Shells that displayed alternating bands of luminescence and non-luminescence were labeled as "high-contrast banded luminescent" (HCBL; Figure 5C) while shells that displayed alternating bands of bright and dull luminescence were labeled as "low-contrast banded luminescent" (LCBL;

Figure 5D). Shells that were dominantly luminescent were labeled as "luminescent" (L). Figure 5 shows examples of LCBL, HCBL, SMFL, and NL shells. However, this method is still not fool-proof for identifying diagenetic alteration. For example, Barbin and Gaspard (1995) showed that parts of unaltered modern brachiopod shells display luminescence while Rush and Chafetz (1990) and Qing and Veizer (1994) showed that some altered fossil shells are non-luminescent.

Using these PL and CL images as a reference (Appendix B), only non-luminescent areas of each specimen were sampled with a dental drill using a $500 \mu \mathrm{~m}$ stainless-steel bur. I sampled each specimen as many times as possible, ranging from one to eight areas (average $\sim$ four), to best provide a seasonally averaged value for the whole specimen. This sampling technique also reduces the chance of skewed data that would result if part of the specimen is chemically altered, or if slight contamination from the matrix or epoxy occurred in one of the sampling sites. When possible, I also sampled the rock matrix surrounding each specimen. Approximately $300-500 \mu \mathrm{~g}$ of powder was extracted from each sampling site and was stored in a labeled micro-centrifuge tube and analyzed separately. About $150 \pm 50 \mu \mathrm{~g}$ of each powder sample was then digested in concentrated phosphoric acid (specific gravity $=1.91-1.93$ ) on a ThermoFinnigan Gas Bench II device. The $\mathrm{CO}_{2}$ released was analyzed on a ThermoFinnigan DeltaPlusXP isotope ratio mass spectrometer at the Geology and Geophysics Stable Isotope Laboratory, Texas A\&M University (TAMU).


[^1]Stable isotope data are reported using delta ( $\delta$ ) notation which compares the relative abundances of minor and major isotopes in a sample, such as ${ }^{18} \mathrm{O} /{ }^{16} \mathrm{O}$ or ${ }^{13} \mathrm{C} /{ }^{12} \mathrm{C}$ in carbonate, to those of an established standard:

$$
\delta(\%)=\left(\left[\mathrm{R}_{\text {sample }} / \mathrm{R}_{\text {standard }}\right]-1\right) * 1000
$$

where $R($ ratio $)=($ abundance of minor isotope / abundance of major isotope $)$
The data reported herein were calibrated to the Vienna Pee Dee Belemnite (VPDB) standard using NBS-19 reference material $\left(\delta^{13} \mathrm{C}=1.95 \%, \delta^{18} \mathrm{O}=-2.20 \%\right)$. As an inhouse check for the TAMU stable isotope laboratory, one NBS-19 sample is analyzed at the start and end of each 9 -sample run. Analytical precision, the standard deviation (1 $\sigma$ ) of replicate analyses of the NBS-19 standard, averaged $\pm 0.09 \%$ for $\delta^{18} \mathrm{O}$ and $\pm 0.05 \%$ for $\delta^{13} \mathrm{C}$ (Appendix C). The full procedure used in this study appears in Appendix A.

## CHAPTER III

## RESULTS AND DISCUSSION

### 3.1 Specimen quality

Of the 31 specimens examined under plane light (PL), all but one (CQ3-1) were determined to have preserved microstructure (Figure 6). Using CL microscopy, 12 of the specimens were determined to be almost completely devoid of a luminescent texture and were thus labeled as NL. Twelve were dominantly non-luminescent but displayed some luminescent areas along shell margins and fractures, and were labeled as SMFL. Six specimens displayed a luminescent banding texture (four LCBL and two HCBL), and CQ3-1 was completely luminescent (L). This luminescent specimen was not analyzed for isotopic data. CQ3-1 and all six of the shells which displayed banded luminescence are Chaoiella. Considering that the shells of this genus are characterized by a thick layer of coarsely fibrous calcite, a structure that is seldom found in productoid brachiopods, it seems likely that this shell microstructure is linked to banded luminescence. Similar banding in fossil cephalopods is believed to be caused by seasonality, stress, and periods of slow growth (Barbin et al., 1995).

### 3.2 Data and observed trends

For this study, 95 samples from the 24 NL and SMFL specimens were isotopically analyzed (Figures 6 and 7). Considering their luminescent quality, these specimens are believed to provide the most representative data for coeval seawater conditions. The six
specimens with luminescent banding were also analyzed to better understand the nature of this banding. Co-occurring matrix was also sampled and analyzed, when possible.

## Variability

In order to discern the significance of possible temporal trends in stable isotopic data, it is of utmost importance to measure the variability within each specimen and between specimens of similar age. Specimens were sampled serially as many times as practical from the anterior end to the dorsal end, and especially thick shells were also sampled serially from the outer margin to the inner margin. The mean intra-specimen variability (1 $\sigma$ ) for specimens with more than one sampled area was calculated to be $\pm 0.2 \%$ ( $\delta^{18} \mathrm{O}$ ) and $\pm 0.1 \%$ ( $\delta^{13} \mathrm{C}$ ) for NL and SMFL specimens, and $\pm 0.3 \%\left(\delta^{18} \mathrm{O}\right.$ and $\left.\delta^{13} \mathrm{C}\right)$ for HCBL and LCBL specimens. This low intra-sample variation suggests that the data is not skewed by poor sampling methods (e.g., sampling inconsistencies) or sample contamination (e.g., from matrix or altered shell), and that the data is representative of the true values of the fossil shells. It is also indicative that seasonality changes were only on the order of $\pm 0.1-0.3 \%$.


[^2]

Figure 7. Oxygen and carbon isotopic compositions of 24 NL and SMFL brachiopod specimens versus age. Data includes those provided by this study (NL and SMFL shell data only), Popp (1986), Korte et al. (2005), and Grossman et al. (2008). Data trends are given for Uralian data from this study and Korte et al. (2005).
*Temperatures were calculated using the equation reported in Hays and Grossman (1991) modified from O'Neil et al. (1969).


