Neodymium Isotopic Composition of Ordovician - Early Silurian Conodonts.

by

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We accept this thesis as conforming to the required standards

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ABSTRACT

Neodymium (Nd) and samarium (Sm) isotopic ratios were determined in conodont apatite to attain a seawater proxy to test recent paleogeographic reconstructions, and by association, other reconstructions involving paleobiogeography and paleoceanography. Conodont samples were chosen from the major cratons and microplates to achieve a global picture of the Ordovician and Early Silurian paleogeography. Fourty-five samples yielded satisfactory ε_{Nd} values for a few time slices in this interval.

The results of the analysis reveal that conodonts are useful proxy tools. They have Nd and Sm isotopic abundances that are within accurate and reproducible analytical limits. The pattern of values reveals a consistent picture of the changes in the Ordovician to Early Silurian oceans. The $\varepsilon_{Nd}(T)$ values for Laurentia are strongly negative in the Early Ordovician and this is in marked contrast to other cratons and microplates. The evolution of the signature over time reveals an increasingly radiogenic component for Laurentia (-22 to -18 changing to -13 to -5). The isotopic values and the secular variation curve are a function of both regional and global tectonic processes, the most obvious being the Taconic Orogeny and the closure of the Iapetus Ocean with the northward drift of Baltica and Avalonia.

In this study, both global and regional scale paleogeographic models of other authors are considered. The ε_{Nd} data help define ancient ocean masses and are relevant to the patterns of conodont biogeography. However, there are not precise correlations with the various realms and provinces. Finally, the data are used to test paleoceanographic circulation models and the data generally support large scale circulation patterns based on Ekman transport.

The use of Nd isotopic signatures representing ancient oceans provides an independent method to test recent paleogeographic reconstruction models. The isotopic signals can integrated into the construction such models so that a more coherent picture of ancient environments can emerge.

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"The time is ripe for a concerted effort, for a merging of the relevant approaches, and required disciplines. Biology, geology and chemistry, together -- the fundamental triad of paleobiologic science--seem certain to give a better answer than any single discipline alone"

J. W. Schopf, 1988

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Chapter 1 Introduction and Objectives

The Ordovician is the longest period (~70 Ma) in the Phanerozoic. It is characterized by several events that are recorded in both the rock and fossil records. For the first time in the Phanerozoic there are several distinct oceans and paleoplates following the breakup of the supercontinent Rodinia in the Proterozoic (Hoffman, 1991; Dalziel, 1991). The Period is marked with major changes in sea-level, both at a regional and global scale and was punctuated by five separate bioevents that shape the chronostratigraphic nature of the record (Barnes et al., in press). During the early Middle Ordovician a major faunal changeover occurred, with the Paleozoic Fauna replacing the Cambrian Fauna (Sepkoski, 1981) and in the Caradoc, volcanic eruptions deposited widespread bentonite ash layers (Huff et al., 1991) that may have affected both biotic and abiotic systems. Towards the end of the Ashgill, there was a continental glaciation at the southern pole that was the result of a shift from greenhouse to icehouse conditions and this may have caused a possible global oceanic circulation event that was partially responsible for the end Ordovician mass extinction and the subsequent Silurian biotic recovery.

The lithological and fossil record provide data to interpret the various factors that controlled the environment during the early Paleozoic. Both have limitations that make reconstruction of the environment (e.g. paleogeography, paleoceanography) difficult. From the rock record sedimentary analysis, basin correlation, paleomagnetics, and igneous events assist in establishing the paleogeographic constraints. However, tectonic deformation can make stratigraphic correlation difficult and paleomagnetism, the dominant method for determining paleogeography, is also limited by overprinting from orogenic events and its inability to establish paleolongitude (Fowler, 1990). To counter these limitations, the fossil record and faunal biogeography are often integrated with paleomagnetic results, however, these taphonomic and samping biases. Additionally, paleoceanographic reconstructions can be strengthened by using General Circulation Models, but such models are in their infancy when applied to the Paleozoic. Other independent approaches that can utilize and test paleoenvironmental reconstructions are required and a geochemical technique is adopted herein.

Neodymium (Nd) isotopic investigations of geological materials have come to the forefront of geochemistry in the last 30 years. Several studies have used the systematics of this isotope to study earth processes and earth evolution. Nd has a short marine water column residency time compared to the total mixing time of the oceans, hence one of its primary uses is in defining major water masses. In the mid to late 1980's a body of evidence accumulated that showed that authigenic, detrital, and biogenic minerals from sediments could be used to track the Nd isotopic composition of the overlying water mass and also for tracking ancient seawater masses as the Nd isotopic signature of the water mass equilibrates and incorporates the signature into the mineral matrix. This allows the Nd isotopic composition of sedimentary materials, including fossils, to be used as a proxy signature for oceans that were contemporaneous with their deposition. This has important implications for studying paleogeography, paleobiogeography, and paleoceanography.

Conodonts are the hard tissue remains of an extinct group of marine, early chordates. They are composed of hydroxy-apatite and as such, represent a potential source of sites for light rare earth element (LREE) and other trace element incorporation. This enrichment and long term mineral stability makes them a good proxy tool in establishing geochemical signals for ancient seawater . Conodont apatite has only recently been studied for the usage of the Nd isotopic system to track ancient geological parameters and these investigations set the ground work for this thesis and are discussed in later sections.

The goal of this thesis is to use the Nd isotopic composition of conodonts as a proxy for recognizing ancient oceans and to test various proposed models of early Paleozoic paleogeography. By testing these models, evaluation of other models of paleobiogeography and paleoceanography can be assessed. Over 60 conodont samples were chosen through five time slices of the Ordovician - Early Silurian and they represent most of the major paleoplates that contributed sedimentary material into the paleoceans. The objectives of the study are as follows:

- to determine the range of Nd isotopic signatures for the major oceans during the Ordovician to Early Silurian using conodonts as a proxy tool

- to correlate the variation in isotopic signals with different sedimentary sources and to estimate the model residence ages of the sample, relating it to its potential sedimentary sources

- to test various proposed models of Ordovician and early Silurian paleogeography using the variation in the isotopic signatures

- to evaluate the correlation between the Nd isotopic signature of the ancient ocean masses and the patterns of conodont provincialism during this time

- to test various proposed models of early Paleozoic paleoceanography

The data contained in this thesis is a substantial addition to the small existing Nd database for the Early Paleozoic. It is the first approach using conodonts globally. The sample distribution is reasonably extensive and contributes to a more comprehensive understanding of the earth's evolution during the Ordovician and early Silurian.

This thesis draws upon information from many areas of study and a basic explanation of these fields is provided in Chapter 2. It includes information on Nd isotopic systematics, paleoenvironmental parameters for the Early Paleozoic, a discussion on conodont biology and geochemistry and a review of the Ordovician chronostratigraphic and biostratigraphic time scale.

Chapter 2 Background Information

2.1 The Neodymium Isotopic System

2.1.1 Theory and Systematics

Neodymium (Nd) and samarium (Sm) are trivalent members of the rare earth elements (REEs). This group consists of 17 elements and includes the lanthanide series. Sm and Nd are radiogenic and this makes them ideal markers to constrain the origin of REEs and depositional environments (Piepgras et al., 1979; Elderfield & Greaves, 1982; Elderfield, 1988). ^{147}Sm alpha decays ($t_{1/2}$ = 1.06 x 10^{11} years) to ^{143}Nd. The fractionation of Sm and Nd in continental crust and the associated mantle ratios of the radiogenic species of Nd to the non-radiogenic species (^{144}Nd) are used to estimate the major inputs of REEs into a system (Piepgras & Wasserburg, 1980; Elderfield & Greaves, 1982; Elderfield, 1988). The REEs fractionate within the earth's magma, particularly in the silicate portion of the melt, and this leads to crustal rocks having different Sm/Nd values and systematically different ^{143}Nd/^{144}Nd values (DePaolo, 1988). These data can track the evolution of changes in the crust over time as the bulk planet is, at the time of formation, assumed to be homogeneous with respect to Sm/Nd. At time T in the past, magma was generated and crystallized in the upper crust, enriching it in various components and leaving the upper mantle reservoir of magma depleted (DePaolo, 1988).

Sm and Nd are tightly coupled and fractionation is likely to occur only in the silicate fraction during magmatism. As lithophile elements they were likely not involved in the formation or condensation of the earth's core which otherwise could have led to large isotopic fractionation (DePaolo, 1988). Their minor differences in atomic weight results in only a slight fractionation but with similar properties they react to evolutionary processes in a complementary manner. Further, they are preferentially incorporated into the crust and major rock-forming minerals and are less likely to be mobile at near-surface conditions (DePaolo, 1988).

Variations in the ^{143}Nd/^{144}Nd ratios are typically too small to be meaningful, so they are normally compared to a standard reference material. For Sm-Nd it is the Chondritic Uniform Reservoir (CHUR) which represents the homogenous bulk earth with ^{147}Sm/^{144}Nd and ^{143}Nd/^{144}Nd ratios the same as in average chondrites (DePaolo & Wasserburg, 1976). The ^{143}Nd/^{144}Nd ratio of any rock sample can be compared to the CHUR as a deviation in 10^4 units using:

$$\varepsilon_{Nd}(0)=\left(\frac{^{143}Nd/^{144}Nd_m}{^{143}Nd/^{144}Nd_{CHUR}(0)}-1\right)\times 10^4 \qquad \textbf{[2.1]}$$

where:

$^{143}Nd/^{144}Nd_m$ is the measured value of the sample

$^{143}Nd/^{144}Nd_{CHUR}(0) = 0.511847$ (Jacobsen & Wasserburg, 1980)

Chondritic values best represent the bulk earth since they have not been affected by magmatic processes (DePaolo, 1988). From extensive measurements on chondrites, Jacobsen & Wasserburg (1980) established the standard chondritic values of 0.511847 for $^{143}Nd/^{144}Nd$ and 0.1967 for $^{147}Sm/^{144}Nd$. The differences in the mantle regimes can be seen in the differentiation between continental crust with an $\varepsilon_{Nd}(0)$ range from 0 - -20 (average: -14) and younger basaltic material having an $\varepsilon_{Nd}(0)$ range of 0 - +10 (average: +8) (DePaolo & Wasserburg, 1977; Piepgras et al., 1979). Generally, crustal material has negative epsilon values, with Precambrian sources being > -10 while depleted mantle material has more positive values.

By assuming that rocks comprising the crust come predominately from the mantle and knowing the systematic changes to ^{143}Nd due to the decay of ^{147}Sm, the $^{143}Nd/^{144}Nd$ value of a sample can be corrected back to an initial $^{143}Nd/^{144}Nd$ value that represents the ratio at the time of crystallization from the mantle (Figure 2.1) and can be compared to the CHUR using:

$$\varepsilon_{Nd}(T)=\varepsilon_{Nd}(0)-\left(\frac{10^4\left[^{147}Sm/^{144}Nd_{CHUR}(0)\right]\left[e^{\lambda_{Sm}T}-1\right]}{^{143}Nd/^{144}Nd_{CHUR}(0)}\right)\times$$

$$f_{Sm/Nd}\times\frac{^{143}Nd/^{144}Nd_{CHUR}(0)}{^{143}Nd/^{144}Nd_{CHUR}(T)} \qquad \text{(DePaolo, 1988)} \qquad \textbf{[2.2]}$$

where:

$$^{147}Sm/^{144}Nd_{CHUR}(0) = 0.1967 \quad \text{(Jacobsen \& Wasserburg, 1980)}$$

$$^{143}Nd/^{144}Nd_{CHUR}(0) = 0.511847 \quad \text{(Jacobsen \& Wasserburg, 1980)}$$

$$\lambda_{Sm} = 0.00654 \text{ b. y.}^{-1}$$

$$^{143}Nd/^{144}Nd_{CHUR}(T) = {}^{143}Nd/^{144}Nd_{sample}(0) - {}^{147}Sm/^{144}Nd_{sample}(0)\left[e^{\lambda_{Sm}T} - 1\right] \quad [2.3]$$

$$f_{Sm/Nd} = \left[\frac{^{147}Sm/^{144}Nd_{sample}}{^{147}Sm/^{144}Nd_{CHUR}(0)} - 1\right] \quad [2.4]$$

The epsilon expression can be simplified by approximating $\lambda_{Sm}T \cong e^{\lambda_{Sm}T} - 1$ and ignoring the second brackets in equation 2.2;

$$\varepsilon_{Nd}(T) = \varepsilon_{Nd}(0) - Q_{Nd} f_{Sm/Nd} T \quad [2.5]$$

where:

$$Q_{Nd} = \frac{(10^4 * \lambda_{sm} * {}^{147}Sm/^{144}Nd_{CHUR}(0))}{^{143}Nd/^{144}Nd_{CHUR}(0)} \quad [2.6]$$

$$Q_{Nd} \cong 25.13 \text{ Ga}^{-1}$$

Thus, the variations in the ε_{Nd} parameter depend on time (T) and the degree of chemical fractionation ($f_{Sm/Nd}$). The $f_{Sm/Nd}$ is a chemical fractionation parameter and is an expression of the $^{147}Sm/^{144}Nd$ deviation from the CHUR. It is representative of the slope of a sample's evolution curve (Figure 2.1). Upper crustal rocks generally have a $f_{Sm/Nd} \cong -0.4$ (Goldstein et al., 1984; Bennett & DePaolo, 1987).

Nd isotopes can be used in determining the model ages of sedimentary material and from this a possible sedimentary provenance. Model age, also referred to as crustal residence age (T_{CR}), is the time during which the rare earth components (e.g. Nd isotopes) resided in the continental crust. There are two methods for determining the crustal residence age: the CHUR model (T_{CHUR}) and the depleted mantle model (T_{DM}) (DePaolo & Wasserburg, 1976; McCulloch & Wasserburg, 1978; Jacobsen & Wasserburg, 1980; DePaolo, 1988). The point at which the sample evolution curve intersects the $\varepsilon_{Nd} = 0$ line (chondritic evolution curve) is the age in which the parent material was extracted from a chondritic mantle, the T_{CHUR} age (Figure 2.2).

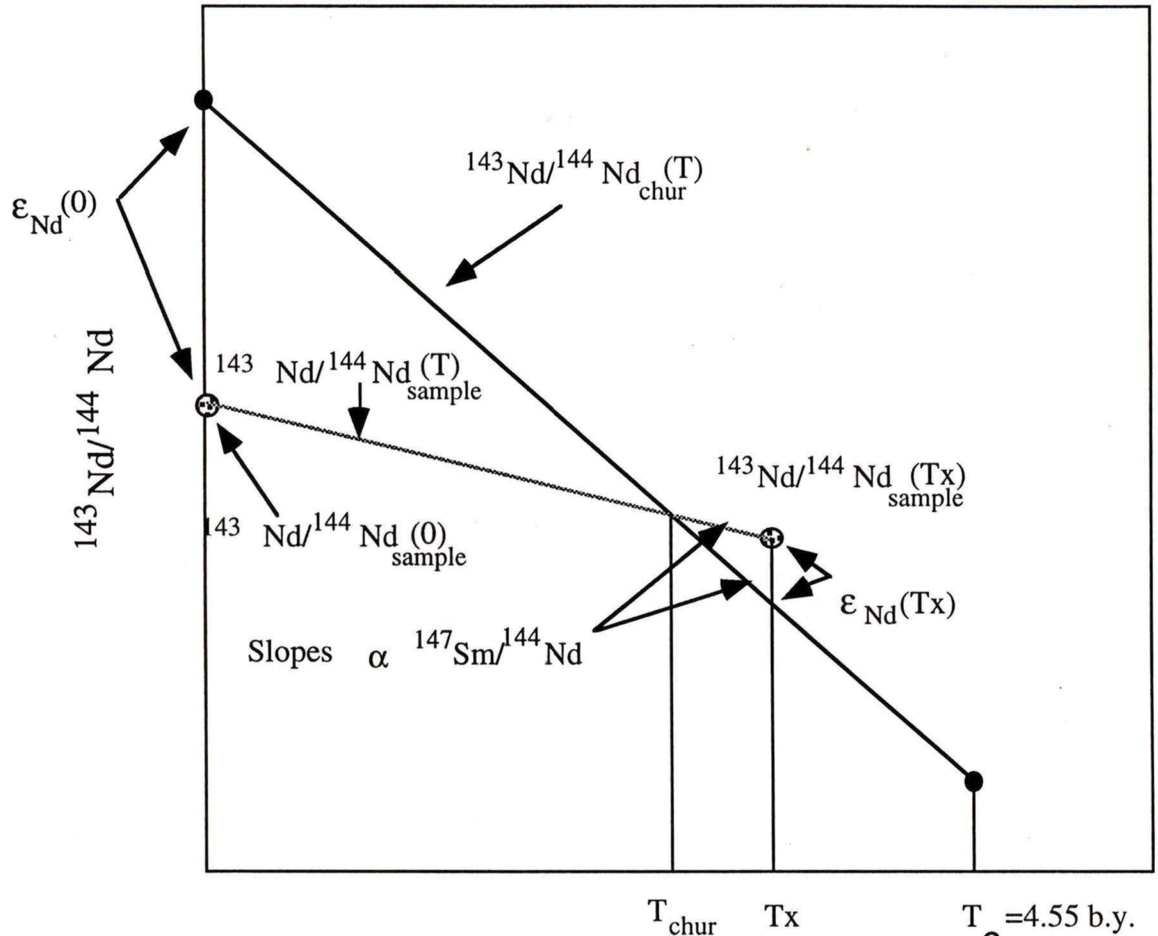


Figure 2.1: Nd isotopic evolutionary parameters as defined in equations 2.1 - 2.5 (after DePaolo, 1988).

However, T_{CHUR} is not always the appropriate model to determine crustal residence age (Goldstein et al., 1984; Keto, 1987; Keto & Jacobsen, 1987) and it can be inconsistent with the radiometric stratigraphic age (Hamilton et al., 1983). Continental crust is derived from a part of the mantle that is also the source for mid-ocean ridge basalts, which are the products of a depleted mantle (DePaolo, 1981). Indeed, a depleted mantle has existed through most of geologic time (DePaolo & Wasserburg, 1976) and McCulloch & Bennett (1994) confirmed, based on a wide variety of isotopic data, that the continental crust is extracted from an increasingly depleted mantle source. In the determination of residence ages, DePaolo (1981) developed the T_{DM} model to more appropriately represent the crustal residence age that is defined as the age in which the parent material was extracted from the depleted mantle. The age is obtained by the intersection of the sample evolution line with the depleted mantle evolution curve (Figure 2). Depleted mantle values can be obtained by using the present day CHUR values and the present day depleted mantle value of $\varepsilon_{Nd}(0) = +10$, assuming the linear evolution of $\varepsilon_{Nd} = 0$ at the origin of the Earth (Figure 2.2).

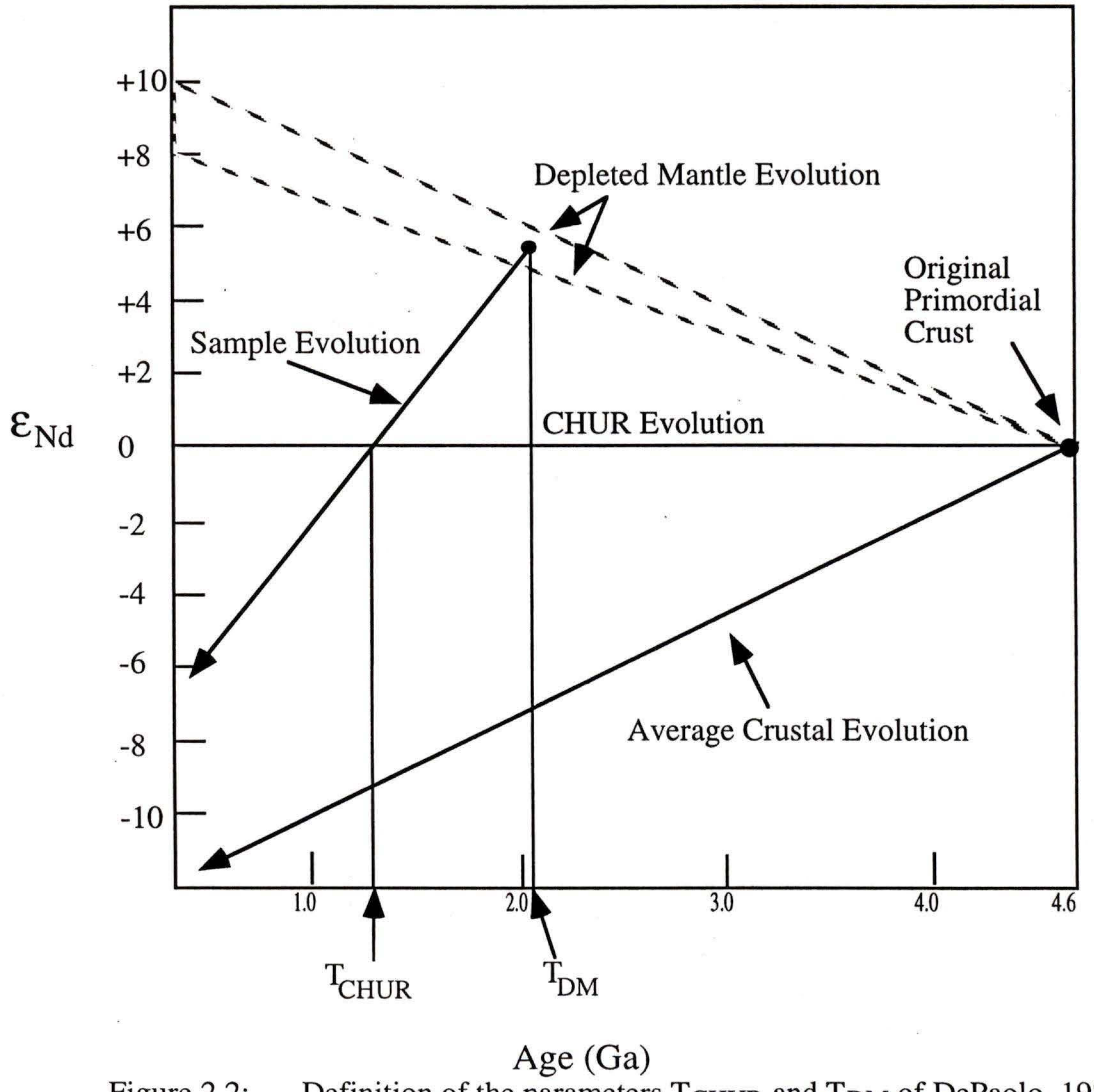


Figure 2.2: Definition of the parameters T_{CHUR} and T_{DM} of DePaolo, 1981 (after DePaolo, 1988).

