STRONTIUM AND CARBON ISOTOPE STRATIGRAPHY OF THE
LLANDOVERY (EARLY SILURIAN): IMPLICATIONS FOR TECTONICS
AND WEATHERING

A Thesis

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ABSTRACT

A high resolution Sr isotope data set is generated for the Llandovery Series from a thick, fossiliferous drill core in Estonia. Observed $^{87}\text{Sr}/^{86}\text{Sr}$ values are at a minimum in the early Llandovery Rhuddanian Stage (~ 0.7079 to 0.7080), and then trend to more radiogenic ratios in the beginning part of the late Llandovery Telychian Stage. An $^{87}\text{Sr}/^{86}\text{Sr}$ high near ~ 0.7084 is observed in the Telychian at the top of the studied section. The range of values is in general agreement with previous sample sets of brachiopods and conodonts recovered from localities in North America and Europe that record a rising trend in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio throughout the Llandovery from approximately 0.7080 to 0.7084 .

The major increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during the late Llandovery may be due to increased riverine flux of radiogenic Sr into the oceans due to: 1) weathering of non-volcanic continental silicate rocks that were uplifted during early Silurian continent-continent collisions, and 2) weathering of exposed felsic volcanics in the Balto-Scandinavian region that formed during subduction of continental crust. The presence of felsic volcanic rocks is consistent with the occurrence of an unusually thick K-bentonite bed (Osmundsberg K-bentonite) representing a large-magnitude ash fall in the early Telychian. Furthermore, a

negative $\delta^{13}\text{C}$ excursion in marine carbonate and organic matter is quasi-synchronous with the increase in Sr at the level of resolution currently available. As atmospheric CO_2 was apparently being drawn down in the preceding Aeronian Stage (positive $\delta^{13}\text{C}$ excursion), the large amounts of ash may have been a catalyst for the ensuing Telychian glaciation, causing a major regression and further contributing to the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ through increased continental weathering.

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CHAPTER 1

INTRODUCTION

The early Silurian Llandovery epoch (~443 to 428 Ma) is a time of biotic recovery following the major episodes of Late Ordovician glaciation and mass extinction (Sheehan et al., 1996; Krug and Patzkowsky, 2004). The Llandovery is generally described as a time of cyclical changes in sea level and climate (Melchin et al., 2006) related to intermittent glaciations that diminished in magnitude during the transition to a middle Paleozoic greenhouse period (Harris and Sheehan, 1996; Melchin and Holmden, 2006; Kaljo and Martma, 2000; Brand et al., 2007; Caputo, 1998). A role for atmospheric CO₂ in driving these changing climatic conditions has also been emphasized (e.g., Azmy et al., 1999; Kaljo and Martma, 2000; Kiipli et al., 2004). However, the timing and causes of paleoclimatic changes with possible links to carbon cycling during the Llandovery remain poorly understood, in part due to a lack of high-resolution, integrated geochemical proxy investigations of changes in seawater chemistry.

Sample sets of calcitic brachiopods and conodonts recovered from localities in North America and Europe record a rising trend in the ⁸⁷Sr/⁸⁶Sr ratio

throughout the Silurian, starting after the late Ordovician glaciation (Ruppel et al., 1996; Azmy et al., 1999; Veizer et al., 1999). This increase (~ 0.7079 to 0.7088) has been interpreted to reflect an overall warming of the Silurian climate that led to enhanced weathering of relatively radiogenic continental silicate rocks (Azmy et al., 1999). The Llandovery portion of the $^{87}\text{Sr}/^{86}\text{Sr}$ curve is characterized by exceptionally high rates of rising $^{87}\text{Sr}/^{86}\text{Sr}$ (Azmy et al., 1999), and significant inflection points have been linked to global sea level changes. However, the density of Llandovery $^{87}\text{Sr}/^{86}\text{Sr}$ analyses in previous studies is relatively low, and correlations with tectonic events (e.g., Bergstrom et al., 1998), eustatic sea level (Johnson et al., 1991), and climate are not well established.

Furthermore, although previous workers have established high resolution records of changes in marine carbonate $\delta^{13}\text{C}$ that may be used to infer changes in global carbon cycling during the Llandovery (Heath et al., 1998; Kaljo and Martma, 2000; Kiipli et al., 2004), corresponding study of Sr isotope stratigraphy has not been undertaken in these same sections. In addition, because the reproducibility of these carbonate $\delta^{13}\text{C}$ shifts outside of the Baltic region has not been thoroughly examined, the relative roles of global versus local effects on the observed trends remain poorly understood. Lastly, it is also possible to gain important environmental information and at the same time address potential diagenetic effects by comparing changes in carbonate $\delta^{13}\text{C}$ with that of coeval organic matter $\delta^{13}\text{C}$ in the same sections.

To better understand the timing and causes of rising $^{87}\text{Sr}/^{86}\text{Sr}$ during the Llandovery, the goal of this study is to construct a high resolution dataset that can

be tied to established Llandovery biostratigraphic zones and $\delta^{13}\text{C}$ stratigraphy. The primary locality utilized here is a particularly thick borehole section from Estonia (Ikla core) (Fig. 1), which was previously studied in great detail for carbonate $\delta^{13}\text{C}$ and biostratigraphy by Kaljo and Martma (2000), sequence stratigraphy by Johnson et al. (1991), and volcanic event (K-bentonite) stratigraphy by Kiipli et al. (2006). The Pancake Range section in Nevada (Harris and Sheehan, 1998) (Fig. 1) provides a secondary, less biostratigraphically well constrained dataset. The results of this study reveal a previously undocumented coincidence among three distinct late Llandovery (earliest Telychian Stage) stratigraphic signals: 1) a rising inflection point in the Silurian $^{87}\text{Sr}/^{86}\text{Sr}$ curve, 2) negative excursion in $\delta^{13}\text{C}$ of both carbonate and organic matter, and 3) an unusually thick K-bentonite bed representing a large-magnitude ash fall.

Figure 1: Paleogeographic reconstruction of the Llandovery, with shaded regions showing locations of Pancake Range locality (Laurentia) and Ikla core locality (Baltica) (after Harris and Sheehan, 1998, and Kaljo and Martma, 2000).

CHAPTER 2

GEOLOGICAL SETTING

During the Llandovery, Baltica moved to a more equatorial setting from its temperate belt setting in the middle Ordovician, which created significant climatic changes for the region (Torsvik et al., 1996). The rocks of the Llandovery in Estonia were formed along the western shoreline of the Baltica paleocontinent, and represent four distinct facies. At the most proximal locations, lagoonal dolomites and dolomitic marls mark the nearshore facies. The high-energy shoals are represented by grainstones with organic build-ups. A wide variety of limestone lithologies can be found in the shallow to mid-shelf facies, with marlstones, mudstones, and micritic limestones in the transition of the deeper outer shelf to the basin. The basin rocks are predominately graptolitic dark shales and claystones, rich in pyrite and organic carbon, which could represent anoxic conditions in this deep water setting.