Inter-specimen variability ( $1 \sigma$ ) between NL and SMFL specimens within each stratigraphic horizon was also calculated (representing the variation between specimens of similar age), which averaged $\pm 0.5 \%$ for $\delta^{18} \mathrm{O}$ and $\pm 0.4 \%$ for $\delta^{13} \mathrm{C}$. Inter-specimen variability was not calculated for HCBL or LCBL specimens as there were too few from within similar stratigraphic horizons; therefore variability between these specimens would have been dominated by temporal variation. Although it is small, it is important to consider this magnitude of variation when comparing data temporally or geographically, as differences smaller than the inter-sample variability would not have any significance.

To test if any significant variation existed between specimens from reef deposits and those from non-reef deposits of similar age, the Mechetlino (non-reef lithology) data were plotted separately (Figure 8d). Although inter-specimen variability was higher in the Mechetlino (non-reef) specimens, the average values did not extend above or below those of the slightly older specimens (Chatlik) or the slightly younger specimens (Kungur and Nizhneizginsk). For these reasons, the Mechetlino data will not be discussed independently of the reef deposit data.

## Oxygen isotope record

In general, the $\delta^{18} \mathrm{O}$ data for the NL and SMFL specimens show relatively constant values in the late Asselian ( $\sim 296 \mathrm{Ma}$ ), Sakmarian ( $\sim 293 \mathrm{Ma}$ ), and into the late Artinskian ( $\sim 276.3 \mathrm{Ma}$ ) (Figures 6 and 7). The specimens from this interval are from shikhan
bioherms near Sterlitimak described in Chapter II. A mean $\delta^{18} \mathrm{O}$ value of $-2.6 \pm 0.5 \%$ $(\mathrm{N}=6)$ from late Asselian specimens remains unchanged in the early Sakmarian specimens averaging $-2.7 \pm 0.1 \%(\mathrm{~N}=4)$. This increased slightly to a $\delta^{18} \mathrm{O}$ value of $-2.2 \%(\mathrm{~N}=1)$ for the early Artinskian specimen and then decreased again to $-2.9 \%$ for the middle Artinskian specimen $(\mathrm{N}=1)$. However, only one specimen each was analyzed for the early and middle Artinskian and therefore the data may not be sufficiently representative of this time interval. There are two datasets for the late Artinskian: specimens from Chatlik ( $\sim 276.3 \mathrm{Ma}$; reef lithology) show an increase in $\delta^{18} \mathrm{O}$ to $-2.2 \pm$ $0.1 \%(\mathrm{~N}=4)$ and specimens from Mechetlino ( $\sim 275.7 \mathrm{Ma}$; non-reef lithology) also show an increase to a mean of $-0.9 \pm 0.7 \%(\mathrm{~N}=4)$. This increasing trend continued into the early Kungurian; the specimens from Kungur and Nizhneizginsk average $-0.3 \pm 0.7 \%$ 。 ( $\mathrm{N}=4$ ).

Of the six HCBL and LCBL specimens, three have similar $\delta^{18} \mathrm{O}$ values compared with the NL and SMFL specimens and three have lower values (Figures 6 and 8a). Two specimens (one LCBL shell from the Kungurian, and one HCBL shell from the late Artinskian) have values that are $\sim 2 \%$ lower than co-occurring taxa from this study. A third specimen (an LCBL shell from the late Artinskian) has a slightly lower ( $\sim 0.3 \%$ ) $\delta^{18} \mathrm{O}$ value from the other specimen of the same age. The remaining HCBL and LCBL specimens fall within a similar range of values acquired from the NL and SMFL specimens of similar age. As a result, the differences in $\delta^{18} \mathrm{O}$ appear to not be correlative with whether the shell displays an LCBL or HCBL texture. However, when also
considering the slightly higher intra-specimen variability that exists in the LCBL and HCBL specimens, future studies using specimens with banded luminescence should use greater scrutiny in specimen screening and sampling.

## Carbon isotope record

The $\delta^{13} \mathrm{C}$ data from the NL and SMFL specimens show a gradual decrease from the late Asselian ( $\sim 295 \mathrm{Ma}$ ) mean $\delta^{13} \mathrm{C}$ value of $5.9 \pm 0.3 \%(\mathrm{~N}=6)$ to a mean of $5.0 \pm 0.5 \%$ $(\mathrm{N}=4)$ in the early Sakmarian specimens (Figures 6 and 7). This decreasing trend continued with a mean of $4.7 \%$ in the early Artinskian ( $\mathrm{N}=1$ ) and $4.3 \%$ in the middle Artinskian ( $\mathrm{N}=1$ ). There are two $\delta^{13} \mathrm{C}$ datasets for the late Artinskian: specimens from Chatlik show an increase to $5.4 \pm 0.6 \%(\mathrm{~N}=4)$ and specimens from Mechetlino also show an increase to a mean of $5.9 \pm 0.3 \%(\mathrm{~N}=4)$. This increasing trend appears to level off in the early Kungurian; the specimens from Kungur and Nizhneizginsk have a mean $\delta^{13} \mathrm{C}$ value of $5.8 \pm 0.2 \%(\mathrm{~N}=4)$.

The carbon isotope data acquired from the six HCBL and LCBL specimens show an interesting trend (Figures 6 and 8b). All six give much lower $\delta^{13} \mathrm{C}$ values than cooccurring specimens from this study. Data from the two late Asselian shells are $\sim 2.5 \%$ o lower while the remaining four shells are $\sim 1 \%$ lower. It appears that these differences in $\delta^{13} \mathrm{C}$ values are not correlative with the banding texture and are more likely related to biological processes, considering all six specimens belong to the genus Chaoiella. This suggests that this genus preferentially incorporates ${ }^{12} \mathrm{C}$ relative to the other brachiopods
analyzed. Such taxon-dependent vital effects have been previously suggested in other brachiopods (e.g., Popp et al., 1986; Mii et al., 2001).

## Matrix data

On average, matrix $\delta^{18} \mathrm{O}$ values are higher than those in co-occurring shells by about $1.5 \%$ for the Asselian and Sakmarian (Figures 6 and 8b). This ${ }^{18} \mathrm{O}$ enrichment in matrix relative to shell is unlike most previously published data (e.g., Mii et al., 1999) with the exception of some Moscovian samples from the Moscow Basin (Mii et al., 2001). Matrix $\delta^{18} \mathrm{O}$ values are lower than those of co-occurring shells in the Artinskian and Kungurian specimens. The cause of this transition is interesting and remains to be elucidated. Average matrix $\delta^{13} \mathrm{C}$ values from each locality are consistently lower than co-occurring shells, as expected, and follow a trend similar to the shell data, except for the late Artinskian and Kungurian specimens, for which matrix $\delta^{13} \mathrm{C}$ values become highly variable (Figures 6 and 8b).