Keto & Jacobsen (1987) stated that a single stage mixing model can be used to determine the T_{DM} using:

$$T_{DM}^{Nd} = (\frac{1}{\lambda_{Sm}}) \times \ln\left[1 + \frac{\left({}^{143}Nd/{}^{144}Nd\right)_m - \left({}^{143}Nd/{}^{144}Nd\right)_0^{DM}}{\left({}^{147}Sm/{}^{144}Nd_m - \left({}^{147}Sm/{}^{144}Nd\right)_0^{DM}\right)}\right] \qquad \textbf{[2.7]}$$

where:

$\lambda_{Sm} = 6.54 \times 10^{-12}$ yr^{-1}

$\left({}^{143}Nd/{}^{144}Nd\right)_0^{DM} = 0.512359$ (Keto & Jacobsen, 1987)

$\left({}^{147}Sm/{}^{144}Nd\right)_0^{DM} = 0.2136$ (Keto & Jacobsen, 1987)

However, according to the authors, T_{DM} may not always represent the mean age of the source material. Fluvial transport can bias the sample towards a younger age and the $^{147}Sm/^{144}Nd$ values in biogenic minerals are commonly different from the source rocks, as such, a two stage model should be used to yield a more accurate residence age:

$$T_{2DM}^{Nd} = T_{DM}^{Nd} - \left(T_{DM}^{Nd} - T_{STRAT}\right)\left[\frac{f_{cc} - f_m}{f_{cc} - f_{DM}}\right] \qquad \textbf{[2.8]}$$

where:

T_{STRAT} is the time of deposition

$T_{DM}^{Nd} - T_{STRAT}$ is the sample evolution from the time of differentiation of crustal source areas from the mantle to the time of deposition

f_m is the sample evolution

$f_{cc} = -\ 0.4$ (continental crust) (Keto & Jacbosen, 1987; c.f. Goldstein et al., 1984)

$f_{DM} = 0.08592$ (depleted mantle) (Keto & Jacobsen, 1987)

T_{DM} and double stage mixing model values from rocks and biogenic minerals have been used in a variety of studies to answer questions concerning crustal growth and recycling and in determining aspects of sedimentary provenance and source material (e.g. DePaolo, 1981; O'Nions et al., 1983; Allegre & Rousseau, 1984; Miller & O'Nions, 1984; Miller et al., 1986; Keto & Jacobsen, 1987; Thorogood, 1990; Evans, 1992; Leng & Evans, 1994; McCaffrey, 1994). However, it is important to note that T_{DM} or any double stage mixing model value, on its own, does not have any geochronological significance.

It does not point to a direct source for the sediments but rather it represents an average age of all the sedimentary material deposited in a basin, and its integrated geologic history (Michard et al., 1985; McLennan et al., 1990).

2.1.2 Nd Isotopes in the Marine Realm

The Sm-Nd isotopic system has been used to study a variety of earth processes that involve the mantle and the crust. The release of crustal material through orogenic, weathering and erosional processes delivers Sm, Nd and other REEs to freshwater and marine systems. Based upon their short oceanic residence times (10^3 - 10^4 years [Elderfield & Greaves, 1982]) and tight coupling behaviour, Sm and Nd isotopes are useful for studying the geochemical evolution of the oceans (Piepgras et al., 1979; Piepgras & Wasserburg, 1980; Elderfield & Greaves, 1982; Wright, 1990). REE and the Nd isotopic system have been extensively studied in the marine realm in a wide array of applications including: the use of Nd as a water mass tracer (e.g. Piepgras et al., 1979; Piepgras & Wasserburg, 1980, 1982, 1983, 1985, 1987; Groussett et al., 1988; Andersson et al., 1992); the variation of REE signatures in the water column associated with redox gradients and Fe/Mn cycling (e.g. German et al., 1991; Sholkovitz et al., 1992); the incorporation of REEs into ferromanganese nodules (for review see Elderfield et al., 1981); and the use of Nd and REEs in biogenic and authigenic minerals to reconstruct paleoenvironments (e.g. Wright et al., 1984; Wright, 1985; Keto, 1987; Keto & Jacobsen, 1987, 1988; Staudigel et al., 1985).

It is important to note that the major inputs of Sm and Nd are continental in origin coming from riverine systems and from aeolian transported detritus. The $^{143}Nd/^{144}Nd$ values of a drainage basin depend on both the age and the lithology of the basin (Goldstein & Jacobsen, 1987). Hydrothermal input of Nd into the marine system is thought to be insignificant (Piepgras & Wasserburg, 1985; Shaw & Wasserburg, 1985) except in the areas associated with deep-sea hydrothermal springs or mid-ocean ridge systems (Piepgras & Wasserburg, 1980). The variation of $^{143}Nd/^{144}Nd$ and the short residence time for Nd result in each oceanic water mass having a specific $^{143}Nd/^{144}Nd$ or $\varepsilon_{Nd}(0)$ value (O'Nions et al., 1978; Piepgras et al., 1979; Piepgras & Wasserburg, 1980, 1982, 1983, 1987) and this variation can be used to track water masses.

2.1.3 Present Day Oceanographic Studies

The Nd isotopic values for today's oceans are reasonably well known. The Atlantic ocean has the least radiogenic values (~-14 to -9), the Pacific has the most radiogenic values (~-5 to 0) and the Indian Ocean shows an intermediate range (~-11 to

-7) (Piepgras et al., 1979; Piepgras & Wasserburg, 1980, 1982, 1983; Goldstein & O'Nions, 1981; also for review see Bertram & Elderfield, 1993 and references therein). The values for the Atlantic represent input from older continental crust (Piepgras & Wasserburg, 1982; Goldstein et al., 1984) and are equal to the average continental crust values, again indicating that the run-off is dominated by crustal sources (DePaolo, 1988). The signature of the Pacific suggests that input is from younger continental crust and the erosion and transport of the young island arc terranes that flank the Pacific basin. The Indian Ocean, however, is controlled by different factors than simply continental input. Goldstein et al. (1984) report $\varepsilon(0)$ values for the Indus and Ganges Rivers of -16 - -12. a signature that is significantly different from the Indian Ocean itself. Albarède & Goldstein (1992) stated that the signal displayed by the Indian Ocean is imparted from the circum-Antarctic Ocean where mixing of Atlantic and Pacific waters occur and giving a Nd isotopic signal that is the average of the two water masses. It is evident that the Nd isotopic composition of any ocean mass is a function of the source material's Nd isotopic composition and of the physical and biogeochemical processes that can internally modify the terrigenous input signal (Bertram & Elderfield, 1993).

This isotopic system is sensitive enough to pick up different water masses in the same water column. For example, there are at least two distinctive $\varepsilon_{Nd}(0)$ signatures associated with the Atlantic. The least radiogenic values (~-14) are associated with samples taken ≥ 1000 m deep and are associated with North Atlantic Deep Water (Piepgra & Wasserburg, 1983). Additionally, Atlantic waters are influenced by outflow from the Mediterranean that sinks under surface Atlantic waters to a depth of 1000 m. At this depth density equilibrium is reached and the water spreads out laterally (Dietrich et al., 1980). This outflow has a $\varepsilon_{Nd}(0)$ of ≥ -9.8 and is distinguished from the overlying and underlying waters. This inflow modifies the eastern Atlantic waters to a more radiogenic value (Piepgras & Wasserburg, 1983). The source of the more radiogenic values for the Mediterranean could be from input from younger continental crust, isotopically juvenile volcanics or the remobilization of deposited volcanic ash (Piepgras & Wasserburg, 1983).

The sensitivity of this isotopic system to different water masses enables it to monitor oceanic circulation processes. Albarède & Goldstein (1992), using their own data and published values, compiled information on over 270 ferromanganese nodules to construct a present day Nd isotopic oceanographic map. Ferromanganese nodules are enriched with REEs relative to shales and scavenge REEs directly from seawater and not the underlying sediments (Goldberg et al., 1963; Piper, 1974; O'Nions et al., 1978; Piepgras et al., 1979). In an interesting observation, Albarède & Goldstein (1992) noted that this pattern significantly correlates with the present day ocean circulation patterns and the geology of the ocean floor.

2.1.4 Paleoceanographic Studies

Piepgras & Wasserburg (1980), assessing $\varepsilon_{Nd}(0)$ as a tracer in modern oceans, hinted that it may also be applicable for use in testing paleogeographic reconstructions. Albarède & Goldstein (1992) suggested that since Nd is in such small amounts in seawater, ferromanganese nodules, that form over millions of years and are excellent depositories of Nd, can be used to estimate the Nd signatures of ancient water masses over geological time. Fossils composed of apatite are enriched with the light rare earth elements (LREE) and Nd more so than other sedimentary materials and the signatures reflect contemporaneous seawater values at the time of deposition (Wright et al., 1984; Shaw & Wasserburg, 1985; Keto & Jacobsen, 1987). Therefore bioapatite, being mineralogically stable over time, should also provide Nd signatures of ancient oceans and provide information on paleoceanographic conditions. Indeed, in order to recover information about ancient oceans, nodules, fossils, and phosphatic deposits are the only reliable indicators of ancient Nd isotopic signatures (Grandjean et al., 1987). For recent biogenic material, the REE signature is attained after death of the parent animal, becoming incorporated into the lattice (Wright et al., 1984; Shaw & Wasserburg, 1983, 1985). This signature is an isotopic fingerprint of the bottom waters at the time of death.

Wright et al. (1984) analyzed the REE pattern and Nd isotopic composition of early Paleozoic conodonts from the continental United States Their analysis showed similar $\varepsilon_{Nd}(0)$ values for samples that were of similar ages from the western United States. A sample from New York State also had a similar isotopic signature but the systematics were anomalous and suggested that either this area shared waters from both the Proto-Atlantic and the Proto-Pacific, or because of fractionation in the sample, the similarities were a coincidence. With the small sample size (n=3), the latter is more probable.

Shaw & Wasserburg (1985) analyzed the Nd signature in conodont apatite to test its use as a proxy for ancient seawater. The Devonian - Mississippian values from conodonts supported the mixing between the Proto-Pacific Ocean and Proto-Atlantic Ocean which could be tested using paleogeographic reconstructions. Their secular variation curve of Phanerozoic time from both biogenic apatite and phosphorites revealed that the Proto-Pacific and Proto-Atlantic attained distinctive signatures approximately at 200 Ma, likely associated with the breakup of Pangaea

Staudigel et al. (1985) analyzed the REE pattern and Nd isotopic signature of fish teeth to provide a more quantitative approach to testing paleocirculation. They found that although the REE pattern may be affected by diagenesis, the $^{143}Nd/^{144}Nd$ ratios were independent of any diagenetic overprint. Their data also does not support the hypothesis that the isotopic signature is picked up from sediment pore water, rather it supports the proposal by Wright et al. (1984) that the signature is attained from the surrounding water mass. Grandjean et al. (1987) performed a similar study on fish debris and also found that even though the REE abundance patterns between samples were variable the $\varepsilon_{Nd}(0)$ values were consistent.

Keto (1987) and Keto & Jacobsen (1987) analyzed a small collection of Ordovician conodonts for ε_{Nd} to assess the paleoceanography of the Iapetus Ocean (for introduction to the Ordovician oceans see section 2.3.1). They used the known pattern of conodont provincialism to gauge their sampling and found that North American Midcontinent Realm samples had $\varepsilon_{Nd}(T)$ from -16 to -9 and lower, while the North Atlantic Realm had higher, more radiogenic, values. They concluded that up until at least the late Middle Ordovician there were two distinct ocean masses constituting the Iapetus. One had typical Iapetus values of -9 to -5 (associated with Baltica) while the other had Panthalassa values of -20 to -10 (associated with Laurentia). They suggested that a barrier between these waters, such as island terranes or mid-ocean ridge, must have impeded circulation. Plots of their data plus additions from Hooker et al. (1981) and Shaw & Wasserburg (1985) (Figure 2.3) illustrate that the convergence of these isotopically distinct waters coincided with the timing of the Taconic Orogeny in the late Middle Ordovician.

Stille et al. (1989) and Stille & Fischer (1990) used Mn deposits and authigenic glauconite along with icthyolith material to determine the Nd isotopic composition of the Tethys Ocean during the Mesozoic. They related their findings to the depositional environmental parameters and to the tectonic events associated with the breakup of Gondwana. Finally, Whitaker & Kyser (1993) determined the ε_{Nd} values in molluscan shells to assess the changing circulation in Cretaceous Western Interior Seaway through a 20 Ma span. They also considered the roles of volcanic activity, diagenetic flux and tectonic activity on ε_{Nd} distribution in the seaway.

These recent studies illustrate that biogenic minerals give reliable and consistent proxy signals for contemporaneous water masses at the time of deposition, that the Nd signature is picked up from the overlying water masses during burial and early diagenesis and is not a product of some diagenetic overprint, and that Nd isotopic system is an ideal tool to study paleoceanographic water masses.

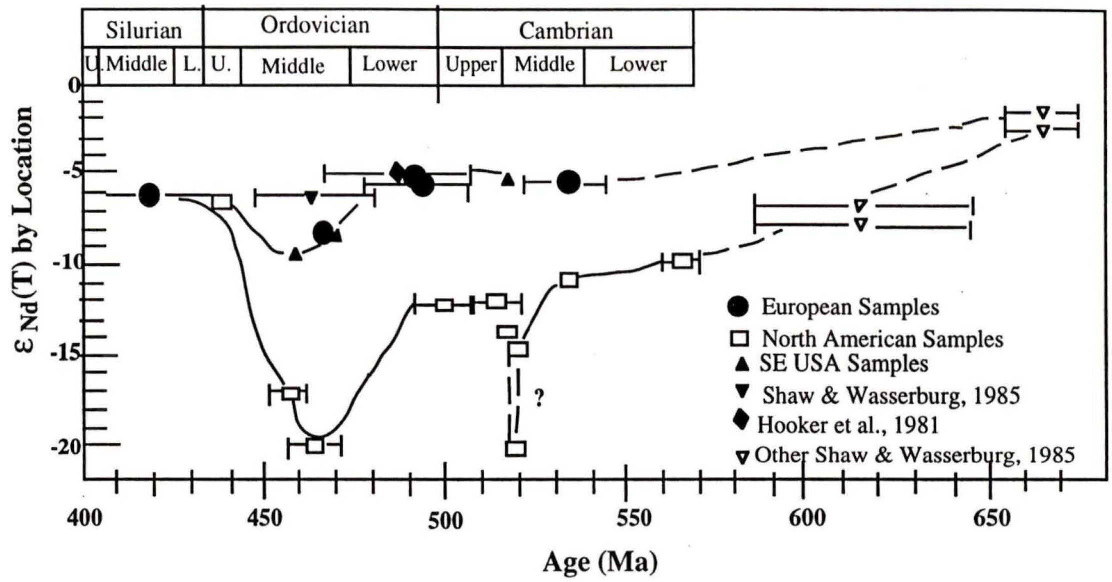


Figure 2.3: Keto & Jacobsen's (1987) Nd isotopic secular variation curve for Phanerozoic time as derived from bioapatite. Time scale is that of Van Eysinga, 1975.

2.2 The Nature of Conodonts and Conodont Geochemistry

2.2.1 The Conodont Animal

Conodonts are microfossils composed of calcium-hydroxy fluorapatite, with a composition comparable to francolite; $Ca_5Na_{0.14}(PO_4)_{3.01}(CO_3)_{0.16}F_{0.73}(H_2O)_{0.85}$ (Pietzner et al., 1968). They are the only hard-tissue evidence of an extinct group of organisms that had a geological range from Cambrian to Triassic with several intervals of rapid speciation. This makes them exceptional for biostratigraphic control, especially in the Ordovician and Silurian when they also have a widespread distribution in marine strata, making them one of the most important groups for global biostratigraphic correlations.

Conodont elements vary morphologically (Figure 2.4) and have an average size range of 0.2 mm to 2 mm long (Briggs, 1992). The elements grew by exterior concentric accretion of apatite lamellae around a central cavity, with layers of organic matter between lamellae. The lamellae are composed of apatite crystallites that have a average thickness of 0.2 μm to 1.2 μm (Barnes et al., 1973a). Additional information on conodont microstructure can be found in Barnes et al. (1972, 1973a), Barskov et al. (1982), Krejsa et al. (1990), Burnett & Hall (1992), and Sansom et al. (1992). Sweet (1988) has provided a review of the biology, ecology, and history of the Conodonta.

The biological affinities of conodonts are still a topic for debate (Aldridge & Briggs, 1986; Aldridge et al., 1986; Sweet, 1988; Krejsa & Slavkin, 1987; Krejsa et al., 1987, 1988, 1990; Sansom et al., 1992; Kemp & Nicoll, 1995a, b). The discovery of soft-bodied impressions of the conodont animal at Granton, Scotland (Briggs et al., 1983; Aldridge et al., 1986) and the subsequent finds elsewhere of other conodont soft-tissue preservation (Mikulic et al., 1985a, b; Smith et al., 1987; Aldridge & Theron, 1993; Gabbott et al., 1995) show a small eel-like organism exhibiting features that can be attributed as chordate (caudal fin rays, notochord, myomeres).

Arguments have been made concerning the presence of homologous structures, neural crest, and comparisons of soft-tissues between conodonts and chordates, and whether these structures confirm a chordate and/or vertebrate affinity (Barskov et al., 1982; Krejsa et al., 1988, 1990; Sansom et al., 1992; Purnell, 1993; Sansom et al., 1994; Kemp & Nicoll, 1995a, b). Although the choices for affinities have substantially narrowed from the number of options in the past (for review see Hass, 1963; Müller, 1981; Aldridge, 1987), a complete consensus on the phylogenetic status of conodonts has not been reached. Most workers place them within the Vertebrata (Barskov et al., 1982; Aldridge et al., 1986; Briggs, 1992; Sansom et al., 1992; Aldridge et al., 1993a; Purnell, 1993) and either in the class Conodonta (Aldridge & Smith, 1993) or in the Craniata (Aldridge et al., 1986; Krejsa & Skavkin, 1987; Krejsa et al., 1987, 1988, 1990; Briggs, 1992; Aldridge & Theron, 1993). Recent work by Gabbott et al. (1995) on preserved muscle tissue suggests that conodonts are crownwards of, or are more evolutionarily advanced than the myxinoids based upon the preservation of extrinsic eye muscle and comparative degrees of cephalization. Although there are some questions concerning their position within the subphylum Vertebrata, their position within the phylum Chordata has generally been accepted (for review see Janvier, 1995 commentary).

2.2.2 The History of Conodont Geochemistry

In the last two decades, conodonts have been used for various geochemical investigations. As noted previously, they provide excellent biostratigraphic correlations and have widespread distribution in marine rocks of Cambrian to Triassic age. These two factors make them ideal for studies involving global bioevents and the correlation, evolution and tectonics of sedimentary basins. Epstein et al. (1977) established the conodont colour alteration index (CAI) with many applications including the thermal history of basins. The index represents systematic changes in the colour of the conodont elements with increasing temperature, overburden and time. The original index was expanded by Rejebian et al. (1987) and has broad applications to the study of sedimentary

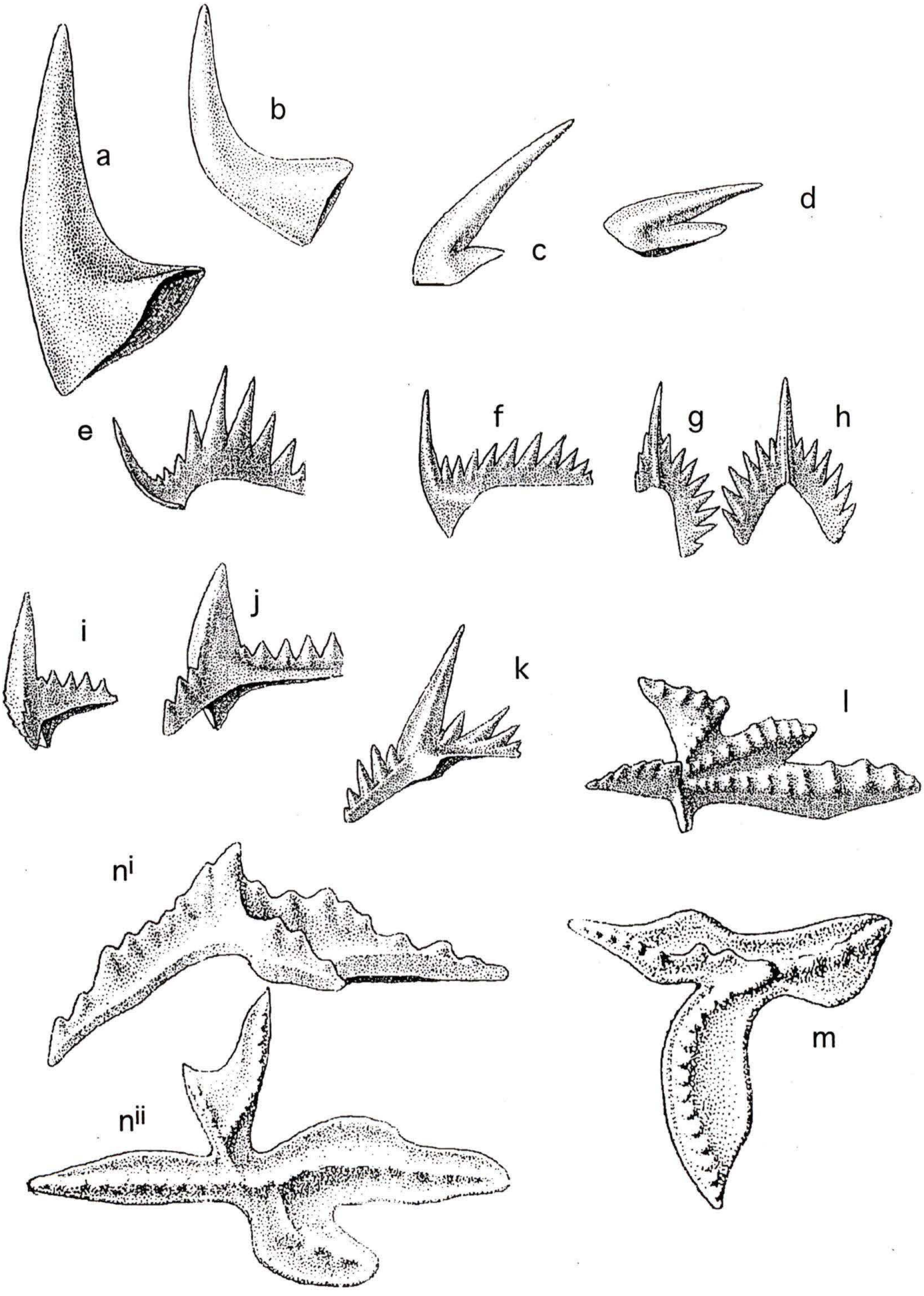


Figure 2.4: Morphological variation in conodont elements. a-d: coniform elements in lateral view. e-h: ramiform elements; e and f in lateral view; g and h in posterior view. i-n: pectiniform elements; i, j, k, and n^i are in lateral view; l, m, n^{ii} are in upper view. All drawings taken from Dzik et al., 1994.

basin tectonics and mineral and hydrocarbon exploration (Harris et al., 1978; Legall et al., 1981; Nicoll & Gorter, 1984a, b; Nowlan & Barnes, 1987). Other investigations have employed conodont apatite to establish absolute age dating via U-Th-Pb mass spectrometric isotope dilution (Kovach & Zartman, 1981; Tucker et al., 1990), fission track (Sachs et al., 1980), and SHRIMP (Compston & Williams, 1992) techniques.