The Ikla borehole section in Estonia (Fig. 2) is representative of deep shelf to basinal facies of a shallow carbonate ramp. It is the most complete Llandovery core extracted from the region because its distal location kept even the largest

Figure 2: Generalized Llandovery paleogeographic map of the northern Baltic region, showing the location of the Ikla core (after Kaljo and Martma, 2000).

shoreline regressions from progressing out far enough to produce unconformities (Kaljo, 2000). The preserved fauna consists primarily of deep-water graptolites and chitinozoans. Lithologies are primarily micritic limestone and marlstone with carbonate nodules at the base and top of the core sequence, transitioning into more argillaceous limestones in the middle part. Near the top of the core, two submarine disconformities are present above and below a thin sequence of argillaceous limestones, which in this locality is the Rumba formation (Kaljo and Martma, 2000).

The Ikla core is well biostratigraphically dated using generalized graptolite zones, as described by Koren et al. (1996), as well as first appearances of key chitinozoans, as described by Nestor et al. (1994). The Ohne formation is dated by appearances of the global chitinozoan *Conochitina electa* and the Baltica chitinozoan *Dimorphograptus confertus*, with *Conochitina electa* also present across two nearby core sections, Kirikukula and Ruhnu, providing a tie point across the region. The boundary between the Kolka formation and the Ikla formation is defined in part by the presence of Baltica chitinozoans *Pernerograptus revolutus* in the Kolka, and *Demirastrites triangulates* in the Ikla. Most important, however, is the first occurrence of the global chitinozoan *Eisenackitina dolioliformis*, which aids in the dating of the Rumba formation as late Aeronian to early-middle Telychian (Kaljo and Martma, 2000; Grahn, 2006). The occurrence of the brachiopod *Stricklandia laevis* in the Rumba formation in the nearby Viki core further constrains the age to Telychian in age (Johnson, 1991). In the Kirikukula core to the northwest of the Ikla core, the global

chitinozoan *Angochitina longicollis* and Baltica chitinozoan *Conochitina proboscifera* also appear, in the Velise formation. In the Ruhnu core to the west of the Ikla core, the occurrence of the Baltica chitinozoans *Coronograptus cyphus* in the Kolka formation, *Demirastrites triangulates* in the Ikla formation, and *Rastrites linnaei* at the Staicele/Rumba boundary all help in constraining the ages of the formations. *Angochitina longicollis* and *Conochitina proboscifera* also appear in the Velise formation of the Ruhnu core, as in the Kirikukula core (Kaljo and Martma, 2000).

The studied Llandovery section in Nevada (Fig. 3) represents a marginal marine to shelf sequence deposited during platform evolution from a carbonate ramp to rimmed shelf phase (Harris and Sheehan, 1998). The Pancake Range section lies east of the margin of the rimmed shelf, which rapidly deepens to the west. Eustatic changes in sea level have been interpreted for this section using sequence stratigraphy based on methods in Johnson, 1996 and on depositional facies (Harris and Sheehan, 1998). The studied interval is contained within the Laketown Dolomite, which here can be split into five separate members, with Tony Grove Member at the base, followed by the High Lake, Gettel, upper High Lake tongue, Jack Valley, and Decathon members. Above the Laketown Dolomite is the Sevy Dolostone, which was not sampled in this study. Three sequences comprise the lower ramp phase of the Laketown Dolomite, which represent the Tony Grove and the lower half of the High Lake. Each of these sequences is dominated by burrowed packstone lithologies, with occurrences of

Figure 3: Generalized Llandovery paleogeographic map of the Great Basin, showing the location of the Pancake Range section (after Harris and Sheehan, 1998).

wackestones and grainstones. Sequence boundaries are defined by surficial features, such as karst surfaces, soils, facies successions, and cyclestacking patterns, and also by large unconformities across the basin representing lowstands. The upper three sequences (upper half of the High Lake, Gettel, High Lake tongue, Jack Valley, and Decathon) during the rimmed shelf phase consist of burrowed mudstones, wackestones, packstones, and grainstones, alternating throughout the sequences (Harris and Sheehan, 1997).

The Pancake Range section is biostratigraphically dated using occurrences of macrofossil assemblages, which are also abundant throughout the section. The Rhuddanian and middle Aeronian is defined by the *Virgiana* dominated brachiopod interval. The upper Aeronian to lower Telychian is defined by an interval dominated by the brachiopod *Pentamerus*. The remainder of the Llandovery is defined by the *Pentameroides* brachiopod interval. While in the other intervals, associated brachiopods are rare, in the *Pentameroides* interval they are more common, although the *Pentameroides* brachiopod still dominates. The latest Llandovery and lower Wenlock are defined by a faunal change where brachiopod diversity increases, including communities such as *Spirinella* and *Atrypina*. (Sheehan, 1980). In the Pancake Range, the Ordovician-Silurian transition is marked by a rapid change in fauna, where the early Silurian cosmopolitan *Virgiana* community (primarily *Virgiana utahensis*) becomes the dominant brachiopod, and brachiopod diversity drops dramatically from the Ordovician assemblages, indicating the transition into the Silurian. In the High Lake member, *Verticillopopra* dasycladacean algae are present, as well as

Amplexoides radicosi and *Tryplasma* sp. corals. In the Gettel, *Palaeocyclus* sp. and *Tryplasma* sp. corals have also been identified (Harris and Sheehan, 1998). Paleogeographically, this section sits on the western margin of Laurentia, near 10-15° S latitude (Harris and Sheehan, 1998).

CHAPTER 3

METHODS

To determine a high-resolution data set for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, carbonate samples from an Estonian drill core and from field collecting in the Pancake Range of central Nevada were analyzed. To obtain carbonate for analyses, rock samples were first sawed to produce flat surfaces and cleaned of any excess sediment; a drill bit was used to obtain carbonate powders for isotopic analyses. Only unaltered, fine-grained micritic components were selected for analysis. Powders were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentration in the Radiogenic Isotope Laboratory at the Ohio State University using Sr purification and mass spectrometry procedures described by (Foland and Allen, 1991). Sr was extracted from powders using ultrapure reagents; powder aliquots of ~25 mg were pretreated with 1M ammonium acetate (pH 8) and then leached in 4% acetic acid. The leachate, which was separated from undissolved residue, was then spiked with an ^{84}Sr tracer. Samples were purified for Sr using a cation exchange resin and a 2N HCl based ion-exchange. Purified Sr was then loaded with HCl on a Re double-filament configuration. Isotopic compositions were measured using dynamic multicollection with a MAT-261A thermal ionization mass spectrometer.