### 3.3 Discussion

Korte et al. (2005) published $\delta^{18} \mathrm{O}$ data from some Uralian brachiopods that show very high values (above $-1 \%$ ) during the Asselian. However, those from this study, as well as from data published by Grossman et al. (2008) from Uralian and North American brachiopods are much lower, averaging below -2\% (Figure 7). Furthermore, the Uralian data published by Korte et al. (2005) indicate a decrease of more than $2 \%$ in
$\delta^{18} \mathrm{O}$ from the Asselian to the Artinskian (295-280 Ma), while the data from this study are relatively constant for the Asselian and Sakmarian (295-290 Ma). In this study, all ten specimens analyzed from this interval were well-preserved and collected from the shikhan bioherms near Sterlitimak. Considering the likely pristine nature of these shells, it is very possible that the high glacial volume during the Asselian (Isbell et al., 2003; Fielding et al., 2008) did not have a significant impact on $\delta^{18} \mathrm{O}_{\mathrm{w}}$ in the Laurussian epicontinental seas where my specimens originated. Although this disagrees with the high Asselian and Sakmarian $\delta^{18} \mathrm{O}$ values reported by Korte et al. (2005), their data were reportedly taken from brachiopod shell fragments, not wholly-preserved shells, which may be a cause of the anomalous $\delta^{18} \mathrm{O}$ records. Another possibility is that the data from this study represent interglacial conditions, while those of Korte et al. (2005) represent glacial conditions. To clarify these results and make stronger conclusions regarding Asselian and Sakmarian changes in $\delta^{18} \mathrm{O}$, further work is necessary.

Despite the discrepancy in the Asselian and Sakmarian data, the early and middle Artinskian $\delta^{18} \mathrm{O}$ data from this study generally agree with those previously published (e.g., Korte et al., 2005; Grossman et al., 2008) (Figure 7). However, the late Artinskian data from this study show a more dramatic increase in $\delta^{18} \mathrm{O}$ than these previous studies: values increased by $2 \%$ to $3 \%$ in less than five million years during the Artinskian and Kungurian. This would correlate to a drop in average ocean temperatures of more than $10^{\circ} \mathrm{C}$ if caused by a cooling climate and increased glacial volume, but the evidence for the onset of glaciation exists later in the Kungurian (Fielding et al., 2008). Therefore,
these high values are more likely a result of the effect that regional aridification could have had on $\delta^{18} \mathrm{O}_{\mathrm{w}}$. Evaporite deposits are common in Kungurian sediments of the Ural Mountains, as reported by Chuvashov and Chernykh (2000), which suggests that this is likely the case.

The $\delta^{13} \mathrm{C}$ data from this study do not agree with those from brachiopods previously studied by Grossman et al. (2008) and Korte et al. (2005) (Figure 7). Asselian and Sakmarian data from this study are about $1 \%$ higher than those of Korte et al. (2005) and show a decreasing trend while previous data are relatively constant during this time. Furthermore, $\delta^{13} \mathrm{C}$ data from this study sharply increase in the late Artinskian attaining values that are more than $2 \%$ higher than those of North American brachiopods of similar age (Grossman et al., 2008). These differences make it difficult to interpret temporal trends in $\delta^{13} \mathrm{C}$ during early Permian. However, considering that values are relatively constant during most of this interval, it appears that no global carbon cycle perturbations arose during this time. Variability among the data is more likely a product of regional differences in ocean circulation.

## CHAPTER IV

## SUMMARY AND CONCLUSIONS

I have presented data from 24 well-preserved brachiopod specimens from Russian Platform of the early Permian, along with six specimens that displayed banded luminescence, and more than 20 matrix analyses. Matrix $\delta^{13} \mathrm{C}$ data was consistently lower than shells of the same age, as expected, while $\delta^{18} \mathrm{O}$ values were higher in the matrix during the Asselian and early Sakmarian, after which matrix values were lower. No explanation for this $\delta^{18} \mathrm{O}$ trend is postulated. Significant differences were not apparent in $\delta^{18} \mathrm{O}$ and $\delta^{13} \mathrm{C}$ values between specimens from reef and non-reef deposits. All of the Chaoiella specimens have lower $\delta^{13} \mathrm{C}$ values than other co-occurring taxa, and all of the specimens with a luminescent texture were Chaoiella. This suggests that vital effects in Chaoiella play a role in both isotopic chemistry and luminescent characteristics.
$\delta^{18} \mathrm{O}$ values of Asselian through Sakmarian data are not consistent with the decreasing trend reported from other Uralian data (Korte et al., 2005). These latter data were obtained from shell fragments, not wholly-preserved shells, which may account for this difference. The low values presented in this study, along with those already published by Grossman et al. (2008), give evidence for the possibility that the early Permian deglaciation event was not recorded in epicontinental sea brachiopods. This suggests that the high glacial volume during the Asselian (Isbell et al., 2003; Fielding et al., 2008)
had little effect on $\delta^{18} \mathrm{O}_{\mathrm{w}}$ in the Laurussian epicontinental seas. However, a second possibility is that these low $\delta^{18} \mathrm{O}$ values are representative of sea level highstands during interglacial conditions, while the high values reported by Korte et al. (2005) represent sea level lowstands during glacial conditions.

The increasing trend in $\delta^{18} \mathrm{O}$ from the Artinskian through Kungurian in this study is consistent with other studies, and might suggest a return to cooler, possibly glaciated, conditions (e.g., Korte et al., 2005, 2008; Grossman et al., 2008). However, considering that the geologic evidence for the onset of glaciation exists later in the Kungurian, these high $\delta^{18} \mathrm{O}$ values are more likely the product of increasingly arid conditions on the continents surrounding the Laurussian epicontinental seas. This is supported by Kungurian evaporite deposits that are common in the vicinity of the Ural Mountains (Chuvashov and Chernykh, 2000).