Several studies have shown that conodonts exhibit a primary isotopic signature (e.g. Sr, O, Nd) that is representative of the signature of seawater, contemporaneous with the time of deposition (Shaw & Wasserburg, 1985; Wright, 1985; Wright et al., 1987; Grandjean-Lecuyer et al., 1993). Modern biogenic apatite will scavenge trace elements and isotopes in higher concentrations than seawater but in similar proportions (Wright et al., 1984). A pure apatite unit cell has two calcium ion sites, Ca1 and Ca2, with 4 and 6 calcium ions respectively, that will accept cation substitution (Eanes, 1973). Le Geros (1981) studied the substitution of various ions into the lattice of apatite and found that ions with ionic radii greater than calcium will substitute for calcium ions preferentially over those ions with smaller ionic radii. Examples of those with larger radii are strontium, the lanthanides and the actinides. Wright (1989) gave an account of the two stage substitution of cations for calcium based on adsorption and diffusive models. Since incorporation occurs during early post-mortem processes, the various chemical elements and isotopes in seawater will equilibrate with the conodont apatite and carry the environmental conditions of the seawater into the lattice. Once incorporated, the product is a trace element-enriched apatite that is exceptionally stable against further diagenetic processes (Wright, 1990).

Previous studies that using conodont isotopic signatures as a proxy signature for ancient seawater include: strontium secular variation (Kovach, 1981; Burke et al., 1982; Kürschner et al., 1992), $\delta^{18}O$ and paleoseawater temperatures (Luz et al., 1984; Geitgey & Carr, 1987), rare earth elemental patterns (Wright, 1985; Wright et al., 1987; Grandjean-Lecuyer et al., 1993), cerium anomalies (Wright, 1985; Wright et al., 1987), chemostratigraphy (Wright, 1985; Wright et al., 1987), and Nd isotopic composition (Kovach, 1983; Shaw & Wasserburg, 1985; Keto, 1987; Keto & Jacobsen, 1987, 1988; Bertram et al., 1993). Wright (1985) and Wright et al. (1987) showed that the incorporation of rare earth elements into biogenic apatite is approximately one weight percent at the sediment/water interface and that all biogenic apatites are enriched in the light rare earth to medium rare earth range. Sm and Nd in the seven to nine fold configuration have an ionic radius similar to that of calcium, hence these ions will actively incorporate into the apatite, giving conodont REEs a characteristic dome-shaped pattern (Wright et al., 1984, 1987). These studies also showed that conodonts have the highest concentrations of Sm and Nd of all biogenic apatites.

Kovach (1983), Shaw & Wasserburg (1985), Keto (1987), and Keto & Jacobsen (1987, 1988) used the Sm-Nd isotopic system to study conodonts and other phosphates as ancient seawater tracers. Their studies proved that conodonts carry a Nd isotopic signature that is undisturbed and accurately traces ancient seawater masses. Although Keto's (1987) thesis was the cornerstone study that established the potential of conodonts as a proxy for tracing ancient ocean masses, important investigations for the preliminary work include Wright et al. (1984) and Wright (1985). Shaw & Wasserburg (1985) should also be given significant credit because they found that conodonts from the same rock sample showed varying concentrations of Sm and Nd, but that this did not significantly affect their isotopic signatures. They determined that conodont Nd isotopic geochemistry could be used to test the presence or absence of individual ocean masses, as a tracer of the evolution of a seawater mass and to test models of paleogeography, paleobiogeography, and paleoceanography. Keto (1987) and Keto & Jacobsen (1987, 1988) used this information to test global paleogeographic reconstructions and to study the evolution, growth and destruction of various ocean and land masses.

2.3 The Ordovician and Early Silurian Interval

2.3.1 Paleogeography

There are several paleogeographic models that reconstruct the position of the continents and ocean masses for the Ordovician and Early Silurian, either on a global or regional basis (e.g. Keppie, 1977; Cocks & Fortey, 1982; Paris & Robardet, 1990; Scotese & McKerrow, 1990, 1991; Perroud et al., 1992; Torsvik et al., 1992; Trench et al., 1992; Li et al., 1993; Dalziel et al., 1994; Astini et al., 1995; Torsvik et al., 1995). These models rely heavily on data provided by paleomagnetism, biogeography, and sedimentary facies distribution (Scotese & McKerrow, 1990, 1991). One of the main objectives of this thesis is to test paleogeographic reconstructions on a global scale. It is imperative that samples of conodonts for Nd analysis be chosen, where possible, from most of the major cratons and microplates that would have existed and contributed erosional material into the oceans. To properly gauge the choice of samples, a principal model was chosen, that of Scotese & McKerrow (1991). To date, it is the most widely accepted model comprising a global reconstruction based on paleomagnetic, paleoclimatic, faunal biogeographic, and tectonic data. It is an updated version of their extensively cited 1990 model and has a +15% uncertainty in latitude for major land masses and a +30% uncertainty in longitude (Scotese & McKerrow, 1991). The major differences between the 1990 and 1991 model are in the positioning of some peri-Gondwana land masses, North and South China, and the addition of predicted subduction zones.

According to this model, the major oceans surrounding the land masses during the Ordovician - Early Silurian were the Panthalassa, the Iapetus, and the Paleotethys. The major cratons at the time were Laurentia (North American craton, Greenland, Arctic Canada, Northern Scotland), Gondwana (South America, Africa, Australia, New Zealand, East Antarctica, South-Central Europe, North and South China, plus other suspect terranes of the Middle East), Baltica (Balto-Scandia, East Russian Platform), Siberia, and Kazakhstan (Figure 2.5).

The Panthalassic was the largest ocean, analogous to today's Pacific. It covered the northern hemisphere and encircled the aggregation of land, reaching from the eastern margin of Gondwana to the western margin of Laurentia. The Iapetus Ocean separated Laurentia from Baltica and Siberia to the east and Avalonia and Gondwana in the south. It opened in the Neoproterozoic (~750 Ma) when Baltica and possibly South America rifted away from eastern Laurentia (Williams & Hiscott, 1987; Hoffman, 1991; Dalziel, 1991, 1992; Soper, 1994) and began to close as subduction zones developed off the eastern Appalachian region. Additionally, Avalonia rifted and moved northwards towards Baltica, until both collided with Laurentia during the Acadian Orogeny beginning in the Late Silurian (Scotese & McKerrow, 1990; Soper et al., 1992; Trench & Torsvik, 1992). The Paleotethys Ocean in this model separates Kazakhstan and Baltica from the 'inner' eastern margins of Gondwana (Australia, China microplates, Middle East and European terranes).

An additional body of water is the Tornquist Sea that separated Gondwana (north African margin and the Avalon terranes) from Baltica (Cocks & Fortey, 1982, 1990; Vannier et al., 1989; Fortey & Mellish, 1992;). Also mentioned in other reconstructions is the Rheic Ocean that opened between Avalonia and the north African margin of Gondwana during the rifting of Avalonia. However, there is no faunal evidence to suggest the presence of such a distinct water mass until the late Early Silurian (Cocks & Fortey, 1982; Fortey & Cocks, 1992).

Paleopoles for Laurentia are well constrained (Van der Voo, 1988) and show Laurentia as straddling the equator and slowly rotating counterclockwise during the Ordovician to early Silurian (Scotese & McKerrow, 1991). This model placed Baltica in a high southerly latitude during the Early Ordovician and moving to more equatorial position, likely rotating counterclockwise, by the end of the Period. This is supported by paleomagnetic data and the reconstructions of Torvisk et al. (1990), Perroud et al. (1992), Trench & Torsvik (1992) and Torsvik et al. (1992). Data from Africa, Australia, South America and Antarctica indicate that Gondwana was situated over the South Pole with some of its margins extending into equatorial regions. The Scotese & McKerrow (1991) reconstructions showed both Siberia and Kazakhstan as stable continents with both in equatorial positions as neighbors to Laurentia and Baltica, and moving to more northerly positions. However, Kazakhstan may be an extension of Siberia (Scotese & McKerrow, 1990) or be an amalgamation of accreted terranes that sutured in the Devonian (Apollonov, 1991, 1995; Scotese & McKerrow, 1991). Siberia had terranes accreted to its margin which are not accounted for in this reconstruction.

Figure 2.5: Paleogeographic location of the cratons, microplates, and oceans as reconstructed by Scotese & McKerrow, 1991. Only the those continental blocks mentioned in the text are labeled.Abbreviations: af=Africa; aus=Australia; eng=England; Kaz=Kazakhstan, ne=New England & Maritime Canada ; sa=SouthAmerica; sce=south-central Europe; sc=South China; tr=Turkey.

In addition to the major cratonic land masses, there were also a series of displaced peri-Gondwana terranes that included Avalonia, Meguma, Armorica and Bohemia (sensu Van der Voo, 1988). Other than Avalonia, these terranes are not well constrained. The position of Avalonia (Ardennes of Belgium, northern France, Avalon Peninsula of Newfoundland, southeast Ireland, part of Nova Scotia, southern New Brunswick, southern England, Wales, and parts of northeast United States) during the Early Ordovician is well known and was situated off the north African margin of Gondwana in a high southerly latitude (Johnson & Van der Voo, 1985, 1986; Van der Voo, 1988;

Scotese & McKerrow, 1990, 1991; Channell et al., 1992). At some time in the Arenig (Torsvik & Trench, 1991), Avalonia broke away from Gondwana and drifted north until it collided with Baltica and Laurentia (see discussion on the Iapetus Ocean above; see section 2.4 and Figure 2.8 for Lower Paleozoic chronostratigraphic subdivisions). The timing and placement of docking is difficult to establish (for review see Soper et al., 1992; Trench & Torsvik, 1992). Many studies have the microplate docking with Baltica in the Late Ordovician and then subsequently both colliding with Laurentia in the late Silurian (Scotese & McKerrow, 1990, 1991). Other models suggest that Avalonia had separate east and west portions with different docking times and locations (Soper & Woodcock, 1990; Soper et al., 1992) although there is no direct evidence to support the idea that Avalonia consisted of discrete east and west fragments (Cocks & McKerrow, 1993). Faunally, it is known that Avalonia shows increased affinities with Baltica during the late Middle - Late Ordovician and then subsequently increasing similarities with Laurentia (Cocks & Fortey, 1992).

Another major displaced terrane is the Armorican massif of Van der Voo's (1988) Cadomia. It was situated on the northern margin of Africa but its composition is problematic and is commonly viewed as a loose agglomeration of terranes including France, Spain, and portions of the British Isles (for review see Van der Voo, 1988). Paleomagnetic results indicated that for the Early Ordovician the microplate was at high paleolatitudes (Perroud & Bonhommett, 1981; Perroud et al., 1986; Tait et al., 1994a, b). The positioning of Armorica is not well established especially in the Late Ordovician (Tait et al., 1994a, b) but Perroud et al. (1984) suggested it was separated from Gondwana with a widened seaway extension of the Paleotethys. Timing of the separation of Armorica is not constrained although Noblet & Lefort (1990) suggest that separation did not occur until well after the Arenig.

Armorica has a loose definition in the literature and Van der Voo (1988) defined it as a loose mosaic of elements, from 70°S to 40°S including France, Spain, Germany (Thuringia) and southern Britain, and also Avalonia. For the purposes of this study, the Armorica microplate is defined to include Spain, Italy, Germany and Turkey. On the Scotese & McKerrow (1991) maps, Turkey is adjacent to south-central Europe and due to this juxtaposition in the southern Paleotethys, it will be included as an element in the microplate.

The primary use herein of the Scotese & McKerrow (1991) model, however, does not preclude other models from being tested. Most paleogeographic models to date have been broadly similar, but another model differs considerably in the positioning of Gondwana in relation to Laurentia (Dalla Salda et al., 1992a, b; Dalziel et al., 1994). The rotation of Gondwana is significantly different and this model proposed that Laurentia had broken out of the Proterozoic supercontinent of Rodinia by the Early Cambrian (Hoffman, 1991; Dalziel, 1991) and during the middle Ordovician collided with the Argentine margin of South America (Figure 2.6). Several lines of evidence for this model

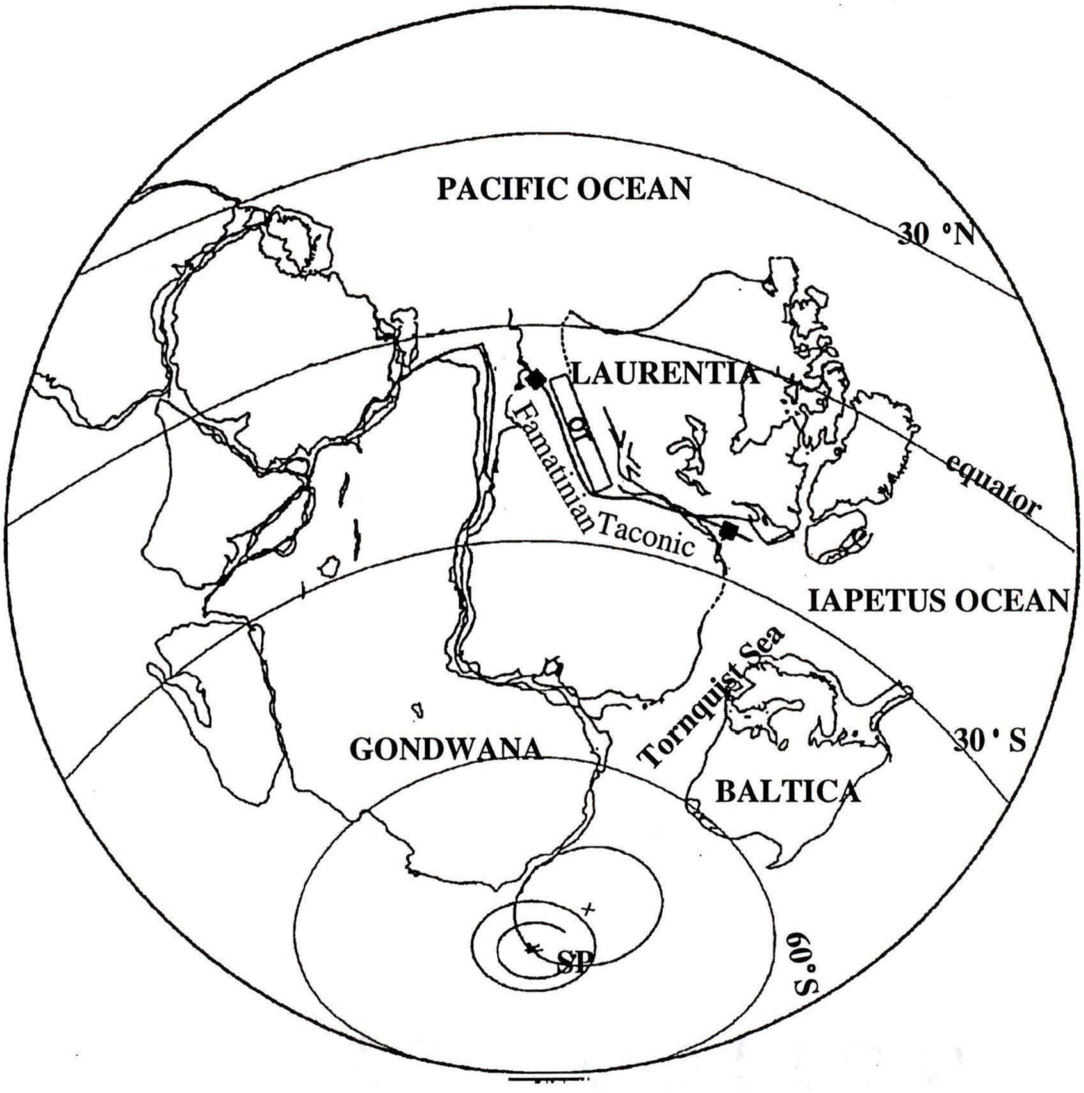


Figure 2.6: Paleogeographic reconstruction of Dalziel et al. (1994) during the middle Ordovician (~450 Ma).

include faunal similarities and carbonate platform correlations of eastern Laurentia and the Precordillera of Argentina. Astini et al. (1995) offered an alternative explanation for the similarities between the Precordillera and eastern Laurentia rather than invoking a continent-continent collision. They suggested that the Precordillera terrane, possibly derived from the southeastern Laurentian Ouachita area, originated by rifting from

Laurentia in the Late Proterozoic - Early Cambrian and drifting across the Iapetus Ocean until collision with the Famatina margin in the Middle Ordovician (~460 Ma). The accretion of the terrane and eastward subduction is considered to have coincided with the development of the Famatina volcanic arc.

A third paleogeographic model that differs slightly from the others is Paris & Robardet's (1990) reconstruction of the Mediterranean region which affects the location of the Avalonia microplate and the distribution of adjacent ocean masses (Figure 2.7).

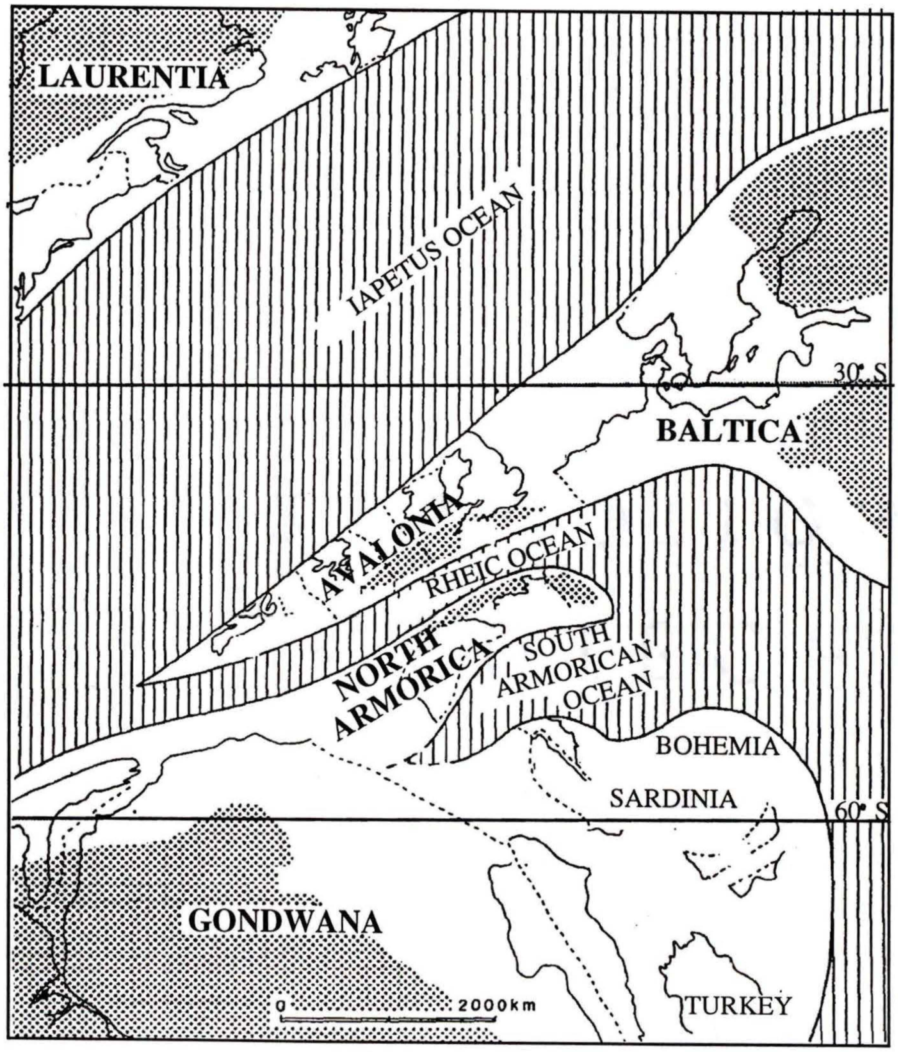


Figure 2.7: Early Ordovician paleogeographic reconstruction of Paris & Robardet (1990)

Rather than having Avalonia as a peri-Gondwana terrane, as in other models, they suggest that it was part of Baltica and was separated from the Armorica microplate by the Rheic Ocean. However, Paris & Robardet (1990) relied on the faunal distributions of planktonic organisms which Fortey & Cocks (1992) and Fortey & Mellish (1992) argue are not sufficiently sensitive for deducing paleogeography and further that the distribution of other benthic faunal groups does not support such a reconstruction.

The pattern of Nd isotopes from conodonts can not provide direct evidence for paleogeographic positioning by delineating paleolatitude or paleolongitude, but it can identify separate major water (ocean) masses and thereby indicates the relative juxtaposition of cratons and microplates and their changing positions through time.

2.3.2 Biogeography and Conodont Faunal Provincialism

The early Paleozoic was a pivotal time for biological change when the Cambrian Fauna, dominated by trilobites, inarticulate brachiopods, archeocyathids, was replaced by the more diverse Paleozoic Fauna (e.g. articulate brachiopods, graptolites, cephalopods) during the early Middle Ordovician (Sepkoski, 1981). It was a time of large scale continental/cratonic separation, the formation of distinct oceans, diversification of faunas, and strong faunal provincialism.

Conodonts showed maximum provinciality during the Ordovician, more so than at any other time in the geological record (Charpentier, 1984). However, global models of conodont provincialism have been hindered by several factors. The paucity of sampling because of the lack of carbonates in high latitude areas has hindered regional comparisons with the well sampled areas such as Laurentia and Baltica (Barnes et al., 1973b; Bergström, 1973; Lindström, 1976). Different taxonomic interpretations and the changeover from form element taxonomy to multielement taxonomy created some early discrepancies in the database (Barnes et al., 1973b; Bergström, 1973; Barnes & Fåhræus, 1975). As well, there is considerable variation in the literature on the definition of a province, either as a region of endemism that is constrained by the presence or absence of taxa, or as a statistical entity (Rosen, 1988). Commonly, the term province and realm are used interchangeably and also when defining geographic differences in the distribution of faunas, rather than strictly being concerned with endemism (Rosen, 1988).