The Laboratory value for the SRM 987 standard is $(^{87}\text{Sr}/^{86}\text{Sr}) = 0.710242 \pm 0.000010$ (one-sigma external reproducibility). For the $^{87}\text{Sr}/^{86}\text{Sr}$ values the associated uncertainties given are for two-sigma mean internal reproducibilities, typically based upon 100 measured ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ reported ratios are normalized for instrumental fractionation using a normal Sr ratio of $^{86}\text{Sr}/^{88}\text{Sr} = 0.119400$. No modifications to the measured normalized $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been made.

For organic carbon isotope analysis, samples were cut into billets using a rock saw, and the billets were cleaned using a sonicator. After drying, each sample was powdered using a mortar and pestle or an electric drill. In Dr. Ken Foland's Radiogenic Isotope Laboratory at the Ohio State University, one gram of powder was weighed out in 50 mL FALCON test tubes and dissolved in 20 mL of 6N HCl and centrifuged. The remaining residue was then washed three times using 20 mL of water and a centrifuge. The samples were then dried overnight in an 80°C oven, and homogenized using a mortar and pestle once dry. Each sample was then weighed on a micro balance, depending on organic content, in Dr. Andrea Grottoli's Stable Isotope Biogeochemistry Laboratory at the Ohio State University, and analyzed for organic $^{13}/^{12}\text{C}$ ratios using a Finnigan Delta Plus IV coupled with a Costech Elemental Analyzer with continuous flow by CONFLOIII (EA-SIRMS).

For $\delta^{13}\text{C}_{\text{carb}}$, samples of the Pancake Range section were drilled on clean carbonate surfaces for approximately 500µg of powder. For each sample, A 75-95µg subsample was analyzed for $\delta^{18}\text{O}$ ($\delta^{18}\text{O}$ = permil deviation of ^{18}O : ^{16}O

relative to Vienna Pee Dee Belemnite Limestone standard (V-PDB)) and $\delta^{13}\text{C}$ ($\delta^{13}\text{C}$ = permil deviation of ^{13}C : ^{12}C relative to V-PDB) using an automated Carbonate Kiel device coupled to a Finnigan Delta IV Plus stable isotope ratio mass spectrometer in Dr. Andrea Grottoli's Stable Isotope Biogeochemistry Laboratory at The Ohio State University. Samples were acidified under vacuum with 100% ortho-phosphoric acid, the resulting CO_2 cryogenically purified, and delivered to the mass spec. Approximately 10% of all samples were run in duplicate. The standard deviation of repeated measurements of an internal standard was $\pm 0.03\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.09\text{‰}$ for $\delta^{18}\text{O}$.

CHAPTER 4

RESULTS

Sr isotope data from Ikla core show significant variability in the Rhuddanian portion of the core, ranging from 0.707986 to 0.708341, averaging about 0.7081. The Aeronian is much less variable, with values staying between 0.708027 and 0.708127. In the basal Telychian (Rumba Formation), a rapid shift to more radiogenic values occurs, trending from .708075 to .708441 (Fig 4).

One of the most important issues with analyzing trends in Sr is the potential for diagenetic influences to alter the primary seawater values. In general, samples that are diagenetically altered are likely to appear more radiogenic than that of the paleocean. When the rock is diagenetically altered, Sr concentration is in most cases reduced, and younger, more radiogenic values overprint the original ratio (Montanez et al., 1996; Azmy et al., 1999; Brand et al., 2006; Halverson et al., 2007). The preferred criteria used to address diagenesis in this study were the Sr concentrations of the analyzed rock, which was measured along with the isotopic ratio. This method was used over other commonly used diagenetic checks (Mn/Sr, Sr/Ca, $\delta^{18}\text{O}$) for a variety of reasons. High Mn/Sr might be indicative of anoxic carbonate precipitation and not diagenetic

Figure 4: $^{87}\text{Sr}/^{86}\text{Sr}$ record of the Ikla core, stratigraphy after Kaljo and Martma., 2000. Hollow points indicate “bad” data points, where Sr concentration is under 100 ppm. Generalized graptolite zones (after Koren et al., 1995): 1, *acuminatus*; 2, *vesiculosus*; 3, *cyphus*; 4, *pectinatus-triangulatus*; 5, *argenteus*; 6, *convolutes*; 7, *sedgwickii*; 8, *guerichi*; 9, *turriculatus-crispus*; 10, *insectus-spiralus-crenulata-greistoniensis*; 11, *crenulata*. Abbreviations: S., Sheinwoodian; Tely., Telychian; Rum., Rumba; Vel., Velise.

alteration, and Sr/Ca and $\delta^{18}\text{O}$ do not account for possible dolomitization, as Sr and Ca concentrations are jointly reduced by the process, and $\delta^{18}\text{O}$ values increase by 2-4%, which can falsely identify a sample as unaltered. However, since initial ocean concentrations of Sr can differ, as well as the original mineralogy of the oceans (calcite vs. aragonite seas), the criteria for diagenesis is variable. Based upon the range of Sr concentrations in the Ikla core rocks, a threshold of 100 ppm was used to exclude data points from the plotted Llandovery $^{87}\text{Sr}/^{86}\text{Sr}$ curve of the Ikla core (Halverson et al., 2007; Montanez et al., 1996). Also, values that were less than 100 ppm appeared to be more radiogenic than the surrounding data points, giving confidence to this criteria selection (Halverson et al., 2007; Montanez et al., 1996). In addition, the data follows distinct trends through time, particularly in the Telychian, where values become more radiogenic as they get younger. It would be statistically improbable for these trends to be caused by diagenetic alteration, giving additional evidence that the values produced in this study are representative of actual paleocean $^{87}\text{Sr}/^{86}\text{Sr}$ values.