Finally, the $\delta^{13} \mathrm{C}$ data from this study vary both from other Uralian brachiopod data (Grossman et al., 2008; Korte et al., 2005) and North American data (Grossman et al., 2008). This gives evidence to the probable dominance of local carbon cycle variability over global variability during the early Permian. However, further work to explicate the discrepancies between these data should be a priority if stable isotopes are to be used as paleoclimate proxies.

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## APPENDIX A COMPLETE PROCEDURE DETAILS

This appendix contains the complete procedure details pertaining to this project. The procedures used were based primarily on those written by H-S. Mii (01APR94; Mii, 1996), but were adapted for use with a digital microscope camera and an image analysis system. Furthermore, certain procedures that were not specifically used in this project (i.e. partially embedding shells in Procedure B) as well as some extraneous information (e.g. general laboratory cleanup procedures) were deleted. Mii's original procedures can be obtained via http://geoweb1.tamu.edu/faculty/grossman/DiGPaST/BrachProcedure_Mii_01APR94.pdf. Finally, please note that I use the term "specimen" for shells and "sample" for an individual powder sample taken from a specimen.

## Notes are given after certain procedures for further clarification.

## Procedure A. Initial Preparation of Specimens

1. Make a list of specimens on an Excel spreadsheet, including the genus/species and all other relevant information, as well as a unique ID for each. NOTE: See Appendix C1.
2. Prepare and label suitable containers for storing specimens (e.g., plastic sample box of appropriate size).
3. Photograph the specimens and labels for future reference. Include a scale (e.g., scale card or ruler).
4. Determine the best line along which the specimens should be cut for thin-sectioning and sampling, and mark it with a pen/marker/etc. This cutting plane should encompass the thickest part of the shell.
5. Determine whether the specimens will be completely or partially embedded. NOTE: I completely embedded all of my specimens.

## Procedure B. Embedding Specimens

NOTE: I fully embedded specimens, so I have removed the procedures for partially embedding specimens.

1. Select a suitable cardboard box for embedding specimens. Make sure that the specimens all fit in the box with at least $3-4 \mathrm{~mm}$ of space surrounding each specimen (including top and bottom). NOTE: I used between 3-6 specimens per box, which were on the order of 10 x $10 \times 5 \mathrm{~mm}$.
2. Label the sides of the box with the specimen IDs to keep track of the specimens.
3. Mix enough epoxy to fill the box 3-4 mm from the bottom.
4. Place epoxy in vacuum chamber for 10 minutes at about 28-30 torr to de-gas the epoxy and prevent air pockets from forming around specimens as it cures.
5. Before putting specimens in box, pour in a $3-4 \mathrm{~mm}$ layer of epoxy and wait 48 hours for it to cure. This thin layer of epoxy prevents the specimens from being damaged when the bottom of the box is cut away.
6. Arrange the specimens in the box so that there is 3-4 mm of space around them. They should be aligned and propped up with supporting material such that the planned cutting plane of each specimen (from procedure A4) is perpendicular/parallel with the edges of the box. NOTE: I used yellow clay on a few specimens (which became messy) and then small pieces of Styrofoam on the rest.
7. Mix, evacuate (see procedures B3 and B4), and pour enough epoxy to fill up the box in a layer no deeper than 2 cm and wait at least 48 hours for it to cure. Continue adding "layers" of epoxy until the specimens are completely embedded. Note that epoxy must be added in layers because it will not cure if too thick.

## Procedure C. Cutting Specimens

1. After specimens are embedded and epoxy has cured, use the trim saw to separate specimens from each other and to cut away the sides of the cardboard box. Be sure to make the cuts as straight and perpendicular to each other as possible.
2. Label individual specimens with permanent marker now that they are separated.
3. Store the specimens separately in the labeled storage containers.
4. Using the Isomet saw and as thin a blade as is practical, cut the sample along the cutting line marked in procedure A4.

## Procedure D. Preparing Glass Microscope Slides

## NOTE: I used pre-frosted slides, so I have removed the procedures for preparing non-frosted slides.

1. Etch the sample ID on the non-frosted side of the slide(s).
2. Grind down the corners of each slide using 320 -grit sandpaper and then 600 -grit sandpaper. Then grind down the edges on the frosted side of each slide. This prevents you from cutting yourself while working with them and prevents the slide from "grabbing" the cloth of the polishing wheel and damaging it.

## Procedure E. Making Thin-Sections

1. Determine which side of each cut specimen contains the thickest shell and proceed with that half. Store the other half in the labeled storage container.
2. Wash the specimen in distilled de-ionized water and ultrasonicate in distilled de-ionized water. Wash hands thoroughly.
3. Polish the surface of the specimen that is going to be glued to the glass slide using 320 grit polishing powder.
4. Wash the specimen in distilled de-ionized water and ultrasonicate in distilled de-ionized water. Wash hands thoroughly.
5. Polish specimen using 600 grit polishing powder.
6. Wash the specimen and glass slide in distilled de-ionized water and ultrasonicate in distilled de-ionized water. Wash hands thoroughly.
7. Glue the specimen onto the frosted side of the glass slide.
A. Using a glass stir rod spread a few drops of loctite or epoxy (no need to evacuate it) around to completely cover the surface of the specimen that will be glued. Attach specimen to slide.
B. If using loctite, put the sample(s) in the "heating box" overnight.
C. If using epoxy, allow it to cure for at least 48 hours (at room temperature).
D. Use kimwipes and absolute alcohol or acetone to wipe off the excess loctite/epoxy around the edges of the specimen after it has dried/cured.
8. Cut the specimen from the slide with the Isomet saw, leaving a thin-section roughly 500 microns thick.
9. Use the grinding wheel on the right side of the Hillquist petrographic saw to grind the thinsection to proper thickness. NOTE: Some of my specimens started to come off the slide during this step as a result of poor loctite/epoxy quality, so some of the thin-sections are several hundred microns thick. This problem might be avoided by heating billet in a warm oven for 24 hours and storing the billet in a desiccator for at least two hours before attaching it to the slide.
10. Polish the thin-section(s).
A. Polish the thin-section(s) using 320 grit polishing powder.
B. Clean the thin-section(s) with the ultrasonic cleaner. Wash hands thoroughly.
D. Polish the thin-section(s) using 600 grit polishing powder.
E. Clean the thin-section(s) with the ultrasonic cleaner. Wash hands thoroughly.
F. Polish the thin-section(s) using $9.5 \mu \mathrm{~m}$ polishing powder.
G. Clean the thin-section(s) with the ultrasonic cleaner. Wash hands thoroughly.
11. To see the specimen IDs better on the glass slides, mark over the specimen ID etchings with a permanent marker/pen.