The conceptual aspects of conodont provincialism are covered by Pohler & Barnes (1990) who suggested that the hierarchy of realm, province and community is the logical way to address aspects of paleoecology. Following the definitions of Valentine (1968, 1973), Pohler & Barnes (1990) defined a conodont community, the basic unit in the hierarchy, as an assemblage of conodont populations that exist within a geographical area with certain species or genera dominating. A province was defined as an assemblage of communities in a geographical area that is taxonomically more complex than a community. During some intervals of the Ordovician, subprovinces may be distinguished

(Barnes et al., 1973b; Barnes & Fåhræus, 1975). Pohler & Barnes (1990) delineated conodont provinces using barriers to migration such as climate, physiogeographic or oceanographic conditions. A realm, the largest biogeographic unit in this hierarchy, is an assemblage of conodont provinces and is delineated by some large scale ecological barrier (e.g. oceanic clines).

Although conodont provincial models are biased to present day northern hemisphere sampling, two major realms, illustrated in Figure 2.8, are easily distinguished; the Midcontinent Realm that includes most parts of North America, Siberia, Australia, North China and Korea, and the North Atlantic Realm (the European Province of Barnes et al., 1973) that includes most of Europe, the Appalachian Orogen of North America, South China and some portions of Australia (Sweet et al., 1959; Sweet & Bergström, 1962, 1974; Bergström, 1971, 1973b, 1990; Barnes et al., 1973; Pohler & Barnes, 1990).

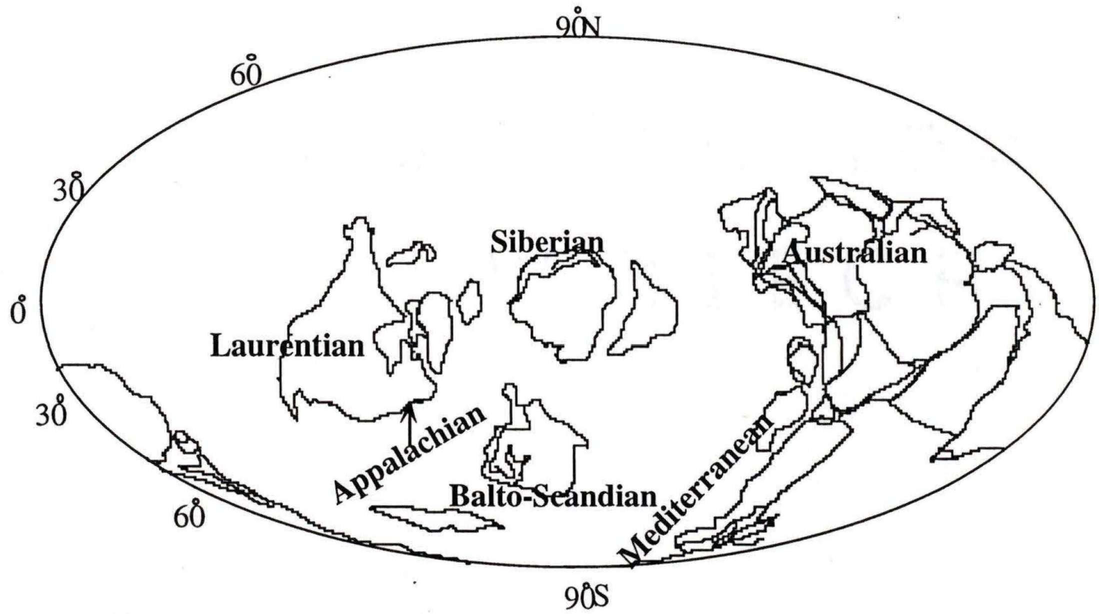


Figure 2.8: Paleogeographic positioning of the major conodont provinces. The map reconstruction is that of the Arenig from Scotese & McKerrow, 1991.

During the Cambrian and the early Tremadoc, most conodont faunas were relatively cosmopolitan, having a wide distribution and consisting of mostly cordylodids and simple cones (Barnes et al., 1970; Barnes et al., 1973b; Bergström, 1973; Miller, 1984). By the late Tremadoc-Arenig, provincialism increased in groups such as conodonts (Sweet, et al., 1959; Sweet & Bergström, 1962; Bergström & Sweet, 1966; Barnes et al., 1973b; Bergström, 1990), trilobites (Whittington & Hughes, 1972, 1973;

Whittington, 1973; Cocks & Fortey, 1990), graptolites (Skevington, 1974, 1976; Berry & Wilde, 1990) and brachiopods (Williams, 1973).

The Midcontinent Realm was developed on shallow water cratons within tropical - subtropical climate belts (Sweet & Bergström, 1974) and consisted of several provinces: the Laurentian (North America), the Siberian (Siberian platform) and the Australian provinces (Australian Gondwana). The North Atlantic Realm was developed in a cooler water environment (Sweet & Bergström, 1974) and consists of the Balto-Scandian Province, the Appalachian Province (Pohler & Barnes, 1990), and the Mediterranean Province (Gutiérrez Marco & Rábano, 1987). It has been suggested that the Midcontinent Realm represents a region of heightened endemism as a result of increased temperature and salinity due to low latitudinal position while the North Atlantic Realm is composed of more cosmopolitan faunas that are widely dispersed both latitudinally and longitudinally (Barnes & Fåhræus, 1975).

In the Early Ordovician, Balto-Scandian conodonts were quite distinct from those of cratonic Laurentia but showed many similarities with faunas from the eastern Appalachians (Bergström, 1990) Similarities between Siberian and Laurentian conodonts were few, likewise between Siberia and Baltica, justifying a separate province status for Siberia (Bergström, 1990) In the Early - Middle Ordovician, Baltica remained distinct from Laurentia, but the Appalachian Province had similarities with both. There are some faunal similarities between Siberia and North America, but these are mostly at the generic level (Bergström, 1990). There are excursions of the North Atlantic fauna into the Midcontinent Realm during certain times in the Ordovician (Sweet et al., 1971; Barnes et al., 1973b; Barnes, 1974). During the middle to late Ordovician there is increasing faunal similarity between Laurentia and Baltica but the provinces still remain distinct, and the southern polar portions of Gondwana represented by the Mediterranean Province fauna (Gutiérrez Marco & Rábano, 1987; Bergström, 1990; Bergström & Massa, 1992) also remained distinct. This latter province suffers from a sampling bias due to the paucity of carbonates and is not yet fully delineated. The glaciation during the Ashgill directly affected the biota by reducing the available living space and changing the thermal regime (Brenchley, 1984; Barnes, 1986; Barnes & Bergström, 1988; Bergström, 1990). Siberian conodonts are still distinct from Laurentia during the Late Ordovician as is the Mediterranean Province. However, there are increasing faunal interactions between Baltica and South-Central China (Bergström, 1990). Early Silurian conodonts (e.g. Panderodus, Ozarkodina, Oulodus) are cosmopolitan by comparison (Pohler & Barnes, 1990).

Controls on provincialism were not due to water depth or lithofacies (Barnes et al., 1973b; Cocks & Fortey, 1990). McKerrow & Cocks (1986) stated that there are two factors that control provinciality: climate and barriers to migration. The effect of temperature and its control of faunal distributions has been invoked as the main reason for provinciality not only in conodonts (Barnes et al., 1973b; Bergström, 1973; Barnes & Fåhræus, 1975) but also in trilobites (Whittington & Hughes, 1972, 1973) and graptolites (Skevington, 1976). The Midcontinent Realm is characterized by significantly warmer water faunas. This is supported by paleomagnetic data that indicates the cratons of Laurentia, Siberia and Australian Gondwana straddling the equator (Van der Voo, 1988; Scotese & McKerrow, 1990, 1991). The North Atlantic Realm consists of cooler water faunas and supports the paleomagnetic data and the relative reconstructions that place peri-Gondwana terranes and Baltica in more temperate and polar regions (Scotese & McKerrow, 1990, 1991). The increasing faunal similarity between Laurentia and Baltica during the Middle to Late Ordovician may be tectonically influenced, with the movement of Baltica into more equatorial latitudes (Torvisk et al., 1990; Perroud et al., 1990; Trench & Torvisk, 1992; Torvisk et al., 1992), and also with the narrowing of the Iapetus Ocean in response to the Taconic Orogeny (Cocks & Fortey, 1982). This narrowing would have allowed for easier dispersal of pelagic and nektobenthic organisms and their larvae between the waters of the two provinces.

An organisms mode of life may be a third factor in the development of provincialism. For example, free swimming adults may have a greater dispersal capability than those organisms which are benthic or sessile, even though these organism may have wide larval dispersal. There still remain questions concerning the habit of the conodont animal. It is thought that although some species may have been pelagic (Seddon & Sweet, 1971, Chamberlain & Clark, 1973; Druce, 1973), others may have been nektobenthic and benthic (Barnes et al., 1973b; Barnes & Fåhræus, 1975; Fortey & Barnes, 1977). Also organisms that live in the upper portions of the water column are affected by latitudinal temperature differences more so than those organisms that live in deep-water since temperature at depth is usually constant (Cocks & Fortey, 1990; Fortey & Cocks, 1992). Indeed, in conodonts, deep-water forms are considered to be cosmopolitan, showing no degree of endemism (Bergström, 1990).

The extent to which an organism is endemic or cosmopolitan is a function of physiological tolerances to abiotic conditions. How a species is distributed is related to its mode of reproduction, biological competition, and life history strategy. Physically, its distribution is also controlled by the water mass it inhabits, and how that water mass circulates. Since Nd isotopic signatures can be used to trace individual paleocean water masses, and to some degree, their circulation and interaction, then this isotopic system can be used to track the evolution of provincialism in organisms such as conodonts, trilobites and graptolites, through the Ordovician to Early Silurian interval by understanding the degree of interaction between relevant water masses.

2.3.3 Paleoclimatology and Paleoceanography

Reconstruction of paleoclimatic conditions, or processes involving paleoceanography, is a daunting task that requires several assumptions concerning past abiotic and biotic conditions. Further back in time, it becomes increasingly difficult to model environmental conditions due to the lack of necessary information and simplification of complex processes (Crowley & North, 1991). The early Paleozoic is especially problematic, with only limited proxy data on variations in temperature, CO_2 and O_2. Climate is complex, controlled by interactions between the atmosphere, hydrosphere, cryosphere and lithosphere and although this study is focused more on testing models of paleoceanography it is intrinsically linked to climate.

Paleoclimates During the Ordovician - Early Silurian

The climate during the Ordovician and early Silurian is considered to have been warm and predominantly in a greenhouse state (Spjeldnaes, 1961, 1981; Frakes, et al., 1992) with a change to glacial conditions during the late Ordovician (Hambrey, 1985; Wilde, 1991; Frakes et al., 1992). Some theories suggest that the changeover to icehouse conditions was rapid and existed only for a short interval in the Ashgill during an otherwise greenhouse state (Hambrey, 1985; Fischer, 1981; Brenchley et al., 1994, 1995). There is some evidence, however, in the form of glacial deposits, that suggest that icehouse conditions were initiated in the late Caradoc and did not revert back until the early Llandovery (Hambrey, 1985; Frakes et al., 1992).

The evidence for greenhouse conditions in the Tremadoc - Arenig is based largely on lithological data. The Early Ordovician shows extensive carbonate deposits with evaporites, a gauge of arid conditions, being rare until the Llandeilo (Frakes et al., 1992). The change from warm to cold climate likely began in the Caradoc (Frakes et al, 1992) and may be affected by extensive volcanism and superplume activity that may have enhanced greenhouse conditions (Barnes et al., in press). The mid-Caradoc was also a time of maximum transgression with the flooding of stable cratons and widespread deposition of carbonates (Barnes et al., in press). Crowley & North (1991) state that there is a proportional relationship between sea-level and CO_2. If this relationship holds, then the mid-Caradoc was also likely a time of high atmospheric CO_2 and warm temperatures.

However, even by early Caradoc times minor glacial deposits were located from 50°C - 70°C latitude (Frakes et al., 1992).

The glaciation, indicated by the distribution of tillites, glacial marine sediments, various other glacial features, and eustatic change, reached a maximum in the late Ashgill, Hirnantian Stage (Brenchley et al., 1994; Frakes et al., 1992). Icehouse conditions are periods of eustatic regression and sea-level during the late Ashgill is one of the lowest in the Phanerozoic (Brenchley et al., 1994). Ice sheets were extensive over the south pole, covering most of polar Gondwana and affecting the peri-Gondwana terranes. Hambrey (1985) estimated that in North Africa a major portion of the ice sheet would have covered 6 - 8 x 10^6 km^2. Glacial lithologic indicators are also found in South Africa and southern Europe, indicating extension of the ice sheets into temperate latitudes (Frakes et al., 1992). Stratigraphic and paleontological evidence suggests that there were between two and four major glacial phases (Barnes, 1986, 1988; Brenchley et al., 1995). Although some glacial deposits were still present in the early Silurian, their distribution was minimal by the mid-Llandovery suggesting that the reversal back to a greenhouse state was initiated by the early Llandovery. During this time, sea-level increased markedly together with carbonate deposition. Greenhouse conditions prevailed until the early-mid Carboniferous (Frakes et al., 1992).

There are few quantitative estimates of temperature for this time. Those derived from $\delta^{18}O$ measurements , generally based on carbonates or biogenic minerals, suggest that low latitude temperatures were greater than 30°C (Luz et al., 1984). By the Late Ordovician, the record shows an increase in $\delta^{18}O$ values suggesting cooling associated with icehouse conditions (Luz et al., 1984; Marshall & Middleton, 1990; Middleton et al., 1991; Wadleigh & Veizer, 1992).

A critical component of climate is the concentration of atmospheric greenhouse gases, particularly CO_2. The CO_2 cycle in the atmosphere is exceptionally complex involving transport between various reservoirs and sinks (for review see Berner, 1991, 1994). Physically, CO_2 is removed from the atmosphere primarily by the weathering of calcium and magnesium silicates (Berner, 1991, 1993a, b, 1994). Walker et al. (1981) stated that over geological time at a scale of greater than 1 Ma, crustal weathering balances the CO_2 that is degassed from various sources. As CO_2 increases in the atmosphere, both the temperature the rate of silicate weathering increases. This process consumes and buries CO_2 resulting in decreasing concentrations in the atmosphere and subsequently, lower temperatures. This negative feedback continues even during times of high sea-level stand, as during the Caradoc, when although silicate weathering was reduced due to the complete flooding of some cratons, CO_2 is buried through the deposition of carbonates. This negative feedback would stabilize climate. Kuhn et al. (1989) suggested that over geologic time, mean global temperatures could not have deviated by more than 15° C. Therefore, the general trend is that temperature over time has remained relatively stable.

Berner (1991, 1994) concluded that the early Paleozoic atmospheric CO_2 was much higher than in today's interglacial climate and could have been greater than 20 times the present day CO_2 levels, while Wilde et al. (1991), using data from Budyko et al. (1987), suggested that it was as much as five times higher than modern day values. Crowley & North (1991) posed an interesting question as to how a large polar glaciation, such as the Late Ordovician event, could occur with elevated CO_2. Brenchley et al. (1994) speculated that glaciation during the Ashgill could have occurred during greenhouse conditions due to changes in the positioning of Gondwana. As it rotated over the pole, its position could have promoted the retention of snow, ice and sea ice. This would have resulted in downwelling of saline-rich ocean water around the polar regions, invigorating circulation. Upwelling nutrient rich bottom waters could have increased productivity leading to a draw-down of CO_2 and lower temperatures. This idea is supported by abruptly increasing $\delta^{13}C$ values during the late Ashgill (for review see Brenchley et al., 1994, 1995).

Since climate, CO_2, and weathering are interconnected, a feedback cycle is an important process when considering inputs of erosional material into the ocean system. This material, whether it be aeolian or fluvial transport, carries with it the REE patterns, Nd and Sm values of the erosional basin. Although Nd isotopic signatures alone can not determine rates of weathering, they can indicate the sedimentary provenance(s) from which material is derived. The data from this study will elucidate the effects that eustasy has on $\varepsilon_{Nd}(T)$ trends. For example, it can be predicted that during periods of low sea-level, the water masses, based on $\varepsilon_{Nd}(T)$ values, will appear as more distinct entities due to reduced interactive circulation and more isolated ocean barriers. However for periods of high sea-level stand, the opposite effect can be predicted where the open ocean masses will more readily interact with shelf and inland sea environments. This will possibly lead to a greater homogenization or blending of the isotopic signatures from various terrane sources.

Paleoceanography During the Ordovician- Early Silurian

This study uses neodymium isotopes as a paleotracer of ancient water masses that can be used to test models of paleoceanographic circulation. Patterns of ocean circulation are a function of two main factors: geography and climate. Geographic land masses and oceanic ridges present barriers to circulation, both surface and deep, and provide potential regions for upwelling. In the paleogeographic maps developed for the Ordovician and early Silurian (e.g. Scotese & McKerrow, 1991) the paleolatitude for the major cratons is reasonably well known. Using these paleogeographic reconstructions, zonal and meridianal barriers between ocean masses can be postulated.

Climate is by far the most important of the two factors. Principal factors for ocean circulation include wind stress (on sea surface), heat flux, and the flux of fresh-water, all of which are difficult to quantify for past geological times. Wind stress is the major contributor to surface ocean circulation and it also modifies sea surface temperatures by mixing surface waters. The flux of fresh-water is a particularly important contributor to deep ocean circulation as salinity increases the density of a water mass and causes water mass subduction. The final major factor is heat flux. Since heat is unevenly distributed between the poles and the equator the transfer of heat also contributes to the overall pattern of surface circulation. It has an important effect on deep circulation since cold water is more dense and sinks under warmer waters. Temperature affects the flux of salinity by either increasing evaporation in warm equatorial waters or by tying up fresh-water as ice at the poles. This interaction between salinity, temperature and density is responsible for today's thermohaline deep water circulation.

It is difficult to quantify the effect of climate on ocean circulation over geologic time. Wind stress and heat flux are not preserved in the geologic record and changes in fresh-water are only indirectly available in the form of lithologic deposits that gauge precipitation and evaporation such as evaporites and tillites. Yet, even with considerable limitations, models of ocean circulation in the Ordovician and Silurian have been attempted for the last two decades. Ross (1975) was among one of the first to model ocean circulation. He invoked a series of oceanic gyres and their relationships to the surrounding land masses to account for faunal distributions. Other models followed, some based on faunal distributions (e.g. Bergström, 1990) while others relied heavily on certain physical assumptions to explain possible patterns of circulation (e.g. Wilde, 1991). Many workers (e.g. Finney & Chen, 1990) simply plotted today's patterns of surface circulation onto early Paleozoic paleogeographic maps.

Most paleoceanographic models are focused on surface circulation since this is the least complicated scenario to model. Predicting and modeling deep-water processes is complex, particularly in the Ordovician where climate was predominately in a greenhouse state (see previous section for discussion) and assessing the role of deep-water formation and cold-saline vs. warm-saline circulation is difficult. Additionally, the extent and role that icecaps played in driving deep-water formation and global circulation in early

Paleozoic is not known. An approach to understanding a whole ocean state is that of Jeppsson (1990), and by extension, Aldridge et al. (1993b) and Jeppsson et al. (1995).

Jeppsson (1990) suggested that sea level changes were an insufficient explanation for faunal changes associated with habitat displacement. He suggested that climate and ocean chemistry played a crucial role. In this model for the Silurian, the ocean existed in two states: Primo (P) and Secundo (S), and that biotic change was associated with a change from a P-state to an S-state. P-episodes were characterized by a wetter climate and high latitude temperatures less than 5°C, which caused cold deep-water, high in O_2, to form. The creation of this type of bottom water resulted in upwelling, higher surface water nutrients and greater productivity and planktonic diversity. Lithologically, this state is associated with less carbonate deposition and increasing clay transport, possibly associated with regressive conditions. S-episodes were the opposite, with a drier climate and high latitude temperatures of greater than 5°C, which resulted in saline maxima at water mass cold edges and sluggish upwelling of O_2-poor waters. The lack of nutrients would have decreased plankton diversity and productivity. The sediments would reflect an S-state by showing increased carbonate deposition and less clay input.

Aldridge et al. (1993b) suggested that in the Llandovery, there were 2 P-states and 2 S-states with biotic changes occurring during the transition from P to S. Jeppsson et al. (1995) suggested that for the Wenlock there were as many as 5 S-states, 3 P-states with 3 P-S events and one S-S event.

Wilde (1991) and Wilde et al. (1989, 1991) realized that the Ordovician and Silurian circulation could be modeled using the Sverdrup-Ekman model of transport due to the presence of a large land mass at 60°S and an eastern meridianal boundary in the southern hemisphere. These models rely on certain astrophysical constants concerning the size, shape, and rotation of the planet. Wilde et al. (1991) discussed the physio-chemical parameters of the Silurian oceans and how they would affect ocean circulation patterns. They modeled surface circulation patterns and correlated these with lithofacies distributions. The Wilde (1991) study for the Ordovician to Early Silurian are more descriptive with respect to circulation patterns and how changes in meridianal boundaries would change the patterns. It also spans the same time interval, as such, the Wilde (1991) models will be the principal test subject for this present study.

Wilde's (1991) models for Ordovician circulation began with the Tremadoc and show relative changes in circulation associated with changing land mass distributions until the early Llandovery. The overall picture of circulation is relatively constant. Zonal circulation dominates the northern hemisphere due to the lack of land barriers to obstruct the north cool temperate and polar currents. The placement of numerous land masses in the tropics and southern temperate latitudes creates weak north-south flow and discontinuous equatorial currents. Much like today's oceans, major regions of upwelling and downwelling are associated with the placement of high pressure systems and flow counterclockwise and clockwise, respectively. The regions of oceanic high pressure, and hence upwelling, are situated in the mid-latitudinal ranges, approximately 30°S. Regions of downwelling and cyclonic pressure are at the temperate to polar regions, 30°S - 60°S. Incorporated into this model is the effect of monsoons and seasonal current reversals. If these factors did occur with enough intensity to alter circulation, the model suggested that seasonal current reversals would occur in the subtropical Paleotethys, along the eastern coast of Gondwana. These conditions were probably relatively constant throughout much of the greenhouse period in the Ordovician with some minor deflections of currents associated with the northward drift of Baltica.