The $\delta^{13}\text{C}_{\text{org}}$ curve from the Ikla core exhibits both similarities (Telychian portion) and differences (Rhuddanian-Aeronian) when compared with the $\delta^{13}\text{C}_{\text{carb}}$ curve generated by Kaljo and Martma (2000) (Fig 5). This general difficulty in matching signals is likely due in part to the low resolution of the data compared to $\delta^{13}\text{C}_{\text{carb}}$ and the fact that $\delta^{13}\text{C}_{\text{org}}$ is likely to be inherently more noisy than $\delta^{13}\text{C}_{\text{carb}}$ due to inhomogeneities in the materials analyzed (e.g., Joachimski et al. 2002). It

Figure 5: $\delta^{13}\text{C}_{\text{carb}}$ data (Kaljo and Martma, 2000) and $\delta^{13}\text{C}_{\text{org}}$ data (this study) of the Ikla core, 3 point running average through the raw data, stratigraphy after Kaljo and Martma, 2000. Abbreviations as in Figure 4.

is also possible that the differences in the carbon isotope curves of carbonates and organic matter are related to changes in atmospheric CO₂ that can affect photosynthetic fractionation (Kump and Arthur, 1999; Joachimski et al. 2002). Here, we wish to emphasize the significant parallel changes in the two curves in the Telychian. A significant $\delta^{13}\text{C}$ minimum occurs in the earliest Telychian Rumba Formation, with $\delta^{13}\text{C}_{\text{org}}$ values near -29 to -30 ‰ and $\delta^{13}\text{C}_{\text{carb}} \sim 0$ to -1 ‰. Both curves begin to increase rapidly in the middle Telychian into the early Wenlock, with $\delta^{13}\text{C}_{\text{org}}$ rising by a magnitude of 3.5 ‰, and $\delta^{13}\text{C}_{\text{carb}}$ by 4.5 ‰. Presumably, this marks the beginning of the Ireviken excursion, which has been shown to show values of 3 ‰ and 4 ‰ in the early Wenlock. TOC ranges from 0.06 % to 0.34 % and shows no discernable trend in relation to $\delta^{13}\text{C}_{\text{org}}$ values (App. B), which indicates a reliable signal recovery. The parallel changes in both carbonate and organic $\delta^{13}\text{C}$ is itself a reliable indicator of preservation of primary seawater values (Joachimski et al., 2002).

While the $\delta^{13}\text{C}_{\text{carb}}$ data from the Pancake Range section is less biostratigraphically controlled, the negative excursion present in the Ikla core appears to be present here as well, showing values of approximately 0 ‰ in the earliest Telychian. The Pancake Range data also trends to more positive values after this negative excursion, reaching 2.5 ‰ in the late Telychian, and even 3 ‰ in the early Wenlock, similar to the trends in the Ikla core (Fig 6).

Figure 6. $\delta^{13}\text{C}_{\text{carb}}$ data from the Pancake Range, with 3 point running average through the raw data, stratigraphy after Harris and Sheehan, 1997. Dark shaded boxes indicate darker colored dolomite lithology, light shaded boxes indicate lighter colored dolomite lithology. Member abbreviations: G, Gettel; HL, High Lake; JV, Jack Valley; D, Decathon.

CHAPTER 5

DISCUSSION

The establishment of a high-resolution Sr isotope curve for the Llandovery from the Ikla core in Estonia reveals that much of the previously recognized overall $^{87}\text{Sr}/^{86}\text{Sr}$ rise (Azmy et al., 1999) is focused in the earliest Telychian Stage (Fig. 7). Furthermore, by analyzing Sr isotopes as well as organic carbon isotopes in the same core that was previously analyzed for $\delta^{13}\text{C}_{\text{carb}}$ (Kaljo and Martma, 2000), it is possible to establish a temporal coincidence among major changes in all three records during the Telychian (Fig. 8). Although the studied interval here includes the earliest Silurian Rhuddanian Stage, the isotope signals from this interval in the Ikla core are clearly more complex than succeeding stages and will require additional study to discern whether these trends indeed record primary, global changes in seawater chemistry or secondary (local) influences. Thus, in the discussion which follows here, the focus is on the records spanning the Aeronian and Telychian Stages only.

The observed Sr isotope increase in the early Telychian can be potentially linked to changes in rates of continental weathering, hydrothermal interaction with basaltic rocks, or changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ of the continental source material

Figure 7: Evolution of $^{87}\text{Sr}/^{86}\text{Sr}$ through the Llandovery and lower Wenlock based on this study, with comparison to data from Azmy et al., (1999). Abbreviations as in Figure 4. Additional generalized graptolite zones (after Koren et al., 1995): 12, *murchisoni*; 13, *riccartonensis*. Additional abbreviations: Wenl., Wenlock; Shein., Sheinwoodian.

Figure 8: $^{87}\text{Sr}/^{86}\text{Sr}$ (this study) and $\delta^{13}\text{C}_{\text{carb}}$ (Kaljo and Martma, 2000) record of the Ikla core, plotted against global eustatic curves (Johnson et al., 1996, and Loydell, 1998, respectively) and glaciations, evidenced by $\delta^{18}\text{O}$ (Caputo, 1998) and glacial sediments (Azmy, 1998). Abbreviations as in Figure 4. Additional abbreviations: H, high stand; L, low stand.

being weathered (Richter et al., 1992; Hodell et al., 1990; Farrell et al., 1992). The weathering of continental silicate rocks will introduce relatively radiogenic Sr (higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) into rivers. The riverine flux may thus increase during tectonic uplift resultant from continental collisions, which may also expose older, highly radiogenic (high $^{87}\text{Sr}/^{86}\text{Sr}$) silicates (Raymo and Ruddiman, 1988). Hydrothermal interaction with newer basaltic ocean crust, or the weathering of continental mafic volcanics both increase the flux of less radiogenic Sr to the oceans (Palmer and Elderfield, 1984), and therefore could have decreased in magnitude to contribute to the early Telychian $^{87}\text{Sr}/^{86}\text{Sr}$ rise.

The stratigraphic evidence from K-bentonite studies of Silurian strata (Bergstrom et al., 1998) reveal a potential link between the early Telychian increase in $^{87}\text{Sr}/^{86}\text{Sr}$ and convergent margin tectonics. K-bentonite beds represent short-lived ash falls that can be correlated over long distances by geochemical “fingerprinting” techniques (Huff et al., 1998). Llandovery K-bentonite horizons are known from European (Baltic) sections and the Appalachians of North America (Bergstrom et al., 1992). However, by far the largest and most significant Silurian K-bentonite is known as the Osmundsberg K-bentonite bed. The Osmundsberg K-bentonite is identifiable from a wide range of localities, including Sweden, Estonia, Norway and the British Isles (Bergstrom et al., 1992; Bergstrom et al., 1998; Lehnert et al., 1999) (Fig. 8). This bed occurs at thicknesses up to 115 cm at some localities, and has been traced over a distance of 2000 km into Estonia (Bergstrom et al., 1998). The Osmundsberg K-bentonite bed has been interpreted to represent a large scale felsic volcanic event, with an

ash fall that lasted a few weeks (Huff et al., 1998). This large-magnitude ash fall is well dated by biostratigraphy to the earliest Telychian lower to middle *turriculatus* graptolite zone (Bergstrom et al., 1998). Significantly, the Osmundsberg K-bentonite bed also occurs in the same sedimentary formation in the Baltic region (Rumba formation) in which the rising $^{87}\text{Sr}/^{86}\text{Sr}$ values are recorded in the Ikla core (Fig 4). The weathering of early Silurian felsic volcanics with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios thus may have been a contributing factor to the coincident rise in $^{87}\text{Sr}/^{86}\text{Sr}$. However, because the $^{87}\text{Sr}/^{86}\text{Sr}$ continues to rise through the remainder of the Silurian, input of radiogenic Sr from the weathering of uplifted non-volcanic silicates could sustain this increase.