## Procedure F. PL/CL Photography and Specimen Preservation Analysis

## NOTE: The images I acquired during these procedures can be found in Appendix B and full resolution versions can be found at http://jordan.noret.info/research/UGR.

1. Load the thin sections into the specimen compartment of the Technosyn Model 8200 MKII cathodoluminescence (CL) stage (cathodoluminoscope) and seal the compartment.
2. Turn on the cathodoluminoscope power and start the vacuum pump. Put pressure on the CL stage gun plate and door to make sure O-rings seal. Leave the vacuum pump running throughout the rest of this procedure. After the specimen chamber is sufficiently evacuated (this usually takes a minimum of 30 minutes), the electron beam will function properly.
3. While waiting for the chamber to fully evacuate, turn on the computer and digital camera attached to the microscope. Open the imaging software on the computer and center/focus the specimen on the screen using plane light in the microscope.
4. Plane light image. Using an exposure time that does not result in too dark or too light of an image (the brightness can be previewed on the computer monitor), capture the plane light image and save to computer. If the thin-section is of proper thickness, this exposure time should be less than 250 milliseconds (usually around $50-100 \mathrm{~ms}$ ). Thicker sections will require longer exposures. NOTE: For the thicker thin-sections described in procedure E10, I had to use exposures of up to 1 second.
5. Cathodoluminescence image. Turn off the microscope light, any other lights in the room, and cover the microscope with a dark cloth to prevent light from the computer monitor from leaking into the microscope stage.
A. Turn on the electron beam ( kV switch). The kV meter should read above 10 kV .
B. Using an exposure time of 5 seconds, capture the image and save to computer.
C. If image in previous step is too bright, try shorter exposure times. If image in previous step is too dark or completely black, try longer exposure times until a strong orange luminescence appears on the specimen (usually the calcite cements exhibit CL). Exposure times should not exceed 60 seconds.
D. If image is still completely black, either the kV knob needs to be turned up or there is no luminescence in the specimen. Use a previously photographed luminescent specimen to determine which is the case. NOTE: For most thin-sections I used exposure times of
between 10 and 20 seconds, but for the thicker thin-sections described in procedure E10, I had to use exposures of approximately 1 minute.

## Step G. Powder Preparation for Stable Isotopic Analysis

1. Obtain powder samples from specimens.
A. Select areas of shell to drill based on the PL/CL photographs, avoiding luminescent areas. Sampling locations should be distributed across whole shell. If possible, serial samples should be taken between the inner and outer shell margins.
B. Working under a binocular microscope, use a dental drill with a stainless steel dental bur to drill holes into the shell and collect the carbonate powder residue (about 300-500 $\mu \mathrm{g}$ from each hole).
C. Give each drill hole an ID and label a corresponding microcentrifuge tube. NOTE: For example, the tube corresponding to the first sample hole in specimen BT1-1 was labeled as BT1-1-1 or BT1-1(1).
D. Carefully sample the shell and transport the powder from each drill hole into its labeled microcentrifuge tubes.
2. Using a microbalance, take about $150 \mu \mathrm{~g}$ of each powder sample and place in a test tube to be analyzed by a stable isotope ratio mass spectrometer.
3. Follow the appropriate procedures in the stable isotope lab to analyze samples for collecurng $\delta^{13} \mathrm{C}$ and $\delta^{18} \mathrm{O}$ data.

## APPENDIX B

## SPECIMEN IMAGES

This appendix contains images of each specimen used for isotopic analysis, as well as the single specimen that was characterized as luminescent, which was not analyzed. Below is a brief overview of the format followed within. Note that images were rotated, resized, and sometimes flipped in order to fit on the page neatly or for easier comparison.
microscope imagery map
Image location 1 refers to images 1PL and 1CL, and so on.
NOTE: scale not determined for these images

## plane light images

Images taken under plane light to determine the preservation of shell microstructure. NOTE: scale bar is 2 mm in length

## cathodoluminescence images

Images taken under cathodoluminescence to determine the preservation of original shell chemistry.
data map
Locations of samples taken from each specimen and data values from each (X1-X3 are matrix samples). For tabular format, see Appendix C.
NOTE: scale not determined for these images



Full resolution images can be found at: http://jordan.noret.info/research/2009/undergrad

The scale bar used in PL/CL images above is 2 mm in length:
Data maps: W8:08GRo $8^{180}$ | BLACK $-\delta^{13} \mathrm{C}$
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr


Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in PL/CL images above is 2 mm in length: $\square \square \square \square$
Data maps: W\&्0
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in $\mathrm{PL} / \mathrm{CL}$ images above is $\mathbf{2 m m}$ in length:

Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in PL/CL images above is 2 mm in length

Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr


Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr


Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in PL/CL images above is 2 mm in length: $\square \square \square$
Data maps: W\&्0
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in PL/CL images above is 2 mm in length:

Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr


[^3]
The scale bar used in PL/CL images above is 2 mm in length:
Data maps: Whevere o $\mathbb{8}^{180}$ \| BLACK - $\boldsymbol{\delta}^{13} \mathrm{C}$
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

The scale bar used in PL/CL images above is 2 mm in length:
Data maps: Whelere o $8^{180}$ | BLACK - $\boldsymbol{\delta}^{13} \mathrm{C}$
Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr


The scale bar used in PL/CL images above is 2 mm in length:

Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

## APPENDIX C

## SPECIMEN NOTES AND DATA

This appendix contains specific information for each specimen such as locality, stratigraphic unit, etc. All $\delta^{13} \mathrm{C}$ and $\delta^{18} \mathrm{O}$ data that was collected is also contained within, sorted in several different ways, as well as previously published data from Russian and North American brachiopods. All $\delta 13 \mathrm{C}$ and $\delta 18 \mathrm{O}$ are given in \% (V-PDB).