The model does not predict major changes in circulation until the Ashgill with the changeover to icehouse/regressive conditions and the closing of the Iapetus Ocean. As Baltica and Avalonia drifted north and closer to Laurentia and Siberia, meridianal circulation was disturbed. Gyre circulation around 60°S was predicted to be limited due to land masses and possible packs of sea-ice. The model suggested that as sea-level regressed and shelves were exposed, meridianal barriers would lead to more intense circulation in the open ocean. Also, the presence of major ice sheets over the southern pole would enhance the formation of cold dense waters and invigorate deep-water circulation at the poles, enhancing global ocean ventilation. This is quite different than during the greenhouse state where deep-water downwelling likely occurred in warm tropical waters.

Wilde (1991) admitted that plotting climatic zones and changes due to seasonality, is difficult and potentially incorrect. The models employ aspects of present day controls of circulation that may not hold true for the early Paleozoic. There is also a degree of uncertainty associated with the paleogeographic positioning of the major and minor land masses. Paleomagnetic studies can only resolve the latitude, and the varying longitude positions for the paleoplates can result in a much different picture than that proposed by Wilde and colleagues. The models described above employ the paleogeographic reconstructions of Scotese (1986), which, except for the positioning of South China, are almost identical to that of Scotese & McKerrow (1991). As previously stated, this latter model has been seriously challenged by Dalziel et al. (1994). Resolution of the juxtaposition of South America could have a dramatic impact on various paleoceanographic circulation models.

Wilde et al. (1991) pointed out that by using interdisciplinary approaches such as using lithofacies and faunal distributions evidence can be gathered that will test the models and that a reasonably consistent model for ocean circulation and environmental conditions will emerge. The Nd isotope data from this present study can assist in testing these models by delimiting the range of values for the major water masses. The change in the Nd isotopic values over time and in association with tectonic forces, will indicate the relative degree of ocean mass mixing.

2.4 The Ordovician - Early Silurian Time Scale

A geochronological scale, or geological time scale, is established by calibrating the stratigraphic record based on a criterion exhibiting unidirectional or measurable change (e.g. lithologic, biological, isotopic). It is a combination of a chronometric scale (statement of age or duration) and a chronostratic scale (rock sequence) (Harland et al., 1990). Several time scales have been developed for the early Paleozoic (McKerrow et al., 1980, 1985; Gale, 1982, 1985; Harland., et al., 1982, 1990; Odin, 1994). However, difficulties arise in correlating the sedimentary rock and biostratigraphic record with ages attained using isotopes. Odin (1994) gave three ways to resolve the conflict between age data and numerical time scales: statistically (e.g. Harland et al., 1990), geochronologically (e.g. Odin, 1985), and graphically using litho-, bio- or chronostratigraphy (e.g. Gale, 1985; McKerrow et al., 1980, 1985).

Odin (1994) considered his geochronographic scale as the most useful, but his approach requires that each interval being assessed be bounded by an isotopic age with the dates being weighted differentially. This approach is less applicable for much of the early Paleozoic where relatively few isotopic ages have been established. Although some Ordovician chronostratigraphic units do have good isotopic dates, the values for other boundaries are quite variable (Odin, 1994).

The graphical method uses geochron ages as anchors and the stratigraphical scale and its stage durations are extrapolated, or interpolated, using various criteria such as lithostratigraphy, biostratigraphy, magnetostratigraphy or chemostratigraphy. This method has several drawbacks: only a few dates are sufficiently constrained to be suitable as anchors (Odin, 1985); the method is often subjective and the criteria used to establish duration, such as sedimentation rates or rates of evolution, are commonly imprecise (Gale, 1985): and error estimates are only those estimates of each geochron used and not an estimate error of the entire scale itself (Harland et al., 1990).

The statistical method assesses the age of each boundary from a data set with ages being given equal weight. This approach tries to calibrate the chronometric and chronostratic scales against each other using statistical applications to produce chronograms. The chronograms take into account both chronostratic and isotopic uncertainty and yield what is statistically the best date for a boundary considering the state of the isotopic data set. Chronogram ages are plotted against the chronostratic scale resulting in a geological time scale. Some degree of graphical interpolation is necessary for those boundaries that are poorly defined or lacking in isotopic data.

The Harland et al. (1990) time scale (Figure 2.9), the most widely adopted time scale at present, was chosen to assist in the determination of the ages of the samples in this study. This time scale is not without its problems. The terminology used for some stages and series is controversial and also tends to artificially split the scale more than is necessary. Improper weighting (i.e. identical weight for all samples) between well and poorly constrained data may cause inappropriate ages (Gale, 1985; Odin, 1985, 1994). However, Harland et al. (1990) acknowledged that the scale is limited by variable isotopic data. They overcame these limitations by excluding values that were rejected by the primary authors, values that are poorly constrained by other stratigraphic methods, and data that appear anomalous.

This geological time scale and the approach used for its determination is the most statistically reliable for the early Paleozoic. It also has the advantage over other scales because it includes and calibrates the biozonation of graptolites and conodonts together with the stage and series boundaries. Finally, the Canadian Institute for Advanced Research, Earth System Evolution Program, within which this present study is a part, has selected Harland et al. (1990) as the most appropriate time scale at present.

The Ordovician chronostratic/biostratic scale itself is problematic due to lack of agreement by the Cambrian/Ordovician Boundary Working Group of the Subcommission on Ordovician Stratigraphy which has yet to formalize a precise definition for the base of the Ordovician and most of the series and stage boundaries. Correlating the key graptolite, conodont, and shelly fossil biozones are complicated by the strong provincialism exhibited by these key fossil groups. For years, the British system of subdividing the Ordovician has been widely adopted, but it is a system that is not easily correlated with other parts of the world and has created a disparity in regional and global correlations (Webby, 1995). Few series and stages have a formalized definition but some options being put to vote are illustrated in Figure 2.10.

The favoured stratotypes for the Cambrian-Ordovician boundary are at Dayangcha, Peoples Republic of China (Chen, 1986) and Green Point, Newfoundland (Barnes, 1988), but both are still under study. The favoured zone fossil for the base of the

Period	Epoch	Stage	Biozones			Age (Ma)
			Graptolite		Conodont	
SILURIAN	Llandovery	Rhuddanian	C cyphus	cyphus	D. kentuckyensis	437
				acinaces		
			C. vesiculosus/atavus			
			A. acuminatus			
ORDOVICIAN	Ashgill	Hirnantian	G. persculptus		A. ordovicicus	439
		Rawtheyan	D. anceps			
		Cautleyan				
		Pusgillian	D. complanatus			
	Caradoc	Onnian	P. linearis		A. superbus	443
		Actonian	D. clingani			
		Marshbrookian				
		Longvillian				
		Soudleyan	C. wilsoni	D. multidens	A. tvaerensis	
		Harnagian	C. peltifer			
		Costonian				
	Llandeilo	Late	N. gracilis		P. anserinus	464
		Middle				
		Early	G. teretiusculus		P. serra	
	Llanvirn	Late	D. murchisoni			
					E. suecicus	469
		Early	D. bifidus		E. variabilis	
					M.flabellum	
	Arenig	Late	D. hirundo		P. originalis	
					P. navis	
					P. triangularis	
		Early	I. gibberulus	D. extensus	O. evae	476
			D. nitidus		P. elegans	
			D. deflexus			
			T. approximatus		P. proteus	
	Tremadoc		A. serratus		D. deltifer	493
			C.heres/S.pusilla			
			S. incipiens			
			D. flabelliforme		C. intermedius	
Cambrian	L. Cambrian	Dogellian				510
						514

Figure 2.9: The Early Paleozoic geological (chronostratigraphic) time scale used to establish the ages of the conodont samples. After Harland et al. (1990) including all series and biozone designations.

Ordovician was that of Cordylodus lindstromi , however in 1995 it appears to have been replaced by Iapetognathus n. sp.

The Tetragraptus approximatus (approximatus) Zone is favoured as the base of the Arenig (Berry, 1991). with candidate global stratotype sections at the Ledge Section on the Cow Head Peninsula of western Newfoundland (Williams et al., 1994) and at Hunneberg, Sweden (Maletz et al., 1995). The subdivision of the Arenig by the additional laevis/triangularis/victoriae biozone still requires a ballot as does the use of Phragmodus undatus/Corynoides americanus to subdivide the Caradoc.

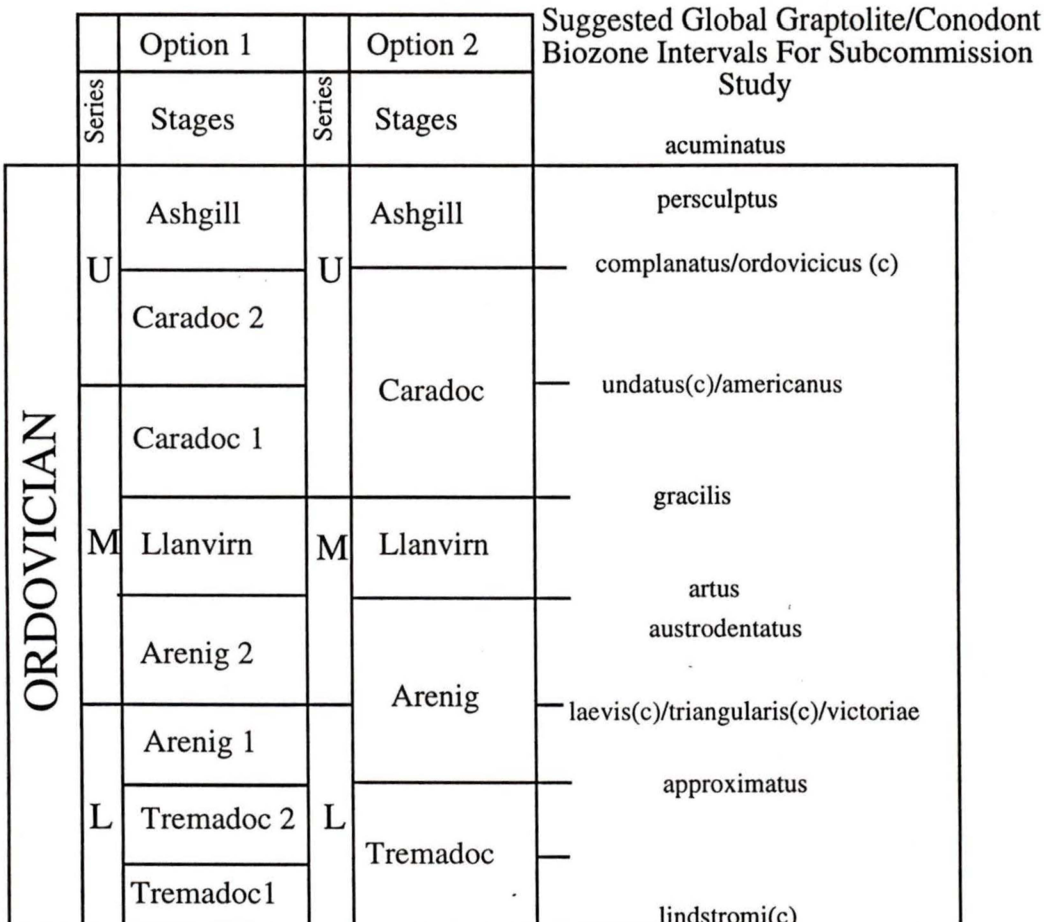


Figure 2.10: Proposed series and stage boundaries and associated conodont (c) and graptolite biozones for study by the Subcommission on Ordovician Stratigraphy of the IUGS. Modified from Ordovician News, Volume 11, 1994.

The biozone at the base of the Llanvirn, stage 3 or 5 depending on the option in Figure 2.10, is complicated by faunal provincialism and it has been suggested that the Llanvirn incorporate the Llandeilo (Fortey, 1995), which on its own is too short in duration to warrant stage status. The base of the Llanvirn in Britain is taken at the

Didymograptus artus Zone. An alternative basal biozone is Undulograptus austrodentatus. The use of the Nemagraptus gracilis Biozone for the base of the Caradoc will be put to vote and a Global Stratotype Section Point (GSSP) is required. The uppermost division likely will coincide with the Dicellograptus complanatus/Amorphognathus ordovicicus biozones (Barnes, 1991).

The Silurian System is less problematic. The Ordovician - Silurian boundary was established in 1985 by the boundary working group of the IUGS with the stratotype at Dob's Linn, Scotland and the level defined by the base of the Parakidograptus acuminatus Zone (Cocks & Rickards, 1988). The system is much shorter in duration and is less complicated by faunal provincialism making international correlation less difficult.

Chapter 3 Methodology

3.1. Conodont Sampling

The conodonts used for this study were collected over many years and are from the personal archives of C. R. Barnes, thesis supervisor. A description of each sample is presented in Table 3.1 and Appendix A. Conodont elements were extracted from calcareous rocks using 10% acetic acid dissolution, followed by separation with a heavy liquid (i.e. tetrabromoethane or sodium polytungstate) and a thorough washing with distilled water to remove any residue left by the heavy liquid. Once dry, samples were hand-picked under a microscope. For a description and review of extraction techniques see Barnes et al. (1987). The elements chosen for this study were carefully picked by C. R. Barnes and had no carbonate and clay debris adhering to them. They were also chosen for having a colour alteration index of ≤ 5; most were CAI ≤ 2 1/2 (Epstein et al., 1977).

The effects of thermal alteration in conodonts on the Nd isotopes is not well defined. Conflicting literature suggests that a CAI value can be either a maximum of 2 1/2 while other literature suggests that values up to 5 are acceptable (Keto & Jacobsen, 1987; Bertram et al., 1993). Conodont samples were viewed through a binocular microscope and colours were assessed by comparing the colouration of the sample to representative specimen CAI suites and photographic templates of the CAI standards provided by Anita Harris of the United States Geological Survey. Samples were mounted onto slide mounts and transported to the Isotope Laboratories in the Department of Earth and Planetary Sciences at Harvard University, Cambridge, MA.

Each sample consists of 10 - 15 conodont elements of the same genus and, for nearly all samples, the same species. This is to test and control for any variability that may be taxonomically induced. Samples were chosen from five time slices through the Ordovician to Early Silurian interval. Samples were also selected for their location in an effort to sample the major cratons and microplates that surrounded and contributed erosional material into the Ordovician to Early Silurian oceans, and across particular environmental gradients. In total, 63 samples were chosen, a number regarded as the maximum that could be analysed for an M.Sc. project given the time consuming laboratory procedures.

3.2 Conodont Age Determinations.

Assignment of ages or placement of samples in the context of the Harland et al. (1990) time scale was difficult task. The amount and accuracy of information varied between samples and not all could be dated with equal precision. A systematic method of assigning ages was used. Based on the literature and the personal knowledge of C. R. Barnes, samples were placed into appropriate biozones (graptolite and/or conodont) and cross-correlated into the chronostratigraphic time scale of Harland et al. (1990). However, this time scale favours the British series and stages and it was commonly necessary to correlate the biozone information with other regional stratigraphic time scales (e.g. IUGS, DNAG) and then to correlate this information into Harland et al. (1990). In practice, this method proved reasonably reliable and accurate, however, if a discrepancy existed between a regional time scale and the Harland et al. (1990) then the latter scale was used to retain consistency.

This method results in the determination of an absolute age and does not permit the easy assignment of errors that might be associated with those ages. If an error needs to be considered, then the error associated with the biozone on the Harland et al. (1990) scale can be invoked. However, the size of the errors that are associated with the biozones are negligible since they would not have a significant effect the final $\varepsilon_{Nd}(T)$ values.

3.3 Initial Preparation, and Isotopic Analysis

3.3.1 Cleaning and Acid Dissolution

All work was performed under clean lab conditions at Harvard University under the guidance of S. B. Jacobsen. All acids used were clean and blanked. Blanks were <0.01 pg/g for Nd in ultrapure water, ~0.03 pg/g for Nd in the HCl and ~0.7 pg/g for Sr in both water and HCl. All beakers were Teflon and cleaned in boiling 50% reagent strength/reagent grade HCl and then in boiling 50% reagent strength/reagent grade HNO_3 prior to use. To ensure that the conodont elements remained intact during transport, they were mounted onto the slide mounts with a water soluble organic glue (gum tragacanth). To remove this possible source of contamination, the elements were removed from their mounts and thoroughly washed three times in ultrapure water and allowed to air dry. The samples were then dissolved in 1 ml of 4N HCl.

The determination of absolute quantities of Sm and Nd in the samples was performed using the isotope dilution technique. Samples were spiked with a tracer enriched in ^{147}Sm and ^{150}Nd prior to separation. However, due to the small size of the conodont elements, it proved impractical to weigh each sample in order to calculate the concentrations of Nd and Sm in the samples, and to calculate the appropriate amount of spike required for the analysis. To overcome this problem, a 1% aliquot (100 μl) was removed from the sample and spiked. The spike solution was a ^{147}Sm-^{150}Nd mixture with a known concentration of ^{150}Nd (0.021717 nm/g) and ^{147}Sm. Prior to dissolution and spiking, the samples were compared with each other with respect to element size. The samples were then categorized as either small, medium or large conodonts. Small elements were spiked with 10 μl, medium with 50 μl, and large with 100 μl. Once spiked, the samples aliquots were dried down to a few drops in quartz covered teflon pots that were heated by overhead lamps. Pure dry N_2 gas was used to purge the fumes from the heated sample.

The aliquots were then redissolved in 40 μl of 4N HCl and then 12 μl - 16 μl of the aliquot were loaded onto single degassed rhenium filaments and analyzed for ^{150}Nd/^{144}Nd, ^{146}Nd/^{144}Nd and monitoring Sm interference by also measuring ^{147}Sm and ^{149} Sm ion beams on a Finnigan Mat THQ Quadrapole Mass Spectrometer. Depending on the state of the THQ's vacuum, Nd was, for some samples, measured as an oxide (^{166}Nd/^{160}Nd). However, this ratio was treated as a ^{150}Nd/^{144}Nd ratio as the effect of the oxide was considered negligible since only a general estimate of the total Nd was being obtained. From the ^{150}Nd/^{144}Nd values, the total mount of Nd in the sample is calculated as per:

$$^{144}Nd = \frac{\left(^{144}Nd/^{150}Nd\right)_{mixture} - \left(^{144}Nd/^{150}Nd\right)_{tracer}}{1-\left(^{144}Nd/^{150}Nd\right)_{mixture} \times \left(^{144}Nd/^{150}Nd\right)_{normal}} \times {}^{150}Nd_{tracer} \qquad [3.1]$$

where: ^{144}Nd/^{150}Nd tracer = 0.009012
^{150}Nd/^{144}Nd normal = 0.2386
^{150}Nd of spike = 0.021717 nm/g

The fraction of ^{144}Nd in Nd is: (^{144}Nd/Nd) atomic = 0.237816 and the atomic weight of Nd is 144.2397 (Wasserburg et al., 1981). Therefore, the total number of nannograms of Nd in the sample is:

$$Nd(ng) = \frac{^{144}Nd(nm) \times 144.2397}{0.237816} \qquad [3.2]$$

To calculate the appropriate amount of spike required by any given sample:

$$\text{Amount of Spike(ml)} = \frac{\left(^{144}Nd_{measured} \times 100\%\right) \times 0.2386}{0.021717} \qquad [3.3]$$

A second 1% aliquot was removed from the sample for future Rb/Sr work and the required amount of spike for each sample was added to the remaining sample. Once spiked, the sample was dried down under heat and pure N_2 gas.

3.3.2 Ion Exchange Chromatography

The ion exchange method used to separate Nd and Sm are the standard techniques used at the Harvard Isotope Laboratories as cited in Jacobsen & Dymek (1988). Samples were redissolved in 1.5N HCl, centrifuged and loaded onto columns for separating the REEs from other major cations using first 2.5N and then 4.0N HCl as elutant. For a full description of this elution and collection process see Appendix B. Total blanks on the columns were between 4.4 pg and 170 pg for Nd. Those samples with less than 25 ng of total Nd were run on columns with blanks between 4.4 and 9.5 pg Nd. Once the REE fraction was collected and dried, the samples were redissolved in 0.75N HCl and were then loaded onto the REE microcolumns for separation of neodymium and samarium. Elution for the REE columns was with 0.2M methyl-lactic acid (MLA), with a pH of 4.65. For a full description of this process see Appendix C.

3.3.3 Mass Spectrometric Analysis

Once these fractions were collected and fully dried down under heat and N_2 gas, they were dissolved in 6 μl of 2.5N HCl and loaded onto degassed double rhenium filaments. The Nd fraction was loaded with 0.83N H_3PO_4. The Nd isotopic compositions of the spike-sample mixtures were measured using a Finnigan Mat 262 multi-collector mass spectrometer in static mode. The Sm isotopic composition of the spike-sample mixtures was measured by ion counting on a Finnigan Mat THQ Thermal Quadrapole Mass Spectrometer operated in peak jumping mode.

3.3.4 Data Reduction

For the Sm isotopic measurement, data was obtained for the masses 146-147-148-149. Mass 146 was used to correct ^{148}Sm for interference from Nd, if necessary. The ^{148}Sm/^{147}Sm and ^{149}Sm/^{147}Sm ratios obtained were used to calculate two independent estimates of the amount of ^{147}Sm in each sample. These two estimates always agreed to better than 0.5%. No correction was made for mass fractionation.

For the Nd isotopic measurement, data was obtained for the masses 142-143-144-145-146-147-150. Mass 147 was used to correct ^{144}Nd and ^{150}Nd for interference from Sm, if necessary. The ^{143}Nd/^{144}Nd and ^{150}Nd/^{144}Nd were first corrected for mass fractionation using the exponential law described by Wasserburg et al. (1981) and using a value of $^{146}Nd/^{144}Nd = 0.724134$. Then the $^{143}Nd/^{144}Nd$ ratio was corrected for spike using the fractionation corrected $^{150}Nd/^{144}Nd$ ratio. The value obtained for the Caltech Nd-beta standard with these procedures was $^{143}Nd/^{144}Nd = 0.511095$ with an uncertainty of 0.000005.