The weathering of uplifted non-volcanic, old (radiogenic) silicates from Silurian continent-continent collisions (Ettensohn et al., 1998; Ettensohn et al., 2002) may have been the critical factor in increasing $^{87}\text{Sr}/^{86}\text{Sr}$ (Richter et al., 1992). Furthermore, it has been shown that modern rivers draining high relief regions associated with active plate boundaries in tropical to sub-tropical latitudes have some of the highest physical and chemical erosion rates in the world (Lyons et al., 2005). The uplifted terranes that may have played a role in the early Telychian Sr increase are in tropical to sub-tropical latitudes (Fig. 8). An early Telychian age for major tectonic changes is consistent with the Silurian tectonic evolution of Laurentia that has been described based on evidence from the northern and central Appalachians (Ettensohn and Brett, 1998). This evidence includes U-Pb dating of volcanism from granites from the New Brunswick portion of the Canadian Appalachians (Bevier and Whalen, 1990), deformation,

plutonism, and foreland basin fill (Ettensohn and Brett, 1998). While the final suturing of Baltica and Laurentia, referred to as the Caledonian orogeny, occurred in the late Silurian/early Devonian, it is believed that initial collision actually occurred in the Telychian and is referred to as the Scandian orogeny (Gee, 1975). The Scandian orogeny is dated to early Telychian, as is the Salinic tectophase I, and likely the two represent the same tectonic event represented on separate parts of the Caledonian suture (Ettensohn and Brett, 1998). The Salinic tectophase is most likely a result of oblique subduction of Avalonian terranes under Laurentia.

The best evidence for a causal connection between the Salinic orogeny and the early Telychian increase in $^{87}\text{Sr}/^{86}\text{Sr}$ is based on the age of a major tectonic unconformity in the sedimentary succession of the Appalachian basin. This unconformity, at the base of the Clinton Group in the eastern United States which is dated to early Telychian, represents the uplift and migration of the forebulge that formed during the beginning stages of the flexural subsidence that created the Appalachian foreland basin. A tectonic origin for this sequence boundary is also supported by an overlying condensed section, indicative of flexural subsidence and relative sea-level rise that cut off sediment supply to the shelf and basin. Evidence for the late Telychian Scandian orogeny is found in Greenland, Norway, Scandinavia (late Llandovery bentonites), and Sweden. This suggests the early Silurian was an important period of global tectonic reorganization, primarily along the Caledonian suture (Ettensohn and Brett, 1998), and may have continued to drive $^{87}\text{Sr}/^{86}\text{Sr}$ to more radiogenic values throughout the Telychian and for the remainder of the Silurian. The

Osmundsberg K-bentonite serves as the best indicator of the effect of early Silurian tectonics to the rise in $^{87}\text{Sr}/^{86}\text{Sr}$, as uplift would follow these subduction sourced volcanic

CHAPTER 6

RELATION TO CLIMATE, SEA LEVEL, AND CARBON CYCLING

The ash fall indicated by the Osmundsberg K-bentonite could have influenced the Sr flux into the oceans, but may have also had a significant effect on carbon cycling that produced important climatic feedbacks and linkages between the atmosphere and oceans in the early Telychian. A large influx of volcanic CO₂ to the atmosphere would be low in $\delta^{13}\text{C}$ (-5 ‰) (Payne and Kump 2007), and could have contributed to the observed negative shifts in the $\delta^{13}\text{C}$ records of carbonate and organic matter in the Ikla core (Rumba Formation). A similar negative $\delta^{13}\text{C}$ excursion during this time is also seen in the Canadian Arctic (Melchin et al., 2006), other studied Baltica cores (Kaljo and Martma, 2000), as well as in the $\delta^{13}\text{C}_{\text{carb}}$ data produced from the Pancake Range (Fig 9; all these observations indicate a global event. This also adds an additional method to correlate multiple sections which use different biostratigraphic zonations. This volcanic outgassing scenario was modeled to explain apparently global negative $\delta^{13}\text{C}$ excursions in the early Triassic (Payne and Kump, 2007).

Glaciation during the late Aeronian-early Telychian interval has been proposed by Caputo (1998), and may also relate ultimately to the ongoing tectonic events of this time period. Although the cause of the glaciation is not well understood, the initial cooling likely began in response to the enhanced bioproductivity during the preceding Aeronian Stage recognized throughout the east Baltic epicontinental sea (Kiipli et al., 2004). This productivity increase caused an increase in organic carbon burial that is supported by the broad positive $\delta^{13}\text{C}$ excursion in the mid-Aeronian seen in the Ikla core and elsewhere (Kaljo and Martma, 2000). Therefore, a decrease in atmospheric CO_2 likely occurred just before the start of the Telychian and may have positioned the climate system at a tipping point (e.g., Kump and Arthur, 1999). The Osmundsberg K-bentonite (Bergstrom et al., 1998) may thus provide a causal linkage among a major volcanic eruption, negative $\delta^{13}\text{C}$ excursion, and rising inflection in the $^{87}\text{Sr}/^{86}\text{Sr}$ curve (Fig. 9).

The negative shift in the Rumba formation is followed by a prominent positive $\delta^{13}\text{C}$ excursion in the remaining Telychian strata of the Ikla core, which has been identified as the beginning of the Ireviken excursion in the nearby Ruhnu core in the early Wenlock (Kaljo et al., 2003). This positive excursion is consistent with post-glacial warming that triggered enhanced marine anoxia and increased productivity from regenerated phosphate, as modeled by Payne and Kump (2007) for similar cyclic changes in Early Triassic carbon isotopes. The positive $\delta^{13}\text{C}$ shift after deposition of the Rumba formation also corresponds to a continuation of rising $^{87}\text{Sr}/^{86}\text{Sr}$ in the rest of the Telychian and could indicate a

Figure 9. $\delta^{13}\text{C}_{\text{carb}}$ data from the Ikla core (Kaljo and Martma, 2000) plotted against $\delta^{13}\text{C}_{\text{carb}}$ data from the Pancake Range (this study). Grey box is emphasizing negative excursion present in both sections, associated with Osmundsberg K-bentonite and $^{87}\text{Sr}/^{86}\text{Sr}$ inflection point. Abbreviations: Tely., Telychian; S., Sheinwoodian; Rhuddan., Rhuddanian; Sheinwo., Sheinwoodian.