## Contents:

C1-Specimen/Locality Information
C2 - Specimen Characterization and Notes
C3 - Summarized Specimen Data
C4 - All Specimen 813 C Data
C5-All Specimen 8180 Data
C6 - All Matrix $\delta 13 \mathrm{C}$ and $\delta 180$ Data
C7-NL and SMFL Data Sorted by Stratigraphic Horizon
C8 - NL and SMFL Data Sorted by Locality
C9 - Matrix Data Sorted by Stratigraphic Horizon
C10 - Matrix Data Sorted by Locality
C11 - Data Sorted by Specimen Genus
C12 - Previously Published Data
C1) Specimen/Locality Information*


[^4]C2) Specimen Characterization and Notes

| $\begin{aligned} & \text { Specimen } \\ & \text { ID } \\ & \hline \end{aligned}$ | $\begin{gathered} \text { Hand } \\ \text { Sample } \end{gathered}$ | Microstucture | cL | Analysis Status | Notes |
| :---: | :---: | :---: | :---: | :---: | :---: |
| SQ17b | good | preserved | SMFL | analyed | Shell shows bright luminescence along intemal fractures sineations. (These are very thin and insignificant in area, but were still avoided when drilling sample.) |
| sa17a | good | preserved | SMFL | analyed | Shell shows bright luminescencee along intemal fractureslineations. (These are very thin and insigignificant in area, but were still avided when drilling sample.) |
| K08-2 | good | preserved | SMFL | analved | Shell shows bright luminescence along intemal fractureslineations. (These areas were avoided when dinliling sample.) |
| K $\mathrm{Q}^{8}$-1 | good | preserved | SMFL | analyed | Shell shows bright luminescence along shell margin. (These areas were avoided when drilling sample.) |
| K01-2 | poor |  |  | not analyed | Poor shell potential for istopic analysis (shell is too thin). |
| K01-1 | good | preserved | LCBL | analyed | Shell displays low-contrast CL banding. |
| AY2-6 | good | preserved | SMFL | analyed | Shell shows bright luminescence along intemal fractureslineations. (These areas were avoided when dinliling sample.) |
| AY2-5 | poor |  |  | notanalved | Poor shell potential for isotopic analysis (shell is too thin). |
| A P 2 -4b | good | preserved | SMFL | analyed | Shell shows bright luminescence along shell margin and internal fractureslineations. (These areas were avoided when drilling sample.) |
| Ar2-4a | good | preserved | SMFL | analved | Shell shows bright luminescence along shell margin and internal fractureslineations. These areas were avoided when drilling sample.). |
| AY2.3 | good | preserved | SMFL | analyed | Shell shows bright luminescence along shell margin and internal fracturesllineations. (These areas were avoided when drilling sample.) |
| AY2-2 | good | preserved | HCBL |  | Shell displays high-contrast CLL banding with lineations of brighter CL parallel to and especially along shell margins. |
| AY2-1 | poor |  |  | not analyed | Poor shell potential for isotopic analysis (shell is too thin). |
| CQ3.2 | poor |  |  | not analyed | Poor shell potential for isotopic analysis shell is too thin). |
| $\mathrm{CaO}^{\text {a }} 1$ | good | not preserved | L | not analved | Shell is opaque under plane light and nearly all of shell is luminescent under CL. |
| CQ15-2 | poor |  |  | not analyed | Poor shell potential for isotopic analysis (shell is too thin). |
| CQ15-1 | good | preserved | NL | analyed | $G$ Good shell with very minor areas of luminescence. |
| Ca12-2 | good | preserved | SMFL | analyed | Shell shows bright luminescence along shell margin. (These areas were avoided when drilling sample.) |
| C012-1 | good | preserved | SMFL | analyed | Shell shows bright luminescence along shell margin. (These areas were avoided when drilling sample.) |
| CQ13-2 | good | preserved | HCBL | analyed | Shell displays high-contrast CLL banding with widespread regions of low-contrast CL banding. |
| ${ }_{\text {CQ }}^{6}$ 3-1 | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| AS4-6 | good | preserved | LCBL | analyed | Shell displays low-contrast CL banding. |
| AS4-5 | poor |  |  | not analyed | Poor shell potential for isosotopic analysis (shell is too tin). |
| ${ }_{\text {Ast4. }}$ | poor | preserved | SMFL | not analyed | Poor shel potential for isotopic analysis shell is too thin). Shell shows briont ummesescence along several lineaions perpendicular to shell marain. (These areas were avided when drilling sample). |
| As4-2 |  |  |  | notanalyed | Poor shell potentialia for istotopic analysis (shenlil is too thin). |
| AS4-1 | poor |  |  | notanalyed | Poor shell potential for isotopic analysis shell is too thin). |
| ${ }_{\text {AA1 }}$-4 | poor |  |  | not analved | Poor shell potential for isotopic analysis shell is too thin). |
| ${ }_{\text {AA1-3 }}$ | poor |  |  | not analyed | Poor shell potential for isotopic analysis shell is too thin). |
| AA1-2 | poor |  |  | not analved | Poor shell potential for isotopic analysis shell is too thin). |
| AAl-1 | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| ST1-4 | poor |  |  | notanalyed | Poor shell potential for isotopic analysis shell is too thin). |
| ST1-3 | poor | preserved |  | $\frac{\text { not analyed }}{\text { analyed }}$ |  |
| ST1-1 | good | preserved | SMFL | analyed | Shell shows bright tuminescencee along large ilineations in the beakr egion. (These areas were avoided when drililing sample.) |
| KY-2 | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| KY-1 | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| ${ }_{\text {BT1-6 }}$ | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| $\frac{\text { BT1-5 }}{\text { BT1-4 }}$ | good | preserved | $\stackrel{\text { NL }}{\text { N }}$ | $\underset{\text { analyed }}{\substack{\text { andured }}}$ | Good shell with very minor areas of luminescence. |
| BTT-3 | good | preserved | LCBL | analyed | Shell displays low-contrast CL banding. |
| BT1-2 | good | preserved | NL | analyed | Good shell with very minor areas of luminescence. |
| ${ }_{\text {BTIT-1 }}$ | good | preserved | ${ }^{\mathrm{NL}}$ | analved | Good shell with very minor areas of luminescence. |
| ${ }_{\text {BT1-K2 }}{ }_{\text {BT1-K1 }}$ | good | preserved | $\frac{\mathrm{NL}}{\mathrm{NL}}$ | analyed analyed | Good shell with very minor areas of luminescence. |