Table 3.1. Conodont Sample Information

Sample No. [# of elements)	Location	Stratigraphic Unit	Stage or Biozone	Chronostratigraphic Unit (after Harland et al., 1990)	Interpreted Age
1 [10]	Texas	Wilberns Fm.	E. notchpeakensis [2]	L. Cambrian (Dolgellian)	511
2 [10]	Australia	Larapinta Gp.	Upper Whiterockian [1]	L. Llanvirn	472
3 [10]	Spitsbergen	Valhalfonna Fm.	D. bifidus (bifidus) [2]	Arenig	479
4 [9]	Devon Is.	Bay Fiord Fm.	O. multicorrugatus [2]	E. Llanvirn	475
5 [10]	Devon Is.	Irene Bay Fm.	mid-Maysville [1]	Ashgill (Pusgillian)	442
6 [10]	Colorado	Harding Sandstone	Rocklandian [1]	Caradoc (Soudleyan)	456
7 [10]	Oklahoma	Oil Creek Fm.	Conodont Fauna 4 [2]	Arenig	477
8 [10]	Anticosti Is.	Ellis Bay Fm.	Conodont Fauna 13 [2]	Ashgill (Hirnantian)	440
9 [10]	Manitoba	Stony Mountain Fm.	upper Richmondian [1]	Ashgill (Pusgillian)	441
10 [10]	Manitoba	Stony Mountain Fm.	upper Richmondian [1]	Ashgill (Pusgillian)	441
11 [9]	Manitoulin Is.	Georgian Bay Fm.	upper Richmondian [1]	Ashgill (Pusgillian)	441
12 [10]	Manitoulin Is.	Manitoulin Fm.	Llandovery [1]	Llandovery (Rhuddanian)	438
13 [10]	Ontario	Whitby Fm.	Maysvillian [1]	Caradoc (Onnian)	444

14 [10]	Newfoundland	Table Head Gp.	P. tentaculatus [2]	L. Llanvirn	472
15 [6]	Newfoundland	Table Head Gp.	P. tentaculatus [2]	L. Llanvirn	472
16 [10]	Wales	Shoalshook Fm.	A. ordovicicus [2]	Ashgill (Pusgillian)	443
17 [7]	Anticosti	Ellis Bay Fm.	B. plicatispinae [2]	Ashgill (Hirnantian)	440
18 [10]	Siberia	Unit R/Member 74	A. acuminatus [2]	Llandovery (Rhuddanian)	438
19 [10]	Siberia	Unit A/Top bed	C. peltifer [2]	Caradoc (Harnagian)	462
20 [12]	Siberia	Unit O/Bed 60	T. unicum [2]	Ashgill (Rawtheyan)	440
21 [7]	Sardinia	Dosmusnovas Fm.	A. ordovicicus [2]	Ashgill (Pusgillian)	443
22 [12]	Spain	Urbana Limestone	A. ordovicicus [2]	Ashgill (Pusgillian)	443
23 [10]	Italy	Tonflaserkalk Lst.	A. ordovicicus [2]	Ashgill (Pusgillian)	443
24 [9]	Ontario	Selby Fm.	base of the Rocklandian [1]	Caradoc (Harnagian)	460
25 [10]	New Brunswick	Tetagouche Gp.	P. alobatus [2]	Caradoc(Soudleyan)	456
26 [10]	Quebec	Levis Fm.	D. dentatus [2]	Arenig	476
27 [10]	Southampton Is.	Churchill River Gp.	Richmondian [1]	Ashgill (Pusgillian)	441
28 [10]	Vermont	Isle la Motte Fm.	Rocklandian [1]	Caradoc (Soudleyan)	453
29 [10]	Wales	Crûg Fm.	A. ordovicicus [2]	Ashgill (Pusgillian)	442
30 [5]	Wales	Ffairfach Gp.	A. inaequalis [2]	M. Llandeilo	467

31 [9]	Norway	Famme Fm.	-----------[1]	Ashgill (Cautleyan)	441
32 [10]	Newfoundland	Green Point Fm.	C. lindstromi [2]	Tremadoc	505
33 [10]	Sweden	Lanna Limestone	B. navis [2]	Arenig	478
34 [10]	Sweden	Segerstad Limestone	E. suecicus [2]	L. Llanvirn	472
35 [10]	Sweden	Ceratopyge Limestone	C. angulatus [2]	Tremadoc	494
36 [10]	Manitoulin Is.	Gull River Fm.	Blackeriveran[1]	Caradoc (Costonian)	463
37 [9]	Australia	Ninmaroo Fm.	Chosodina herfurthi	Tremadoc	494
38 [10]	Australia	Ninmaroo Fm.	C. proavus/H. simplex [2]	Tremadoc	510
39 [10]	Australia	Clearview Lst.	Brachiopod Fauna C/D [2]	Caradoc (Onnian)	444
40 [10]	Australia	Belubula Fm.	Brachiopod Fauna A/B [2]	Caradoc (Costonian)	462
41 [9]	Anticosti Is.	Bescie Fm.	E. birminghamensis [2]	Llandovery (Rhuddanian)	437
42 [7]	Utah	Crystal Peak Dolomite	P. flexuosus [2]	L. Llanvirn	470
43 [10]	Germany	Kalkbalk Lst.	A. ordovicicus [2]	Ashgill (Pusgillian)	443
44 [10]	Newfoundland	Green Point Fm.	D. bifidus (bifidus) [2]	Arenig	485
45 [9]	Newfoundland	Green Point Fm.	I. v. maximus [2]	Arenig	478
46 [10]	Newfoundland	Green Point Fm.	U. austrodentatus [2]	L. Llanvirn	476
47 [10]	Estonia	Leetse Fm.	Latorp Stg. B1 [2]	Arenig	480
48 [10]	British Columbia	McKay Gp.	Conodont Fauna C/D [2]	Arenig	491

49 [10]	Alberta	Survey Peak Fm.	C. angulatus [2]	Tremadoc	505
50 [10]	Alberta	Outram Fm.	O. communis[1]	Arenig	485
51 [10]	Alberta	Skoki Fm.	-----------[1]	L. Llanvirn	473
52 [10]	Newfoundland	Boat Harbour Fm.	C. angulatus [2]	Tremadoc	500
53 [10]	Newfoundland	Catoche Fm.	P. carlae/S. ovatus [2]	Arenig	485
54 [10]	Newfoundland	Catoche Fm.	P. simplicissimus-O. communis [2]	Arenig	485
55 [10]	Argentina	Empozada Fm.	A. superbus (in clasts)	Caradoc (Marshbrook)	446
56 [11]	Turkey	Sobova Limestone	D. hirundo [2]	Arenig	477
57 [8]	Turkey	Seydisehir Fm.	-----------[1]	Arenig	482
58 [10]	Central China	Nanjinguan Fm.	R. manitouensis [2]	Tremadoc	500
59 [10]	Central China	Fenhsiang Fm.	P. deltifer [2]	Tremadoc	494
60 [10]	Central China	Kunitan Fm.	P. serrus [2]	L. Llanvirn	472
61 [10]	Central China	Baota Fm.	-----------[1]	Caradoc (Marshbrook)	447
62 [10]	Kazakhstan	Shabakty Fm.	Euloma-Leiostegium Beds [2]	Tremadoc	508
63 [15]	Siberia	Unit L/Member 46	O. quadrimucronatus [2]	Ashgill (Pusgillian)	443

Notation: [1] unknown or no biozone present, correlated on other stratigraphic information

[2] biozone present

Chapter 4 Results and Discussion

4.1 Summary of Analytical Results

Sixty-three conodont samples of conodonts were acid dissolved and 1% aliquots removed for the determination of total Nd. Of the 63, 12 were insufficient in total Nd to warrant further preparation and separation. Of the remaining samples that were fully processed and run on the FM 262, 3 failed to establish good steady ion beams and ^{144}Nd data are unavailable, although ^{147}Sm values were obtained. Table 4.1 lists the results of the Nd isotopic analysis. Three of the samples show anomalous results. Samples 2 and 16 have erroneously high ^{147}Sm/^{144}Nd ratios and the ε values and T_{2DM} values are unreliable. Sample 14 is difficult to address; although the ^{147}Sm is somewhat low, this does not explain the discrepancy in the $\varepsilon(0)$ value as compared to the values from the same regional location and time interval. The error associated with the $\varepsilon(0)$ value is also high. One sample, 15, is an inarticulate brachiopod from the same conodont sample. It was included for comparative reasons and when this value is compared to other regional samples, it is consistent. However, there is a discrepancy between this sample and 14. The error associated with 14 is higher than 15 and there were some difficulties in establishing a solid ion beam during the mass spectrometer run for 14. There were also some difficulties during acid dissolution. This sample, (14), and sample 2 took longer to dissolve in HCl compared to other samples and it was noted that for both samples, the organic matter content, as indicated by black flecks of material that only dissolved with difficulty, was high. Schaltegger et al. (1994) suggested that the presence of organic matter during acid digestion may prevent complete spike equilibration and that this can lead to anomalous values. It is not known if that is the case with these samples. The data from these three samples is displayed at the bottom of tables 4.1 and 4.2. They will not be addressed in further result sections or in the discussion. For the remaining 42 samples, although there are no replicates for testing reproducibility, there is no analytical or comparative reason to suspect any inaccuracy.

The ^{143}Nd/^{144}Nd values range from 0.510359 to 0.511593 and the $\varepsilon(0)$ values, overall and through time, range from -29.07 to -4.96. Most of the errors associated with the $\varepsilon(0)$ values are within 1 ε-unit while only 4 have errors between 1 - 2 ε-units. Higher analytical errors can be associated with unstable ion beams during the mass spectrometry runs.

Table 4.2 lists the computational results for $f_{Sm/Nd}$, $\varepsilon(T)$, and the single and double stage crustal model ages. The $f_{Sm/Nd}$ range from 0.06024 to -0.55463 with an

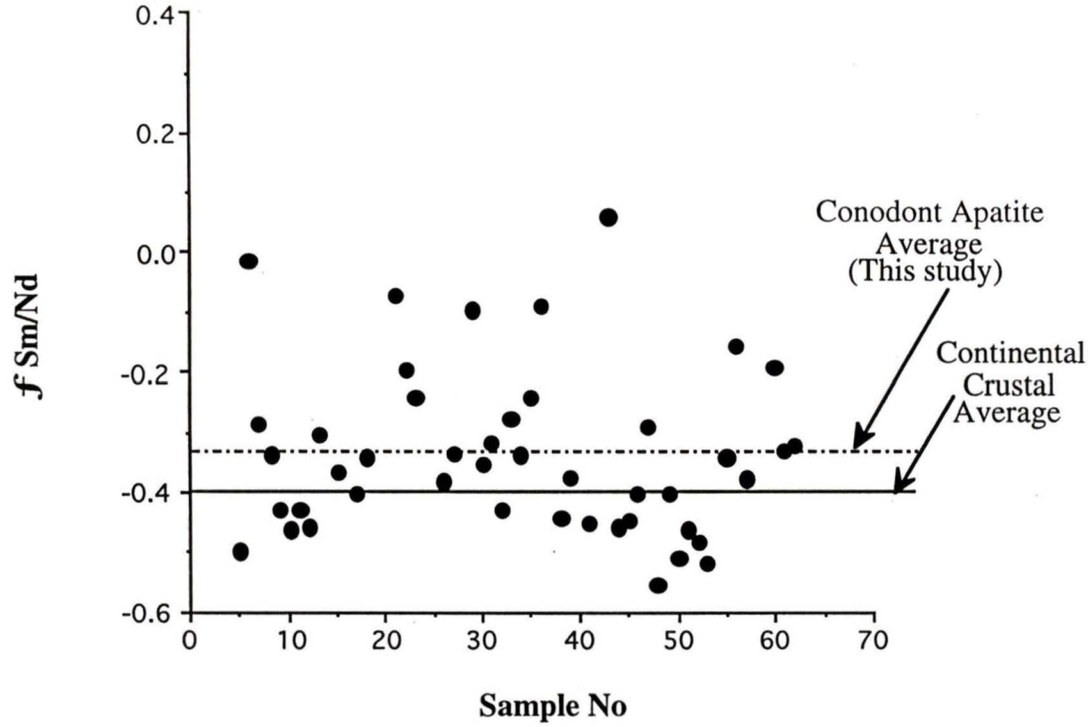


Figure 4.1: Scatter plot of the Sm-Nd enrichment parameter between the conodont apatite samples used in this study. Continental crustal average of 0.4 from Goldstein et al., (1984).

average value of -0.3367. Figure 4.1 illustrates the scatter of the $f_{Sm/Nd}$ values. Many of the samples have a higher $f_{Sm/Nd}$ ratio than the continental crustal average of -0.4 (Goldstein et al., 1984), suggesting some degree of fractionation from the crustal source. This suggests that a double stage model for the determination of model ages is more appropriate (Keto & Jacobsen, 1987). The T_{DM} values range from 6.99 to 1.14 Ga and the T_{2DM} values range from 3.05 to 1.27 Ga.

4.2 Nd Isotopic Values and Crustal Model Ages Through Time and Their Relation to Sedimentary Sources

For a comprehensive analysis, it is important to discuss the Nd isotopic values and the crustal model ages in the context of regional geological associations. There are few studies which have actively tried to assess the isotopic composition of seawater for this interval and most studies have focused on using the Nd isotopic composition of the sediment in the context of quantifying provenance sources. Both these approaches are valuable for comparative purposes, but although there is often overlap between seawater and sediment Nd isotopic values, the conodont values represent ancient seawater signals whereas the sediment values are more a reflection of the protolithic source(s). The result is that the data from sediments tend to be more variable.

All the studies cited herein for comparison have had the Nd isotopic values renormalized to a $^{146}Nd/^{144}Nd$ value of 0.724134. Where possible, the various time scales used in these studies have been recalibrated to the Harland et al. (1990) time scale with the $\varepsilon(T)$ values adjusted appropriately.

4.2.1 The Tremadoc Interval (510 - 493 Ma; Figure 4.2)

The first time slice considered is that of the Tremadoc Series. The samples chosen, as far as possible, were located close to the Cambrian - Ordovician boundary in the lower Tremadoc. $\varepsilon(T)$ values range from -20.8 to -7.1 with the most negative values being associated with the marginal oceans of the Laurentian craton. The T_{2DM} values fall within a range of 2.91 to 1.8 Ga, and again, the oldest ages are associated with Laurentia. These strongly negative signals and the associated T_{2DM} values from Laurentia are likely a result of the averaging of the various Archean provinces which at certain intervals of the Early Paleozoic would have been exposed to erosion.

The sample from Baltica shows a substantially different signature than Laurentia with an $\varepsilon(T)$ value of -7.1. It also shows a younger T_{2DM} value of 1.86 Ga. Baltica is generally composed of Archean continental crust with Svencofennian and Grenville aged material but is has various volcanic terranes, mafic dikes, and other intrusions with mid-oceanic ridge basalt (MORB) characteristics (Andréasson, 1994). The continental margins were uplifted in the Late Cambrian to Early Ordovician (Andréasson, 1994) with the initial deformation of the miogeocline by the early Ordovician (Roberts & Gee, 1985). It is possible that this tectonic activity and subsequent uplift led to the erosion of isotopically younger material, resulting in the more radiogenic signal. Goldstein & Jacobsen (1987) noted that orogenic areas may erode faster than stable older cratonic regions. This would lead to isotopically younger rocks being eroded faster into the sedimentary basin and consequently, the waters in the basin reflect this process by yielding younger ε_{Nd} signals and younger crustal ages. The signature indicates, however, that input is still dominated by continental crust. The Nd isotopic values suggest that the input sources for Baltica seawater could be the result of a mixing between Archean, and possibly predominantly, Proterozoic continental crust and juvenile volcanics.

Kazakhstan shows a slightly more negative signature but with a still reasonably younger continental crustal source than Laurentia with a $\varepsilon(T)$ value of -10.3 and a T_{2DM} value of 2.06 Ga. The regional geology of Kazakhstan is not well established. Apollonov (1995) suggested that in the Ordovician it was composed of two stable micro-continents;

the Kazakhstan - Tienshanian (K-T) and the Balkhash. The former was dominated by Bahama bank-like carbonates and includes the Malyi Karatau seamount and the Batyrby section. The Balkhash was bounded by a volcanic arc. It is difficult to determine the basement or any one particular source of sedimentary material for Kazakhstan due to the lack of good paleomagnetic information and a poor understanding of regional geological history.

The sample from Australia, representing equatorial Gondwana, shows a value similar to that of Kazakhstan with a $\varepsilon(T)$ value of -9.5 and a T_{2DM} value of 2.00 Ga. No published reports exist for the sedimentary provenance of strata from the Georgina Basin, Australia, in the early Ordovician, however sediments from the neighbouring Amadeus Basin show a similar signal to that of the Georgina Basin conodonts with an $\varepsilon(T)$ value of -9.68 and a T_{DM} value of 1.79 (Zhao et al., 1992). The results of the study showed that the major input of sediments to the Amadeus Basin was intimately linked to the surrounding igneous rocks, the Arunta and the Musgrave Blocks, and reflected a close regional source for sedimentary material rather than influx being predominately on a cratonic scale (Zhao et al., 1992). It is possible that the Georgina Basin was similarly influenced, since the Arunta Block separates the Georgina Basin from the Amadeus to the south and southwest.

Based on the Nd isotopic signatures, the marginal oceans of Laurentia (Iapetus and western Panthalassic) may represent distinct water bodies with slightly different source material Additionally, circulation between these oceans may have been restricted. In the Iapetus region, the marginal Baltica waters also represent a distinct ocean mass from that of the Laurentian Iapetus waters. Baltica Iapetus waters were receiving significantly younger ages material than Laurentian Iapetus. The distinct signatures between these regions is also likely due to the lack of water mixing between the masses. The similarity in the signatures of Kazakhstan and northern Gondwana suggest that the east and west margins of the northern Paleotethys were receiving material similar in age and possibly that this region was well circulated. However, the lack of constraints on the position of Kazakhstan make this latter statement difficult to evaluate. The signature of Baltica is slightly different from the Kazakhstan and Gondwana marginal ocean values, indicating that the latter regions were receiving older material. It is also possible that meridianal circulation in the Paleotethys was restricted, although not incomplete such that homogenization of the isotopic signals was not possible.

In comparison, Late Cambrian - Early Ordovician seawater values from inarticulate brachiopods determined by Keto & Jacobsen (1987) for Laurentia (~-19 to -5) were more radiogenic than our values. The reason for this more radiogenic signal from these samples is not clear. Most of these samples are of Late Cambrian age and may be indicative of a younger erosional source that was dominant at the time. The -5 value is from the Riley Formation, Cap Mountain Member represents a Cambrian transgressive event (Miller, 1987) that may have resulted in a change in erosional source. Another possibility is that the values are suspect since they were determined on inarticulate brachiopods and not conodonts. The use of brachiopods as true proxy signals for ancient seawater has not been rigorously tested, nor adequately compared to conodont values. In the Keto & Jacobsen data set, two brachiopod samples from Wisconsin, United States, with ages within error of the estimated ages show radically different isotopic signatures, one with approximately -19, the other with approximately -14. It may be that brachiopod apatite is susceptible to flux and post-depositional changes that will adversely affect the Nd isotopic signals.

A single seawater value from conodonts exists for Kazakhstan, also from the Batyrby section. Keto (1987) and Keto & Jacobsen (1988) report a ε(T) of -10.7, identical to the value obtained during this study. Although in this study there are no conodont samples from Avalonia for this time interval, there is sediment data available in the literature. Thorogood (1990) reported shales from Wales with Nd isotopic values of -7.7 - -8.2 and T_{DM} values of 1.55 - 1.66 Ga.

4.2.2 The Arenig - Llanvirn Interval (492 - 469 Ma; Figure 4.3)

For this time interval, the range of ε(T) for seawater is from -22.7 to -5.6 and the T_{2DM} values range from 2.6 - 1.7 Ga. Marginal ocean masses for the Laurentian craton begin to show a shift towards more radiogenic ε(T) values. The western margin of Laurentia bordering the Panthalassic Ocean has slightly more negative signals with input remaining predominately from older Archean continental crust, as indicated by both the crustal model ages and the stronger negative isotopic signal. The less negative value of -11.7 is the shallow water Skoki Formation from Alberta. When this data point is placed into the context of a reconstruction such as that of Scotese & McKerrow's (1991), this point appears inconsistent with other surrounding values. The neighbouring values (-17 [Outram Formation, Alberta]; -16.5 [McKay Group, British Columbia]) are however, about 10 to 15 Ma older than the Skoki. The more radiogenic signal displayed by the Skoki could be the response to different input sources that were dominant during its deposition. It should be noted that larger time slice intervals may blur the pattern of events.

Gehrels et al. (1995) have reported detrital zircon ages from Ordovician sandstones from the Cordilleran margin that show that in these strata, zircons are predominantly 1.7 - 1.95 Ga. They have suggested that the provenance for these sandstones is the Peace River Arch, which may have exposed Early Proterozoic and Late Archean rocks. They suggested sediments from this arch dominated the sediment load and were transported along the near-shore miogeocline by long-shore currents. However, they stated this process was unlikely in the more off-shore settings, based on grain size, suggesting that the off-shore deposits were likely derived from some other source to the north. It is possible that the sediments from the Peach River Arch were deposited in the Skoki Formation, and the younger age of the sediments is responsible for the more radiogenic signature.

The Iapetus margin of Laurentia generally shows a narrow range of ε-values from -14.8 to -13.3 with a T_{2DM} of 3.05 to 2.28 Ga. The strongly negative value of -22.7 (T_{2DM} = 3.05 Ga) from the Catoche Formation of Western Newfoundland, is not necessarily an outlier compared to the other regional values. This sample represents the onset of a regional transgressive phase and an outer platform facies in contrast to the slope of the coeval Cow Head Group at St. Paul's Inlet. The samples at Cow Head show what is typically an western Iapetus Ocean signature of approximately -14. The difference between this platform facies and that of the outer slope may be a result of the transgressive waters being in contact with sediments from the older Archean sheild. Additionally, as deposits built up at the shelf-slope interface, the degree of circulation between the platform and the outer slope would have been small, resulting in two isotopically distinct water masses.

The younger Table Head Group, which lies stratigraphically above the Catoche represents a collapsing continental margin and progressive drowning (Stouge, 1984). It shows a similar ε(T) value as those of the Cow Head Group suggesting that waters of the carbonate platform were well mixed with the waters of the outer slope. The Levis Formation, near Québec, is a correlative environment to that of the Cow Head Group (476 Ma) and shows similar ε(T) values, indicating that the waters along the Appalachian continental margin were receiving material that was comparable in age and lithology and possibly that the waters on the margins were well mixed.

The margin of Baltica facing the Iapetus Ocean shows values consistent with those of the Tremadoc at -6.9 and -8.8 . This suggests, like previously, that the source of sedimentary material to these waters is a mixture of isotopically younger terranes, possibly volcanic, and older stable continental crust. The T_{2DM} data lies within a narrow range with values of 1.77 and 1.99 Ga. The consistency in the ε(T) values through time suggest that the sources for this region have remained constant. ε(T) and T_{2DM} values for the Armorican microplate are similar and overlap those for Baltica with ε(T) values of

-9.7 and -5.6. Sediment sources for the Armorican microplate in the Arenig have been linked to the Cadomian - Pan-African basement of Gondwana with most of the material likely being transported and deposited during the Arenig transgression (Noblet & Lefort, 1990). Gondwana would represent a possible source of stable continental crust. Avalonia could also represent an additional source as the basement of Armorica is similar to that of Avalonia (Andre et al., 1986), suggesting that these were in close proximity as peri-Gondwana terranes, at least during the time of basement formation.