Figure 10: Paleogeographic map of northern Iapetus region during the Llandovery, showing the location of the Ikla core. Large dots indicate locations of the Osmundsberg K-bentonite, showing thicknesses (in cm). Small dots represent locations of earlier Llandovery K-bentonites. Shaded area between Baltica and Scotland represents potential source area for Osmundsberg K-bentonites, and the shaded area between Nova Scotia and North America represents potential source area for North America K-bentonites (after Bergstrom et al., 1998).

Stages	Baltic Stages	Formations	Graptolite Zones	Conodont Zones
Telychian	Adavere	Velise	insectus- spiralis	P. amorphognathoides.
			crenulata- griestoniensis	P. celloni
		Rumba	turriculatus- crispus	D. staurognathoides
			guerichi	
Aeronian	Raikkula	Saarde	sedgwickii	I. discreta- I. deflecta
			convolutus	
			argenteus	
			pectinatus- triagulatus	D. kentuckyensis
Rhudd- anian	Juuru	Ohne	cyphus	
			vesiculosus	
			acuminatus	

Figure 11: Stratigraphy of Llandovery rocks of South Estonia (after Kaljo and Martma, 2000) correlated with generalized graptolite zones (after Koren et al., 1996) and conodont zones (after Bergstrom et al., 1998). Bold dot indicates approximate location of Osmundsberg K-bentonite (Bergstrom et al, 1998).

periodically important role for enhanced warming in increasing weathering of radiogenic continental silicate rocks.

CHAPTER 7

CONCLUSION

High resolution data of $^{87}\text{Sr}/^{86}\text{Sr}$ during the Llandovery shows that the change in Sr is more complex than previously thought, and aids in interpreting the paleoclimatic and tectonic reasons for this shift. The presence of the Osmundsberg K-bentonite and the negative excursion in $\delta^{13}\text{C}_{\text{carb}}$ in the Rumba formation of the early Telychian in the Ikla core coincide with the start of the rapid positive shift in Sr. This implies that large scale volcanics were present, and that weathering of these volcanics potentially caused the onset of the rise in Sr. These volcanics would have served as a precursor to continental subduction in the early Silurian, which following the Taconic orogeny of the late Ordovician/early Silurian, would have exposed older radiogenic Sr to be weathered, and thus continued the increase in radiogenic values. During the Aeronian, bioproductivity was high, and C burial increased, lowering atmospheric CO_2 into the Telychian which, sent the climate into a glaciation, which contributed to the increased weathering of continental silicate rocks as sea level regressed. Associated with the increase in $^{87}\text{Sr}/^{86}\text{Sr}$ is a large negative excursion in $\delta^{13}\text{C}$, which could be the result of an increased flux of light CO_2 into the atmosphere, furthering

strengthening the hypothesis that large scale volcanics were active. This negative shift is present in both of the Llandovery sections analyzed in this study (Nevada and Estonia), as well as in the Canadian Arctic section studied by Melchin and Holmden, 2006, and in each case precedes the Ireviken excursion, indicating this is a global excursion.

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APPENDIX A
DATA TABLES

Meters	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr error	Sr ppm	$\delta^{13}\text{Ccarb}$	$\delta^{13}\text{Corg}$	$\delta^{18}\text{O}$	Formation
260.0				1.793		-3.726	Riga
265.0				3.659		-3.667	Riga
269.2				3.370		-3.311	Riga
275.0				3.413		-3.606	Riga
280.4				3.588		-3.795	Riga
286.5				3.414	-26.69	-4.234	Riga
288.5				3.114	-26.67	-4.104	Riga
289.2	0.708441	0.000014	136.7	3.236	-26.40	-4.146	Velise
294.3				1.794		-5.212	Velise
296.0	0.708423	0.000009	138.3	2.474	-26.80	-4.746	Velise
300.8	0.708359	0.000008	148.9	2.241	-26.49	-5.437	Velise
305.2	0.708334	0.000011	143.0	1.500	-27.73	-5.265	Rumba
308.1	0.708201	0.000008	227.2	0.386	-27.84	-4.988	Rumba
310.1				0.169		-4.724	Rumba
310.5							Rumba
312.1	0.708217	0.000011	236.1	-0.028	-28.72	-5.038	Rumba
313.2				-0.509		-5.621	Rumba
316.6	0.708184	0.000011	318.1	0.277	-30.02	-3.725	Rumba
318.4				0.005		-4.563	Rumba
320.0				-0.946		-4.960	Rumba
320.3	0.708140	0.000010	242.7		-29.50		Rumba
322.0				0.335		-5.021	Rumba
322.4							Saarde (Staicele Mem)
323.1	0.708160	0.000008	247.1		-28.59		Saarde (Staicele Mem)
323.5				0.960		-4.841	Saarde (Staicele Mem)

Continued

Table 1: Stable isotope data from Ikla Core. Uncertainities are two-sigma mean internal reproducibilities, typically based upon 100 measured ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios given are normalized for instrumental fractionation using a normal ratio for $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.119400. The Laboratory reference value for the SRM 987 standard is ($^{87}\text{Sr}/^{86}\text{Sr}$) = 0.710242 ± 0.000010 (one one-sigma external reproducibility). No modifications to the measured normalized $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been made.

Table 1 continued

324.5				1.506		-4.967	Saarde (Staicele Mem)
327.5				2.119	-29.14	-5.065	Saarde (Staicele Mem)
330.9				1.911		-5.061	Saarde (Staicele Mem)
332.5							Saarde (Staicele Mem)
334.8	0.708067	0.000009	832.1	2.423	-28.79	-5.035	Saarde (Staicele Mem)
337.5							Saarde (Staicele Mem)
338.0				2.562		-5.084	Saarde (Staicele Mem)
340.1	0.708075	0.000009	1098.0	1.927	-27.56	-4.636	Saarde (Staicele Mem)
342.7				2.116		-5.226	Saarde (Staicele Mem)
343.1							Saarde (Staicele Mem)
344.9	0.708090	0.000011	887.1	2.075	-29.25	-4.989	Saarde (Staicele Mem)
347.3				2.395		-4.976	Saarde (Staicele Mem)
350.0				2.416		-5.152	Saarde (Staicele Mem)
352.5				2.428		-5.000	Saarde (Staicele Mem)
353.0	0.708090	0.000008	917.8		-28.01		Saarde (Staicele Mem)
354.5	0.708093	0.000008	341.9	2.376	-28.97	-5.050	Saarde (Staicele Mem)