Hand samples, after cutting with an Isomet saw, were checked to determine if there was "good" potential for shell analysis (i.e. shell is thick), and were otherwise labeled "poor".
Integrity of shell microstructure is checked under plane-polarized light (See Appendix B for photographs taken).
Integrity of shell microstructure is checked under plane-polarized light (See Appendix B for photographs taken).
Cathodoluminescnce (CL) is used to check the chemical preservation of the shells using the following scheme (See Appendix B for photographs taken):
L- - luminescent; shell is dominantly luminescent under CL light, very little or no non-luminescent areas
LCBL - low-contrast banded luminescence shell displays alternating bands of strong-luminescence/weak-luminescence under CL light
HCBL - high-contrast banded luminescence; shell displays alternating bands of luminescence/non-luminescence under CL light
KCBL - high-contrast banded luminescence; shell displays alternating bands of luminescence/non-luminescence under CL light
SMFL - shell margin and fracture luminescence shell mostly non-l-uminescent under CL light, with some luminescent areas along shell margin or fractures within shell
NL - $n$-luminescent; shell completely non-luminescent under CL light; no luminescent areas
C3) Summarized Specimen Data

Ages are from Gradstein etal. (2004).
AVG $=$ mean
AVG $=$ mean
STD $=10$
$\square$ LCBL or HCBL specimen

| $\begin{array}{\|l} \hline 0 \\ 0 \\ 0 \\ 0 \\ \hline 0 \end{array}$ |  |  |  |  |  |  | \% |  | $\stackrel{\square}{\circ}$ |  |  | 9 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{array}{\|l\|l} 0 \\ 0 \\ 0 \\ \hline 0 \end{array}$ |  |  | $\mathfrak{m o g}$ |  | 우욱 | $0$ |  | Bix | $9$ | $8$ | \% ¢ | $\underset{\sim}{9}$ |
| 易 |  |  | \% $0_{0}^{\circ}$ |  |  |  | 80 | ${ }^{\circ}$ | $\because$ |  |  | \% |
|  |  |  | $0$ |  |  | bex in ix | $0 .$ | $\mathscr{G} \mid$ | $y_{0}^{2}$ |  |  |  |
| - |  |  |  |  |  |  |  |  |  |  |  | \% |
|  | $\hat{S}^{2}$ | Rex | Bx |  | $\mathrm{S}_{6}^{x}$ |  | $\mathfrak{y s i x i n ~}$ |  |  |  | $\sim_{0}^{\circ}$ |  |
|  | $2$ | 20 | $\frac{6}{2}$ | $2$ |  |  |  |  |  |  |  | 5 |

${ }^{*}$ N column displays the number of samples analyzed from each specimen However, in the bottom row the
value coresponsins to to total number of specimens, not the toal rumber of a analyses.

Each specimen was sampled as many times as was practical. ס13C ( $1-8$ ) are the $\square$ LCBL or HCBL specimen
data from these different sampling locations (See Appendix B).
Ages are from Gradstein et al. (2004).
$N=$ number of different samples analyzed from each specimen.
AVG $=$ mean
STD $1 \sigma$
Precison $=1 \sigma$ of the NBS-19 samples that were analyzed atternately with the
carbonate samples of this study.
C5) All Specimen $\delta^{18} \mathrm{O}$ Data


[^5] $\delta 13 C$ (X1-X3) and $\delta 180(X 1-X 3)$ are samples taken from the matrix surrounding
each shell analyzed.
Ages are from Gradstein et al. 2004
Precision $=1 \sigma$ of the NBS-19 samples that were analyzed alternately with the
carbonate samples of this study.
$\mathrm{N}=$ number of different analyses done on each rock.