The sample from South China, $\varepsilon(T) = -13.8$, interestingly shows both $\varepsilon(T)$ and T_{2DM} values that suggest input from an older continental source than that contributing to the southern Paleotethys (e.g. Armorica) or the eastern Iapetus waters off Baltica. The rocks of the Yangtze Platform are predominately Late Archean and Paleoproterozoic with surrounding younger orogenic belts (Wang et al., 1995). Input sources could include the platform itself and/or Gondwana. It is also possible that Laurentia was a sedimentary influence since the $\varepsilon(T)$ value is approximately that for Laurentian seawater.

The $\varepsilon(T)$ values for the east and west marginal oceans of Laurentia appear to be somewhat distinct and likely represent differences between dominatly Archean and Proterozoic sources, respectively, and the restricted degree of ocean circulation. It is also clear that there is a distinction between the Iapetus waters off Laurentia and those off Baltica suggesting that circulation between these waters was still restricted in the Arenig. However, the similarities in the Nd isotopic values of Baltica and Armorica suggests that sources for these regions are similar, and possibly that there was ocean mixing in this region.

Other values for the Nd isotopic composition of seawater from biogenic apatites are approximately -12 for Laurentia (Nevada), and for Siberia, -5 (Keto & Jacobsen, 1987). These values were determined on inarticulate brachiopods and so their representation of seawater is not clear. However, the value for Laurentia is not far from the values attained in conodonts of -14 to -13. The -5 for Siberia is interesting, if it represents a true seawater signal, in that the erosional sources are evidently more radiogenic. This isotopic distinctness of Siberia will be addressed in section 4.4.4.

Miller and O'Nions (1984) reported Nd isotopic values from Quebec sediments for the early Arenig with values of -17 and -11. They attributed the wide range in epsilon values to differential input that was not homogenized by erosion and transport. Overall these values and those of Keto & Jacobsen (1987) listed above, fall well into the ranges of the isotopic composition of the eastern Laurentian seawater values as derived by conodonts in this study.

Although no conodont samples were included from Avalonia during this time slice, Evans (1992) reported Nd isotopic values from North Wales for the Caban Conglomerate with a range from approximately -6 to -9.5. These values are within the range reported from other sediments in Wales from other time slices, and is consistent with the Nd isotopic value of seawater attained from conodonts in the Llandeilo - Caradoc interval of this study. These values also overlap the range of signatures for conodont samples for Baltica and Armorica in the Arenig, supporting the view that the southern Paleo-Tethys region was reasonably well mixed.

4.2.3 The Llandeilo - Caradoc Interval (468 - 444 Ma; Figure 4.4)

Sampling distribution for this time interval is limited, however, in the context of the previous time frame, a few conclusions can be made. Laurentia shows a rather large range in $\varepsilon(T)$ values, from -10.05 to -20.2 and a T_{2DM} range from 2.8 to 1.99 Ga. This can be explained by regional variation in depositional environments. The Gull River Formation ($\varepsilon(T)$ = -20.25), in Ontario, represents a lagoonal sequence and interaction with the outer platform and open ocean was was likely restricted. It can be suggested that the source materials to the lagoon facies, Archean continental crust, were deposited without subsequent influence from the more open Iapetus Ocean waters. Without the homogenizing influence of the continental margin and open ocean waters, the older signature dominates.

The Harding Sandstone ($\varepsilon(T)$ = -18.50), in Colorado, represents a shoreline sequence during the major Caradoc transgression with the major sediment source being dominated by Archean continental crust, and possibly reworked Archean clastics. This value is distinctly different from the Iapetus continental shelves/open ocean as represented the Whitby Formation ($\varepsilon(T)$ = -10.05) in southern Ontario. This formation represents the initial phase of collapsed foreland basin which would have allowed an influx of open Iapetus waters. Sediment sources for the shelf/open waters of the Laurentian Iapetus could have included the Taconic region and/or the stable shield to the north.

The $\varepsilon(T)$ for Avalonia (-6.30) can be attributed to a mixture of younger continental crust and juvenile arc material. It is within the range of values for Baltica and the Armorican margin in the Arenig - Llanvirn. The Avalonian basement consists of Late Precambrian igneous rocks and Ordovician volcanics. The volcanics consist of a mixed mantle and continental crust component (Noble et al., 1993). Considering that Avalonia had separated from Gondwana by this period, it is difficult to assess the relative importance of Gondwana as a sediment source to Avalonia marginal waters. Sediment sources could include the microplate itself, since the composition of the various basement rocks, $\varepsilon(T)$ = -4 - -6 (Noble et al., 1993), could easily account for the signal. The overlapping values for Baltica, Avalonia and Armorica suggest that these waters were well mixed. It is important to note that material being shed from Baltica and Avalonia into the Iapetus Ocean would also have had equivalent aged sediments being transported into the southern Paleotethy due to the peneplaned nature of the Baltic platform and that it was covered by epicontinental seas for most of the Ordovician (Gorbatschev, 1985). Therefore, the isotopic similarities could be the result of similarities in source materials. The overlapping values for Baltica, Avalonia and Armorica also suggest that these waters may have been well mixed which is not unreasonable due to the lack of physical barriers between the two plates and that parts of Baltica in the Early - Middle Ordovician were still at high latitudes.

The northeastern margin of Gondwana, represented by a sample from the Clearview Limestone Member, Ballingoole Limestone, of the Bowan Park Group, of east - central Australia, shows a $\varepsilon(T)$ signature of -5.50 that suggests input from juvenile volcanic sources. The Bowen Park Group represents deposition in the western flank of a volcanic setting known as the Molong High (Webby & Percival, 1983; Stait et al., 1985). Although the Molong High has been interpreted as an island arc setting (Cas et al., 1980; Cas, 1983; Powell, 1983, 1984), Vandenberg & Stewart (1992) interpreted it as an offshore vent volcano. The Molong High is a volcanic complex that erupted in the early Ordovician and was overlain by carbonates. Both the eastern and the western flank were sites of shallow water carbonate deposition (Webby & Packham, 1982) until the Late Ordovician when volcanic activity resumed, depositing volcaniclastics predominantly in the eastern flank These volcanics could represent the source for the juvenile Nd isotopic signal, however, because this value is still negative the volcanic material was evidently mixing with other continental crust sources, possibly coming from the craton.

The sample from the Precordilleran terrane of Argentina shows a signal that would indicate input from isotopically juvenile volcanics similar to the Clearview Limestone Member. The structural geology and early evolution of the Argentine Precordillera is controversial (for review see Astini et al., 1995). Possible source regions could have been from the stable Gondwana craton while the isotopically juvenile input could be the result of erosion of rift related volcanics that intruded the basin during the Caradoc (Keller, 1995) or from an arc - continent collision as the Famatina terrane accreted to the margin (Astini et al., 1995). If this terrane had indeed docked onto the Panthalassic margin of Gondwana then the $\varepsilon(T)$ value is not inconsistent with the northeastern margin (e.g. Clearview Limestone). The source material to these two regions may be similar in that the continental source is likely derived from the Gondwana craton with input from volcaniclastics. The similarities in lithology as well as a well circulated eastern Panthalassic margin can account for the similarities in the Nd isotopic values.

The South China sample, with an $\varepsilon(T)$ value of -11.39, is slightly more radiogenic than the sample from the Arenig-Llanvirn in that area. Comparatively, its signature is still most similar to the waters of the Laurentian Iapetus margin. For this time interval, there are no samples from western Laurentia to allow comparison with South China, so it is difficult to propose juxtaposition for this microplate to Laurentia.

Comparative values in the literature from this time interval include Shaw & Wasserburg (1985) who produced one of the first Nd isotopic values as a proxy for seawater using phosphorites of Ordovician age. This sample, from Tennessee had an $\varepsilon(T)$ of approximately -6. This is slightly more radiogenic than values from Tennessee conodonts (Keto & Jacobsen, 1987) where a value east of the Saltzville Fault (Blockhouse Shale) yielded a value of -8 and a younger sample, taken west of the fault (Holston Fm.), yielded a value of -9. Other values for Laurentian seawater during this time interval include -16.8 (Oklahoma: inarticulate brachiopod) and -19.6 (Pennsylvania: conodonts) (Keto & Jacobsen, 1987). Theses samples generally concur with the values presented in this study for Laurentian inner shelf Iapetus waters during the Llandeilo - Caradoc.

Data from Welsh sediments during this interval show an epsilon range from approximately -9 to -4 (Miller & O'Nions, 1984; Thorogood, 1990; Evans, 1992). Thorogood suggests that excursions in the secular variation curve towards more radiogenic sources may be related to the increased volcanic activity during the Caradoc. Nd isotopic values from the Caban Conglomerates for this time interval have values around -10 to -9 for Central Wales and approximately -9 to -8 for North Wales, within the range of the sediment values reported by Thorogood (1990). The seawater values derived from conodonts overlaps the range for the sediments cited above and is also consistent with the sediment values from earlier time slices for the region. The source of Avalonia sediments was questioned by Thorogood (1990) due to the separation of Avalonia from Gondwana during this interval. He stated, that Gondwana was an unlikely direct source of sediments, and rather the values are a reflection of reworked older Late Cambrian - Tremadoc sediments mixed with the Caradoc radiogenic volcanics.

4.2.4 The Ashgill Interval (443 - 439 Ma; Figure 4.5)

Laurentian Iapetus ε(T) values for the Ashgill are similar to those in past intervals but are slightly more radiogenic and fall close in range to values from Baltica and Avalonia. Samples from the interior of the craton show a trend towards much more radiogenic values when compared to the cratonic margin. It appears the inner cratonic area is a region of increased volcaniclastic input, likely erosion and transport of island arc complexes associated with the Taconic Orogeny. There was also a major phase of volcanism in the Middle Ordovician, resulting in several potential sources of isotopically younger material, including the Bronson Hill Anticlinorium (New England Appalacians), the Barnard volcanics (Vermont), the Ascot volcanics (Québec) and the Carolina Terrane (Virginia, North & South Carlonia) (S. Samson personal communication, 1995). These volcanics may explain the difference between inner cratonic values and shelf values for the Iapetus. The erosion of this volcanic material into the inner cratonic regions may dominate the sedimentary load during phases of uplift of the Taconic Orogeny. One sample from the Churchill River Group, Southampton Island still retains a more non-radiogenic signal of -16.1 and indicates that input is still dominantly from older continental crustal sources.

Even though Avalonia had rifted from Gondwana and was drifting northwards with Baltica, there is still a reasonably tight range between these values and those of the Armorican margin. Baltica and Avalonia have ε(T) values of -9.9 and -7.6 respectively while the Armorican region shows a range from -8.8 to -4.7. These values suggest that much like previous intervals, the source material is stable, relatively younger, continental crust mixing with juvenile volcanic material and it also indicates that the waters of this southern ocean are still well mixed. It appears that for the Ashgill, the waters of the southern Paleotethys Ocean and the Iapetus Ocean were increasingly similar. This may be related to the northward drift of Baltica and Avalonia towards Laurentia and the narrowing of the Iapetus Ocean. As the Iapetus narrowed, mixing was likely enhanced, resulting in a homogenization of the Iapetus Ocean and southern Paleotethys waters.

There are only a few data points for this time interval in the literature; one mentioned previously is a sample from Tennessee produced by Keto & Jacobsen (1987) and also sediments from Wales published by Thorogood (1990). Nd isotopic values of -8 to -7 are consistent with previous values from Welsh sediments and the conodonts from this study.

4.2.5 The Early Llandovery Interval (438 - 436 Ma; Figure 4.6)

Data for this interval are sparse but the values attained are generally consistent with those from previous time slices. The Iapetus margin of Laurentia shows an $\varepsilon(T)$ range of ~-12 to -6 illustrating that the source regions and the ocean circulation in this region has been consistently maintained.

The Siberian value of -1.2 is interesting in that it is much more radiogenic than any of the other samples analyzed. This sample represents a displaced terrane that was not part of the stable craton. This terrane, commonly referred to as the Kolyma terrane, is now sutured to the northeast margin of the ancient Siberian platform and is part of the Verkhoyansk-Kolyma Mesozoides, a Mesozoic orogenic belt (Parfenov, 1991, 1995). It is part of the Omulev Mountains and together with the Tas-Kayakhtakh Uplift and the west Selennyakh Ridge, form the Kolyma loop (Parfenov et al., 1993), also referred to as the Moma - Selennyakh tectonic zone (Parfenov, 1995). The geology of this region is complex and heterogeneous, showing Cordilleran-type terrane accretion (Parfenov, 1991, 1995; Parfenov et al., 1993). The stratigraphy of the Kolyma loop suggest deposition in a miogeosynclinal setting of a passive margin (Field Guide, 1979; Parfenov et al., 1993; Parfenov, 1995) and the early Paleozoic lithology consists of carbonate deposits with conglomerates at the base of the Ordovician (Parfenov, 1991). The position of this microplate is not well constrained but Parfenov et al. (1993) and Parfenov (1995), based on paleomagnetic data, suggested that it may have formed a part of the Siberian continent during the Ordovician and Silurian, rifted in the Middle Devonian, and resutured in the Jurassic.

A full synthesis of the tectonics and sequence of events for this region is unavailable. Correlating the conodont Nd isotopic composition with the regional geology and paleogeography is tenuous at present. It is evident that there must have been significant radiogenic input to these waters in order to explain the high $\varepsilon(T)$ value and a source for this is undetermined. Ophiolites juxtaposed to the Paleozoic carbonates are thought to be of early Paleozoic age (Parfenov et al., 1993; Parfenov, 1995). If so they may represent a possible radiogenic source. Paleogeographic positioning could also be a determining factor in the isotopic composition of this seawater, and this will be discussed further in section 4.4.4. Further studies are needed to elucidate the tectonics of the ancient Siberian platform and its outlying terranes. Additional Nd isotopic analyses can assist in constraining the position of this terrane to the craton proper.

The Silurian conodont samples from this study are of early Llandovery (Rhuddanian) age, whereas the published data from other sources are younger (Aeronian-Telychian). However, it is still important to consider these data as a predictive tool to determine changes in the secular variation curves. Data from Evans (1992) on the Caban Conglomerates, Wales, at 430 Ma reported a range from -7 to -9 with one value of -1.2 while data from Leng & Evans (1994) from sediments of the Welsh Basin, also at 430 Ma, showed a Nd isotopic range, mostly between -7 and -2. Slightly older sediments from Wales have $\varepsilon(T)$ values between -6 and -5 (Thorogood, 1990). The range of values suggests that sources to the Iapetus region during the Llandovery were progressively slightly more radiogenic. This may be the result of increased Taconic material being shed into the Iapetus Ocean. Evans (1992) determined that the source of the Caban Conglomerate Formation was from an Avalonia source that shed detritus into the Silurian basin. Similarly Leng & Evans (1994) suggest that Gondwana was not a direct source of sediments to Avalonia during the Late Ordovician - Early Silurian due to the distance between them, that rather the source of the Nd isotopic signal was from a reworking and mixing of detritus from both Gondwana and Avalonia, supporting the conclusions of Thorogood (1990).

4.3 The Nd Isotopic Evolutionary Trends for the Ordovician and Early Silurian Oceans

$\varepsilon(T)$ values plotted as time slices on paleogeographic maps is one way to represent the data and is useful in the context of testing paleogeographic models. However, this representation can be somewhat blurred since some intervals are of longer duration than others and it is important to display the data in a variety of ways to provide a comprehensive understanding of the evolutionary processes. Figure 4.7 shows the $\varepsilon(T)$ versus T_{strat} for each of the cratons and paleoplates samples. To make the scatter plot easier to view and interpret, an envelope encompasses the data into distinct groupings. The envelope does not represent any standard error or deviation associated with the data points; it is merely a subjective representation showing the broad trends in the data.

From figure 4.7 it is apparent that for most of the Early to Middle Ordovician waters of Laurentia are distinct from those associated other cratons and paleoplates. Laurentia shows an $\varepsilon(T)$ range from -22 to -13 whereas Baltica, Avalonia and various peri-Gondwana terranes fall in a range of -5 to -10. As eastern Laurentia shifts over time to more radiogenic values the Nd isotopic composition of these waters become increasingly similar to the other cratons and various microplates. The evolution of these two main envelopes mimic each other although the shifts for Laurentia are more severe. The general trend is towards increasing values until approximately 470 Ma, followed by shifts towards lower values around 460 - 450 Ma. This is followed by the final change towards increasing values. It is also apparent (Figure 4.7) that South China falls within the envelope of Laurentia rather than that of the upper curve which contains all the peri-Gondwana microplates.

Since the shifts in $\varepsilon(T)$ values are most dramatic for Laurentia where sample distribution is most intense, a more detailed analysis of the marginal oceans of this craton is permitted. The general increase towards more radiogenic values can be interpreted as the reduction of erosion of older Archean terranes due to the widespread deposition of carbonates during this time. This elimination of the older continental crustal sources results in the dominant input being of younger continental crust and mixing with isotopically juvenile volcanics produced by arc volcanism and continent - arc collisions.

The excursion in this curve from 470 - 460 Ma still needs further investigation. Even though the Gull River sample represents an epeiric lagoonal facies , if this sample were removed from the plot, it would not affect the overall shape or evolution of the $\varepsilon(T)$ envelope. However, since no outer shelf samples for the Iapetus were included for this time, it is difficult to assess this curve as a regional signal in the inner craton or as a more extensive cratonic signature. That is, does the excursion represent some change in sedimentary source that effects both inner shelf and outer shelf Iapetus waters, or is the signal simply representative of inner shelf waters. Since the excursion is correlated approximately with the Caradoc transgression, it is possible that reworked Tremadoc, or even older, sediments may be driving the signal. It is difficult to assess how outer shelf Iapetus waters off Laurentia would have been influenced by the reworking of old sediments . If not strongly affected by the transgression then these waters would not likely shift and a trend towards more radiogenic values would be maintained. However, if these waters do show an isotopic shift, then it would illustrate the far-reaching effects of sediment reworking and transport associated with a dramatic global increase in sea-level.

Other secular variation curves have been published by Keto & Jacobsen (1987) for North America and Europe while Evans (1992), with additional data from Thorogood (1990), has published curves for the sediments of the Welsh Basin. When the Keto & Jacobsen (1987) curve is recalibrated to the Harland et al. (1990) time scale, it is complementary to this study in the overall trends. The Keto & Jacobsen (1987) Early Ordovician curve is not adequately sampled to confirm the initial trend towards increasingly radiogenic values in the early Arenig, but it does show the abrupt shift towards non-radiogenic input followed by a resumption towards more radiogenic values by the end Ordovician. Their curve also illustrates the presence of two distinct water masses in the Iapetus region, one associated with North America and the other with Europe. They suggest that the values that represent the waters off North America are typically Panthalassic while those off Baltica represent true Iapetus waters. An alternative interpretation of their data is that the values associated with North America, except for western Laurentia samples, do not represent values for the Panthalassa Ocean but rather represent western Iapetus Ocean values and those of Baltica represent the eastern Iapetus Ocean.

The secular variation curves of Evans (1994) and Thorogood (1990) showed that for the Welsh Basin, a shift towards an increased radiogenic component was associated with increased volcanism in the Arenig and Caradoc, but Thorogood (1990) suggested that by the Late Caradoc, the radiogenic component had ceased. By the Ashgill, values had returned to early Ordovician values (~-8) until the Llandovery where another rise in radiogenic input was quickly followed by a decline to values of approximately -8. He suggested that this decline was due to decreased volcanic activity in the Wenlock. Thorogood (1990) also had several Precambrian and Cambrian samples from the Welsh Basin that show a strong juvenile igneous component (~-3 to -5) that were replaced in the Ordovician by input from older continental crust (~-7 to -8). This was attributed to the Cambrian transgression that resulted in the shutting down of erosion of the juvenile igneous basement. There are too few samples from Wales in this study to test the robustness of Thorogood's (1990) curve, but, at the relevant time frames, the values from conodonts are supportive.