Continued

Table 1 continued

356.6							Saarde (Staicele Mem)
357.0				2.586		-3.912	Saarde (Staicele Mem)
357.9							Saarde (Staicele Mem)
358.7				2.091		-4.958	Saarde (Staicele Mem)
361.5				2.338		-4.938	Saarde (Staicele Mem)
362.2							Saarde (Staicele Mem)
363.8	0.708127	0.000008	423.1	1.562	-27.56	-4.025	Saarde (Staicele Mem)
369.0				1.348		-4.246	Saarde (Lemme Mem)
371.5	0.708068	0.000013	907.6	1.276	-28.57	-4.260	Saarde (Lemme Mem)
373.4				1.684		-5.703	Saarde (Lemme Mem)
376.1				1.969		-4.475	Saarde (Lemme Mem)
379.0				1.839		-5.175	Saarde (Lemme Mem)
381.4				2.417		-4.335	Saarde (Lemme Mem)
382.1							Saarde (Lemme Mem)
384.4	0.708069	0.000009	648.0	3.189	-27.45	-4.260	Saarde (Lemme Mem)
386.8	0.708108	0.000019	233.1	2.558	-28.82	-4.737	Saarde (Lemme Mem)
387.9							Saarde (Lemme Mem)
391.0				2.703		-4.494	Saarde (Lemme Mem)
393.5				2.828		-4.246	Saarde (Lemme Mem)
394.0							Saarde (Lemme Mem)

Continued

Table 1 continued

396.0	0.708110	0.000009	206.6	2.396	-28.27	-4.789	Saarde (Lemme Mem)
398.0				3.211		-3.612	Saarde (Ikla Mem)
399.2	0.708056	0.000007	971.6	2.105	-27.38	-5.608	Saarde (Ikla Mem)
402.0	0.708078	0.000009	1108.0	2.736	-28.73	-3.429	Saarde (Ikla Mem)
403.1				2.881		-4.432	Saarde (Ikla Mem)
407.8	0.708027	0.000009	1083.0	2.959	-28.84	-3.613	Saarde (Ikla Mem)
411.6				3.161		-4.337	Saarde (Ikla Mem)
415.3				3.119		-4.535	Saarde (Ikla Mem)
419.7	0.708038	0.000008	1396.0	3.196	-28.22	-4.624	Saarde (Ikla Mem)
421.0				3.354		-4.397	Saarde (Ikla Mem)
421.3	0.708044	0.000008	857.9		-27.94		Saarde (Ikla Mem)
422.5							Saarde (Ikla Mem)
424.0				3.604		-4.448	Saarde (Ikla Mem)
428.9	0.708072	0.000012	318.2	3.676	-28.46	-4.525	Saarde (Ikla Mem)
434.0	0.708043	0.000013	967.9	3.258	-29.05	-4.647	Saarde (Ikla Mem)
438.0				1.731		-4.587	Saarde (Ikla Mem)
443.0				2.496	-29.41	-4.351	Saarde (Ikla Mem)
447.0				1.983		-5.077	Saarde (Ikla Mem)
451.3	0.708046	0.000006	510.3	2.209	-28.16	-5.105	Saarde (Ikla Mem)
455.0				2.356		-4.602	Saarde (Ikla Mem)
458.3	0.708275	0.000011	69.3	1.960	-29.20	-4.996	Saarde (Ikla Mem)
460.0				0.952		-4.473	Saarde (Kolka Mem)
462.5	0.708239	0.000009	136.8	1.975	-28.82	-5.083	Saarde (Kolka Mem)

Continued

Table 1 continued

466.0				2.332		-3.757	Saarde (Kolka Mem)
469.1				1.196		-4.766	Saarde (Kolka Mem)
470.0	0.708151	0.000009	260.3	2.117	-27.64	-3.905	Saarde (Kolka Mem)
471.2				1.580		-5.286	Saarde (Kolka Mem)
473.0				2.297		-3.937	Saarde (Kolka Mem)
475.1				0.837		-4.681	Saarde (Kolka Mem)
477.3				2.412		-3.702	Saarde (Kolka Mem)
480.0				1.801		-4.007	Saarde (Kolka Mem)
481.0				2.014		-3.682	Saarde (Slitere Mem)
482.7				2.090		-4.060	Saarde (Slitere Mem)
484.9				1.982		-4.077	Saarde (Slitere Mem)
487.9	0.708105	0.000009	146.9	1.846	-27.71	-4.158	Saarde (Slitere Mem)
489.7				1.799		-4.645	Saarde (Slitere Mem)
494.0				1.388		-4.866	Saarde (Slitere Mem)
496.0				0.347		-4.187	Pusku beds
497.5	0.708127	0.000007	392.2	0.112	-27.40	-4.767	Pusku beds
498.0				-0.890		-3.686	Pusku beds
498.7				-0.953		-3.499	Pusku beds
500.2				1.024		-4.661	Ohne
502.6	0.708171	0.000008	249.0	1.358	-27.81	-3.808	Ohne
505.0				1.392		-3.913	Ohne
507.7	0.708135	0.000008	104.0	0.915	-27.97	-4.907	Ohne
510.5				0.759		-3.823	Ohne
513.0	0.708341	0.000008	139.1	1.280	-26.91	-3.869	Ohne
515.0				1.465		-3.684	Ohne
516.8	0.708132	0.000012	154.7	1.368	-27.21	-3.478	Ohne
518.4				1.970		-4.034	Ohne
520.0				0.956		-4.727	Ohne

Continued

Table 1 continued

521.6				0.572		-4.690	Ohne
522.8				0.710		-4.232	Ohne
524.5				0.773		-4.904	Ohne
526.0				1.511		-3.503	Ohne
527.8	0.708464	0.000019	35.21	1.327	-26.54	-2.951	Ohne
527.9	0.708020	0.000007	127.3		-27.24		Ohne
527.9	0.708034	0.000011	90.56				Ohne
528.4				2.387		-4.653	Saldus
529.1	0.707986	0.000011	174.3				Saldus
530.0				2.520		-4.615	Saldus
531.1	0.708193	0.000016	120.6		-26.76		Saldus
532.3	0.708111	0.000008	142.0	3.003	-26.60	-3.259	Saldus
533.7	0.708154	0.000009	113.2	3.219	-26.39	-3.285	Saldus
534.6				2.496		-3.407	Saldus