## C7) NL and SMFL Data Sorted by Stratigraphic Horizon


C8) NL and SMFL Data Sorted by Locality


C10) Matrix Data Sorted by Locality

|  |
| :---: |
|  |  |
|  |  |


C11) Data Sorted by Specimen Genus

| 1. Kalitvella Data |  |  |  |  |  | 2. Stenoscisma Data |  |  |  |  |  |  | 3. Chaoiella |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{array}{\|c\|c\|} \hline \text { Specimen } \\ \text { in } \end{array}$ | Age | N | $\delta^{13} \mathrm{C}$ Avg | $\delta^{13} \mathrm{C}$ Sto | $\delta^{10} 0$ Avg | $8^{100} 0$ Sto | Age | N | $\delta^{13} \mathrm{C}$ avg | $\delta^{13} \mathrm{C}$ Sto | $\delta^{100} 0$ avg | $8^{100} 0$ Sto | Age | N | $\delta^{13} \mathrm{C}$ Avg | $\delta^{13} \mathrm{C}$ STD | $\delta^{180} \mathrm{AVG}$ | $8^{100} 0$ STD |
| SQ17b | 274.8 | 2 | 5.88 | 0.16 | -0.86 | 0.33 |  |  |  |  |  |  |  |  |  |  |  |  |
| So17a | 274.8 | 3 | 5.47 | 0.18 | -0.99 | 0.33 |  |  |  |  |  |  |  |  |  |  |  |  |
| K08-2 |  |  |  |  |  |  | 274.5 | 1 | 5.84 |  | 0.25 | 0.00 |  |  |  |  |  |  |
| KQ8.1 |  |  |  |  |  |  | 274.5 | 2 | 6.02 | 0.11 | 0.44 | 0.02 |  |  |  |  |  |  |
| ${ }_{\text {KQY2-1 }}$ |  |  |  |  |  |  | 275.7 | 3 | 6.11 | 0.38 | -0.45 | 0.91 | ${ }^{275}$ | 3 | 4.78 | 0.44 | ${ }^{-2.18}$ | 0.60 |
| AY2-4b | 275.7 | 2 | 6.16 | 0.01 | -1.27 | 0.00 |  |  |  |  |  |  |  |  |  |  |  |  |
| AY2-4a | 275.7 |  | 5.41 | 0.13 | -1.64 | 0.05 |  |  |  |  |  |  |  |  |  |  |  |  |
| AY2-3 | 275.7 | 3 | 5.93 | 0.33 | -0.18 | 0.07 |  |  |  |  |  |  |  |  |  |  |  |  |
| ${ }_{\text {A A } 2 \text { 2-2 }}$ |  |  |  |  |  |  | 2763 | 3 | 517 | 0.12 | . 223 | 016 | 275.7 | 3 | 4.65 | 0.20 | ${ }^{-3.14}$ | 0.21 |
| CQ12-2 | 276.3 | 4 | 6.01 | 0.13 | -2.25 | 0.09 |  |  |  |  |  | 0.16 |  |  |  |  |  |  |
| CQ12-1 | 276.3 | 3 | 5.76 | 0.11 | -2.05 | 0.03 |  |  |  |  |  |  |  |  |  |  |  |  |
| CQ13-2 |  |  |  |  |  |  |  |  |  |  |  |  | 276.5 | 6 | 4.26 | 0.38 | -2.25 | 0.12 |
| CQ13-1 |  |  |  |  |  |  |  |  |  |  |  |  | 276.5 | 4 | 4.79 | 0.06 | -2.16 | ${ }^{0.05}$ |
| AS4.6 |  |  |  |  |  |  |  |  |  |  |  |  | 278.6 | 4 | 3.29 | 0.30 | ${ }^{-3.22}$ | 0.13 |
| As4.3 |  |  |  |  |  |  | 278.6 | 3 | 4.32 | 0.09 | -2.90 | 0.12 |  |  |  |  |  |  |
| ${ }_{\text {AA }} \mathrm{Cl} 1$ | ${ }_{293}^{283}$ | ${ }_{8}^{6}$ | 4.68 5.68 | 0.09 0.05 | -2.17 .2 .60 | 0.10 0.12 |  |  |  |  |  |  |  |  |  |  |  |  |
| KY-1 | 293 | 6 | 4.50 | 0.07 | $\stackrel{-2.51}{ }$ | 0.12 |  |  |  |  |  |  |  |  |  |  |  |  |
| BT1-6 |  |  |  |  |  |  | ${ }^{296}$ |  | 5.55 |  | -232 |  |  |  |  |  |  |  |
| BT1-5 |  |  |  |  |  |  | ${ }^{296}$ | 5 | 6.35 | 0.13 | -2.26 | 0.08 |  |  |  |  |  |  |
| BT1-4 |  |  |  |  |  |  |  |  |  |  |  |  | ${ }^{296}$ | 4 | 3.26 | 0.09 | ${ }^{2} 2.26$ | 0.11 |
| ${ }^{\text {BTT } 1-3}$ |  |  |  |  |  |  |  |  |  |  |  |  | 296 | 2 | 3.67 | 0.47 | -2.40 | 0.40 |
|  | ${ }_{2}^{296}$ | ${ }^{3}$ | ${ }_{5}^{5.67}$ | 0.21 | - $\begin{gathered}-2.20 \\ -38\end{gathered}$ | ${ }_{0}^{0.15}$ |  |  |  |  |  |  |  |  |  |  |  |  |
| AVg | 282.53 |  | 5.57 | 0.13 | -1.84 | 0.15 | 281.66 |  | 5.62 | 0.16 | -1.35 | 0.22 | 282.04 |  | 4.10 | 0.27 | -2.52 | 0.23 |
| STD |  |  | 0.50 |  | 0.89 |  |  |  | 0.69 |  | 1.39 |  |  |  | 0.69 |  | 0.46 |  |

[^6]

## APPENDIX D ONLINE RESOURCES

As a supplement to the materials found within this thesis, some resources have been made available online at the website http://jordan.noret.info/research/2009/undergrad. This website will exist for as long as possible (likely forever) in order to make these resources available for readers of this thesis, as well as future researchers. Outlined below are the resources that can be found on this website. Efforts will be taken to convert these resources if the file formats become obsolete.

## 1. Full-Resolution Specimen Image Repository

This repository makes available the full-resolution images of the specimens shown in Appendix B of this thesis: microscope photography maps, PL photos, CL photos, and sampling maps.

## 2. Specimen Notes and Data Spreadsheet

This is the original spreadsheet used to make Appendix C of this thesis. It contains notes about the specimens and the data collected from them.

## 3. Full-sized Data Plots

This file contains the full-sized versions of Figures 7 and 8 from this thesis.

## 4. Raw Isotope Data

These are the original spreadsheets that contain the raw isotope data collected from each specimen. These are made available to allow for the utmost transparency in this project.

## 5. Google Earth File (.kmz)

This file can be loaded into Google Earth to display the specimen localities along with information on the specimens and photographs of the localities.

# CONTACT INFORMATION 

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[^0]:    Figure 2. Lithology and stratigraphy of the 31 specimens used in this study.

    * All localities are in the Southern Urals of Russia.
    \# Ages are from Gradstein et al. (2004).

[^1]:    Figure 5. CL characterization classes as described in the text: A) NL or non-luminescent, B) SMFL or shell margin
    luminescence. $M=$ Matrix. See Appendix $B$ for all CL/PL images.

[^2]:    $\mathrm{P}=$ Preserved; $\mathrm{NP}=$ Not preserved; see text for CI . characterization scheme (NI., SMFI., ICBI, and HCBI .) $\mathrm{N}=H$ of samples analyzed from specimen; $\Lambda \mathrm{VG}=$ mean; STD $=$ standard deviation ( $1 \sigma$ ) \# Ages are from Gradstein et al. (2004).

[^3]:    .....

    The scale bar used in PL/CL images above is 2 mm in length: The scale bar used in high-PL/CL images above is 1 mm in length:
    

    Full resolution images can be found at: http://jordan.noret.info/research/2009/ugr

[^4]:    *Samples were collected during field work donen by Dr. Thomas Yancey and Dr. Boris Chuvashov. The information on this page was obtained from these individuals.
    \#All samples are tom the mid. Urals in Russia. \# All samples are from the ind id. Urals
    Ages are trom Grastein etal
    2004.

[^5]:    Each specimen was sampled as many times as was practical. ס180 ( $1-8$ ) are the $\square$ LCBL or HCBL specimen
    data from these different sampling locations (See Appendix B ).
    

[^6]:    
    