Meters	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr error	Sr ppm	$\delta^{13}\text{C}_{\text{carb}}$	$\delta^{18}\text{O}$	Formation	Member
2.00				-0.072	-2.781	Ely Springs	Flouride
4.25				0.223	-3.223	Ely Springs	Flouride
6.75				-0.098	-3.230	Ely Springs	Flouride
8.25				0.589	-5.493	Ely Springs	Flouride
8.35				0.808	-5.571	Ely Springs	Flouride
8.60				0.748	-4.610	Ely Springs	Flouride
8.85				0.297	-3.972	Ely Springs	Flouride
9.10				0.938	-5.676	Ely Springs	Flouride
9.20				0.483	-3.311	Ely Springs	Flouride
9.30				0.300	-2.458	Ely Springs	Flouride
9.55				0.415	-4.543	Ely Springs	Flouride
9.80				-0.099	-4.447	Ely Springs	Flouride
10.05				0.626	-3.791	Ely Springs	Flouride
10.30				0.597	-4.181	Ely Springs	Flouride
10.55				0.926	-5.306	Ely Springs	Flouride
10.80				0.463	-3.230	Ely Springs	Flouride
11.05				0.780	-2.902	Ely Springs	Flouride
11.30				0.315	-3.601	Ely Springs	Flouride
11.55				0.239	-2.445	Ely Springs	Flouride
13.05				1.758	-5.929	Ely Springs	Flouride
15.05				0.881	-1.607	Ely Springs	Flouride
17.00				1.501	-5.664	Ely Springs	Flouride
19.00				1.252	-6.421	Ely Springs	Flouride
23.00				2.378	-4.969	Ely Springs	Flouride
25.00				2.742	-6.096	Ely Springs	Flouride
29.00				1.529	-5.655	Ely Springs	Flouride
32.50	0.708611	0.000025	32.68	1.588	-6.026	Ely Springs	Flouride
35.00				2.272	-3.307	Ely Springs	Flouride
37.00				0.573	-4.070	Ely Springs	Flouride
41.00				0.712	-6.692	Ely Springs	Flouride

Continued

Table 2: Stable isotope data from Pancake Range. Uncertainties are two-sigma mean internal reproducibilities, typically based upon 100 measured ratios. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios given are normalized for instrumental fractionation using a normal ratio for $^{86}\text{Sr}/^{88}\text{Sr}$ of 0.119400. The Laboratory reference value for the SRM 987 standard is ($^{87}\text{Sr}/^{86}\text{Sr}$) = 0.710242 $\pm$ 0.000010 (one one-sigma external reproducibility). No modifications to the measured normalized $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been made.

Table 2 continued

41.00				1.086	-6.334	Laketown	Tony Grove
43.00				1.038	-6.738	Laketown	Tony Grove
47.00				0.982	-7.233	Laketown	Tony Grove
51.00				0.845	-6.044	Laketown	Tony Grove
57.00	0.708619	0.000023	24.34	1.676	-3.500	Laketown	Tony Grove
63.00				1.018	-6.620	Laketown	Tony Grove
67.00				1.376	-6.264	Laketown	Tony Grove
71.00				1.003	-5.689	Laketown	Tony Grove
75.00				1.301	-8.033	Laketown	Tony Grove
78.00	0.708801	0.000083	14.23	2.226	-10.573	Laketown	Tony Grove
82.00				1.887	-9.569	Laketown	Tony Grove
88.00				2.587	-10.817	Laketown	Tony Grove
97.00	0.708571	0.000027	20.74	2.191	-9.841	Laketown	Tony Grove
100.00				0.345	-5.375	Laketown	Tony Grove
106.00				-0.126	-2.842	Laketown	Tony Grove
115.00	0.708482	0.000035	10.86	2.123	-8.603	Laketown	High Lake
118.00				1.166	-8.794	Laketown	High Lake
124.00				1.965	-8.895	Laketown	High Lake
133.00	0.708546	0.000034	16.35	1.732	-9.255	Laketown	High Lake

Continued

Table 2 continued

139.00				2.179	-8.803	Laketown	High Lake
145.00	0.708063	0.000028	15.28	0.907	-6.275	Laketown	High Lake
151.00	0.708489	0.000092	12.75	1.673	-7.571	Laketown	High Lake
157.00				1.603	-7.672	Laketown	High Lake
163.00	0.708899	0.000019	22.46	1.672	-8.606	Laketown	High Lake
169.00	0.708145	0.000053	11.16	0.901	-5.814	Laketown	High Lake
175.00	0.708070	0.000063	16.50	0.751	-7.836	Laketown	High Lake
181.00				0.276	-6.305	Laketown	High Lake
184.00	0.708156	0.000055	13.47	0.277	-5.859	Laketown	High Lake
187.00				0.074	-6.245	Laketown	High Lake
190.00	0.708103	0.000024	22.99	1.057	-6.566	Laketown	High Lake
193.00				0.754	-6.332	Laketown	High Lake
196.00				0.693	-7.299	Laketown	High Lake
199.00	0.707994	0.000106	29.11	0.224	-4.716	Laketown	High Lake
202.00				0.137	-5.116	Laketown	High Lake
208.00				0.132	-2.961	Laketown	High Lake
214.00				0.100	-3.145	Laketown	High Lake
220.00				0.529	-5.304	Laketown	High Lake
226.00				0.777	-6.658	Laketown	High Lake
232.00				1.108	-6.120	Laketown	High Lake
238.00				0.608	-5.913	Laketown	High Lake
244.00				0.984	-7.686	Laketown	High Lake
247.00				1.863	-3.249	Laketown	Gettel
251.50				2.062	-4.545	Laketown	Gettel
255.50				2.534	-4.349	Laketown	Gettel
260.00				0.852	-4.620	Laketown	Gettel
260.50				0.899	-5.259	Laketown	High Lake
265.00				1.492	-5.088	Laketown	High Lake
269.50				1.291	-6.107	Laketown	High Lake
274.00				0.700	-7.329	Laketown	High Lake
278.50				1.135	-6.733	Laketown	High Lake
282.00				1.183	-6.240	Laketown	High Lake
285.00				2.170	-3.980	Laketown	Jack Valley

Continued

Table 2 continued

289.50				1.060	-5.843	Laketown	Jack Valley
294.00				3.006	-4.188	Laketown	Jack Valley
298.50				1.647	-3.770	Laketown	Jack Valley
303.00				1.280	-6.034	Laketown	Decathlon
307.50				0.753	-6.328	Laketown	Decathlon
312.00				1.220	-5.281	Laketown	Decathlon

APPENDIX B
ADDITIONAL FIGURES

Figure 13: Ikla core $\delta^{13}\text{C}_{\text{org}}$ v. TOC

Figure 14: Pancake Range $^{87}\text{Sr}/^{86}\text{Sr}$

Figure 15: Pancake Range $^{87}\text{Sr}/^{86}\text{Sr}$ v. $1/\text{Sr}$

Figure 16: Pancake Range $^{87}\text{Sr}/^{86}\text{Sr}$ v. $\delta^{18}\text{O}$

Figure 17: Pancake Range $\delta^{13}\text{C}$ v. $\delta^{18}\text{O}$