Table 4.1 Neodymium isotopic analytical results from Ordovician - Early Silurian conodont apatite

Sample No.	Craton/ Paleoplate	$^{147}Sm^{a}$ (pm)	^{144}Nd (pm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd^{b}$	2 σ	ε(0)	Error
Tremadoc								
35	Baltica	22.00	147.44	0.1492	0.511328	0.000018	-10.14	0.35
38	Gondwana	1.00	9.15	0.1097	0.511072	0.000099	-15.14	1.94
37	Gondwana	0.78	------------	------------	------------	------------	-----------	----------
62	Kazakhstan	2.30	17.16	0.1337	0.511112	0.000043	-14.36	0.84
1	Laurentia	-----------	------------	------------	------------	------------	-----------	----------
32	Laurentia	6.62	58.94	0.1123	0.510663	0.000012	-23.13	0.24
49	Laurentia	30.66	260.23	0.1178	0.510521	0.000022	-25.91	0.43
52	Laurentia	2.50	24.63	0.1016	0.510571	0.000014	-24.93	0.27
58	South China	-----------	------------	------------	------------	------------	-----------	----------
59	South China	-----------	------------	------------	------------	------------	-----------	----------
Arenig - Llavirn								
57	Armorica	1.39	11.38	0.1219	0.511324	0.000015	-10.22	0.29
56	Armorica	4.67	28.14	0.1660	0.511256	0.000039	-11.55	0.76
47	Baltica	93.61	669.40	0.1398	0.511314	0.000015	-10.41	0.29
33	Baltica	4.73	33.28	0.1420	0.511279	0.000049	-11.10	0.96
3	Baltica	-----------	------------	------------	------------	------------	-----------	----------
34	Baltica	3.66	28.07	0.1304	0.511192	0.000023	-12.80	0.45
48	Laurentia	2.06	23.55	0.0876	0.510651	0.000017	-23.37	0.33

Sample No.	Craton/ Paleoplate	$^{147}Sm^{a}$ (pm)	^{144}Nd (pm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd^{b}$	2σ	$\varepsilon(0)$	Error
Arenig - Llanvirn Continued								
53	Laurentia	5.43	57.65	0.0943	0.510359	0.000012	-29.07	0.24
44	Laurentia	1.72	16.14	0.1066	0.510806	0.000019	-20.34	0.37
50	Laurentia	0.78	8.092	0.0962	0.510660	0.000031	-23.19	0.61
54	Laurentia	----------	-----------	-----------	-----------	-----------	----------	----------
45	Laurentia	0.73	6.70	0.1089	0.510867	0.000044	-19.15	0.86
7	Laurentia	11.69	82.96	0.1409	0.510765	0.000026	-21.14	0.51
26	Laurentia	5.11	42.15	0.1212	0.510931	0.000052	-17.90	1.02
46	Laurentia	2.44	20.73	0.1178	0.510904	0.000116	-18.43	2.27
4	Laurentia	1.09	-----------	-----------	-----------	-----------	----------	----------
51	Laurentia	1.98	18.77	0.1056	0.510968	0.000036	-17.17	0.70
15	Laurentia	31.07	248.46	0.1250	0.510899	0.000019	-18.52	0.37
42	Laurentia	----------	-----------	-----------	-----------	-----------	----------	----------
60	South China	5.76	36.25	0.1589	0.511024	0.000014	-16.08	0.27
Llandeilo - Caradoc								
30	Avalonia	1.97	15.45	0.1274	0.511312	0.000030	-10.45	0.59
36	Laurentia	25.08	139.85	0.1793	0.510758	0.000013	-21.28	0.25
24	Laurentia	----------	-----------	-----------	-----------	-----------	----------	----------
6	Laurentia	60.12	308.92	0.1946	0.510894	0.000013	-18.62	0.25
25	Laurentia	----------	-----------	-----------	-----------	-----------	----------	----------
28	Laurentia	----------	-----------	-----------	-----------	-----------	----------	----------
13	Laurentia	2.30	16.82	0.1366	0.511158	0.000029	-13.46	0.57

Sample No.	Craton/ Paleoplate	$^{147}Sm^{a}$ (pm)	^{144}Nd (pm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd^{b}$	2σ	$\varepsilon(0)$	Error
Llandeilo - Caradoc Continued								
40	peri-Gondwana	-----------	-----------	-----------	-----------	-----------	-----------	----------
55	peri-Gondwana	7.58	58.62	0.1293	0.511349	0.000013	-9.73	0.25
39	peri-Gondwana	1.05	8.51	0.1234	0.511354	0.000030	-9.63	0.59
19	Siberia	0.6584	-----------	-----------	-----------	-----------	-----------	----------
61	South China	1.45	11.02	0.1316	0.511074	0.000026	-15.10	0.51
Ashgill								
22	Armorica	13.16	83.11	0.1583	0.511352	0.000017	-9.67	0.33
23	Armorica	2.88	19.33	0.1490	0.511297	0.000044	-10.75	0.86
43	Armorica	6.98	33.42	0.2090	0.511433	0.000013	-8.09	0.25
21	Avalonia	21.71	118.8	0.1827	0.511565	0.000013	-5.51	0.25
29	Avalonia	4.00	22.51	0.1779	0.511405	0.000015	-8.64	0.29
31	Baltica	3.56	26.61	0.1339	0.511162	0.000013	-13.38	0.25
9	Laurentia	8.46	75.60	0.1119	0.511301	0.000090	-10.67	1.76
10	Laurentia	51.04	483.68	0.1055	0.511259	0.000041	-11.49	0.80
5	Laurentia	20.09	203.97	0.0985	0.511070	0.000016	-15.18	0.31
11	Laurentia	2.41	21.50	0.1120	0.511170	0.000021	-13.23	0.41
27	Laurentia	10.04	76.50	0.1312	0.510832	0.000028	-19.83	0.55
8	Laurentia	5.25	40.41	0.1300	0.511090	0.000023	-14.79	0.45
63	Siberia	-----------	-----------	-----------	-----------	-----------	-----------	----------
20	Siberia	-----------	-----------	-----------	-----------	-----------	-----------	----------

Sample No.	Craton/ Paleoplate	^{147}Sm[a] (pm)	^{144}Nd (pm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$[b]	2 σ	ε(0)	Error
Llandovery								
12	Laurentia	3.92	36.83	0.1065	0.511283	0.000046	-11.02	0.90
17	Laurentia	4.82	40.90	0.1178	0.511046	0.000018	-15.65	0.35
41	Laurentia	3.83	35.52	0.1079	0.510992	0.000014	-16.71	0.27
18	Siberia	4.39	34.00	0.1291	0.511593	0.000038	-4.96	0.74
*16	Avalonia	4.31	15.19	0.2837	0.511569	0.000067	-5.43	1.31
*2	Gondwana	17.37	62.24	0.2791	0.511520	0.000019	-6.39	0.37
*14	Laurentia	9.51	78.43	0.1213	0.510189	0.000090	-32.40	1.76

* Indicates samples that show anomalous values

a Uncertainty is 0.5%

b Data normalized to $^{146}Nd/^{142}Nd=0.724134$

c Deviations in parts 10^4 from present day CHUR ($^{143}Nd/^{144}Nd=0.511847$; Jacobsen & Wasserburg, 1984)

Table 4.2 Initial Nd isotopic values and model ages for Ordovician - Early Silurian conodont apatite

Sample No.	Craton/ Paleoplate	Age (Ma)	$f_{Sm/Nd}$	ε (T)	Error	T_{DM} (Ga)	T_{2DM} (Ga)
Tremadoc							
35	Baltica	494	-0.2414	-7.14	0.35	2.43	1.80
38	Gondwana	510	-0.4425	-9.47	1.94	1.88	2.00
37	Gondwana	494	--------------	--------------	----------	--------------	--------------
62	Kazkhstan	508	-0.3201	-10.27	0.84	2.37	2.06
1	Laurentia	511	--------------	--------------	----------	--------------	--------------
32	Laurentia	505	-0.4288	-17.69	0.24	2.54	2.66
49	Laurentia	505	-0.4010	-20.82	0.43	2.91	2.91
52	Laurentia	500	-0.4832	-18.86	0.27	2.42	2.75
58	South China	500	--------------	--------------	----------	--------------	--------------
59	South China	494	--------------	--------------	----------	--------------	--------------
Arenig - Llanvirn							
57	Armorica	482	-0.3801	-5.62	0.29	1.72	1.67
56	Armorica	477	-0.1561	-9.68	0.76	3.51	1.99
47	Baltica	480	-0.2891	-6.93	0.29	2.15	1.77
33	Baltica	479	--------------	--------------	----------	--------------	--------------
3	Baltica	478	-0.2780	-7.76	0.96	2.29	1.84
34	Baltica	472	-0.3372	-8.80	0.45	2.13	1.92

Sample No.	Craton/ Paleoplate	Age (Ma)	$f_{Sm/Nd}$	ε (T)	Error	T_{DM} (Ga)	T_{2DM} (Ga)
Arenig Llanvirn Continued							
48	Laurentia	491	-0.5546	-16.53	0.33	2.06	2.56
53	Laurentia	485	-0.5208	-22.73	0.24	2.54	3.05
44	Laurentia	485	-0.4581	-14.76	0.37	2.20	2.41
50	Laurentia	485	-0.5107	-16.97	0.61	2.20	2.59
54	Laurentia	485	--------------	--------------	----------	--------------	--------------
45	Laurentia	478	-0.4466	-13.78	0.86	2.16	2.33
7	Laurentia	477	-0.2837	-17.74	0.51	3.32	2.64
26	Laurentia	476	-0.3838	-13.31	1.02	2.35	2.28
46	Laurentia	476	-0.4010	-13.63	2.27	2.31	2.31
4	Laurentia	475	--------------	--------------	----------	--------------	--------------
51	Laurentia	473	-0.4633	-11.67	0.70	1.96	2.15
15	Laurentia	472	-0.3643	-14.20	0.37	2.50	2.35
42	Laurentia	470	--------------	--------------	----------	--------------	--------------
60	South China	472	-0.1921	-13.80	0.27	3.69	2.31
Llandeilo - Caradoc							
30	Avalonia	467	-0.3524	-6.32	0.59	1.85	1.71
36	Laurentia	463	-0.0883	-20.25	0.25	6.99	2.80
24	Laurentia	460	--------------	--------------	----------	--------------	--------------
6	Laurentia	456	-0.0106	-18.50	0.25	1.14	2.62

Sample No.	Craton/ Paleoplate	Age (Ma)	$f_{Sm/Nd}$	ε (T)	Error	T_{DM} (Ga)	T_{2DM} (Ga)
Llandeilo - Caradoc Continued							
25	Laurentia	456	--------------	--------------	---------	--------------	--------------
28	Laurentia	453	--------------	--------------	---------	--------------	--------------
13	Laurentia	444	-0.3057	-10.05	0.57	2.37	1.99
40	peri-Gondwana	462	--------------	--------------	---------	--------------	--------------
55	peri-Gondwana	446	-0.3429	-5.89	0.25	1.82	1.66
39	peri-Gondwana	444	-0.3725	-5.48	0.59	1.70	1.63
19	Siberia	462	--------------	--------------	---------	--------------	--------------
61	South China	447	-0.3308	-11.39	0.51	2.38	2.10
Ashgill							
22	Armorica	443	-0.1950	-7.50	0.33	2.76	1.78
23	Armorica	443	-0.2424	-8.05	0.86	2.50	1.83
43	Armorica	443	0.0624	-8.78	0.25	2.79	1.77
21	Avalonia	443	-0.0712	-4.72	0.25	3.88	1.55
29	Avalonia	442	-0.0958	-7.57	0.29	4.03	1.78
31	Baltica	441	-0.3192	-9.85	0.25	2.28	1.98
9	Laurentia	441	-0.4309	-5.89	1.76	1.58	1.66
10	Laurentia	441	-0.4635	-6.35	0.80	1.55	1.69
5	Laurentia	442	-0.4993	-9.64	0.31	1.70	1.96
11	Laurentia	441	-0.4304	-8.46	0.41	1.78	1.86
27	Laurentia	441	-0.3328	-16.14	0.55	2.81	2.48

Sample No.	Craton/ Paleoplate	Age (Ma)	$f_{Sm/Nd}$	ε (T)	Error	T_{DM} (Ga)	T_{2DM} (Ga)
Ashgill Continued							
8	Laurentia	440	-0.3390	-11.04	0.45	2.31	2.07
63	Siberia	443	--------------	--------------	----------	--------------	--------------
20	Siberia	440	--------------	--------------	----------	--------------	--------------
Llandovery							
12	Laurentia	438	-0.4585	-5.97	0.90	1.53	1.66
17	Laurentia	438	-0.4011	-11.24	0.35	2.08	2.09
41	Laurentia	437	-0.4513	-11.75	0.27	1.97	2.13
18	Siberia	438	-0.3436	-1.18	0.74	1.38	1.27
*2	Gondwana	472	0.4189	-11.36	0.37	-1.97	-------------
*14	Laurentia	472	-0.3835	-27.85	1.76	3.55	3.45
*16	Avalonia	443	0.4421	-10.35	1.31	-1.74	2.04

* Indicates anomylous samples

[a] Harland et al., 1989

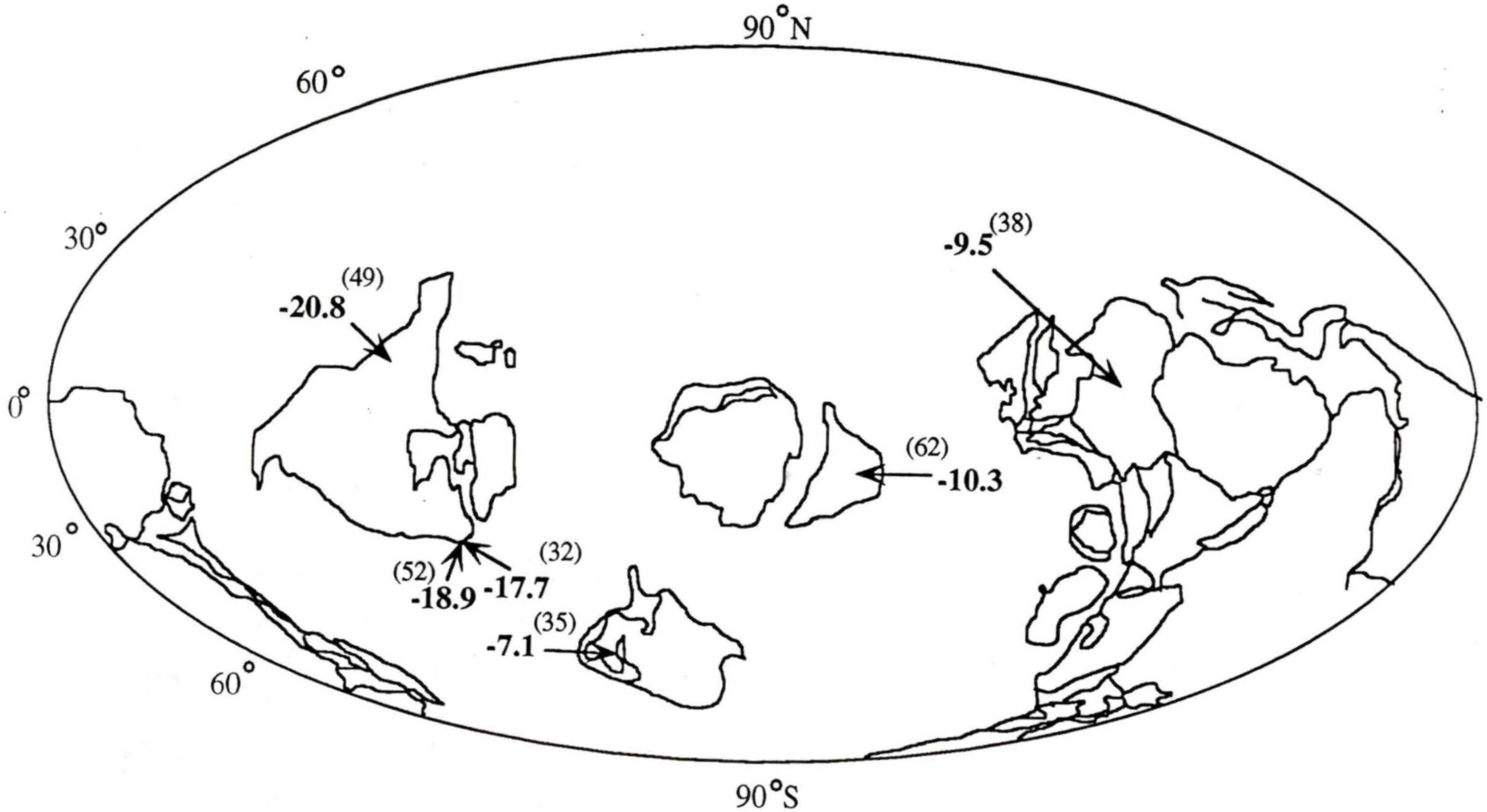


Figure 4.2. Nd isotopic composition of Tremadoc interval (510 - 493 Ma) oceans derived from conodont apatite. Paleogeographic reconstruction after Scotese & McKerrow, 1991. Bracketed numbers refer to sample numbers.

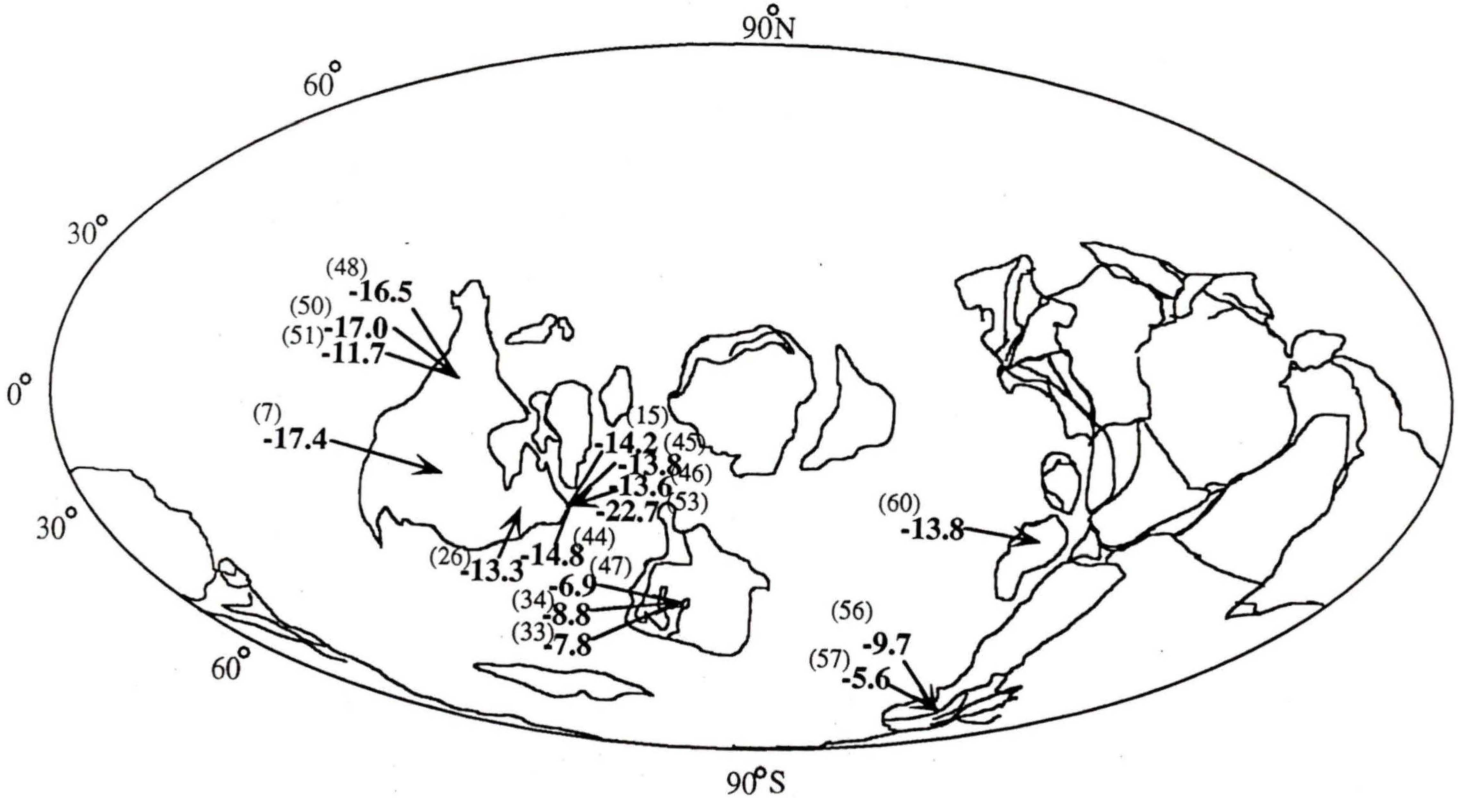


Figure 4.3. Nd isotopic composition of Arenig - Llanvirn interval (492 - 469 Ma) oceans derived from conodont apatite. Paleogeographic reconstruction after Scotese & McKerrow, 1991. Bracketed numbers refer to sample numbers.

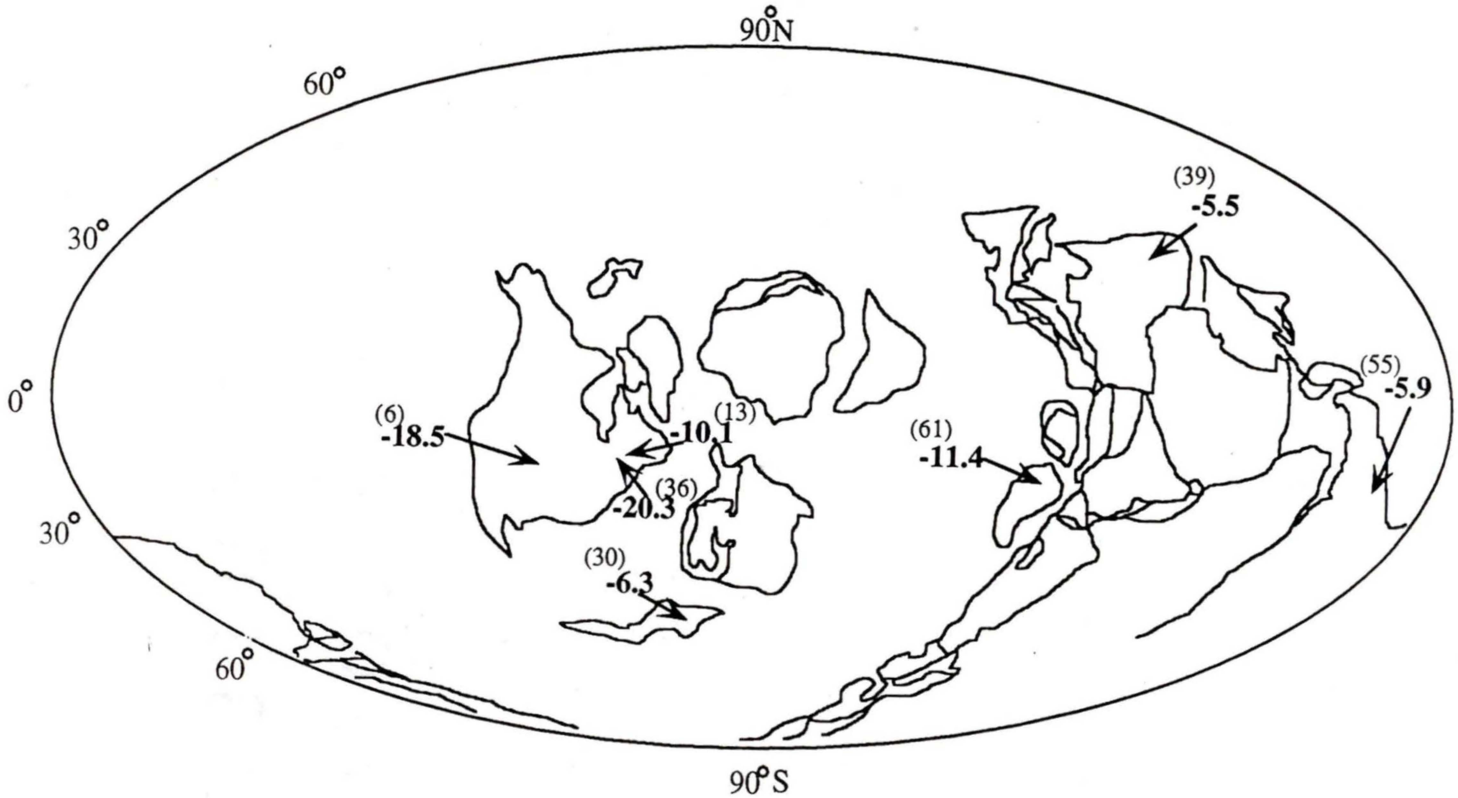


Figure 4.4. Nd isotopic composition of Llandeilo - Caradoc interval (468 - 444 Ma) oceans derived from conodont apatite. Paleogeographic reconstruction after Scotese & McKerrow, 1991. Bracketed numbers refer to sample numbers.

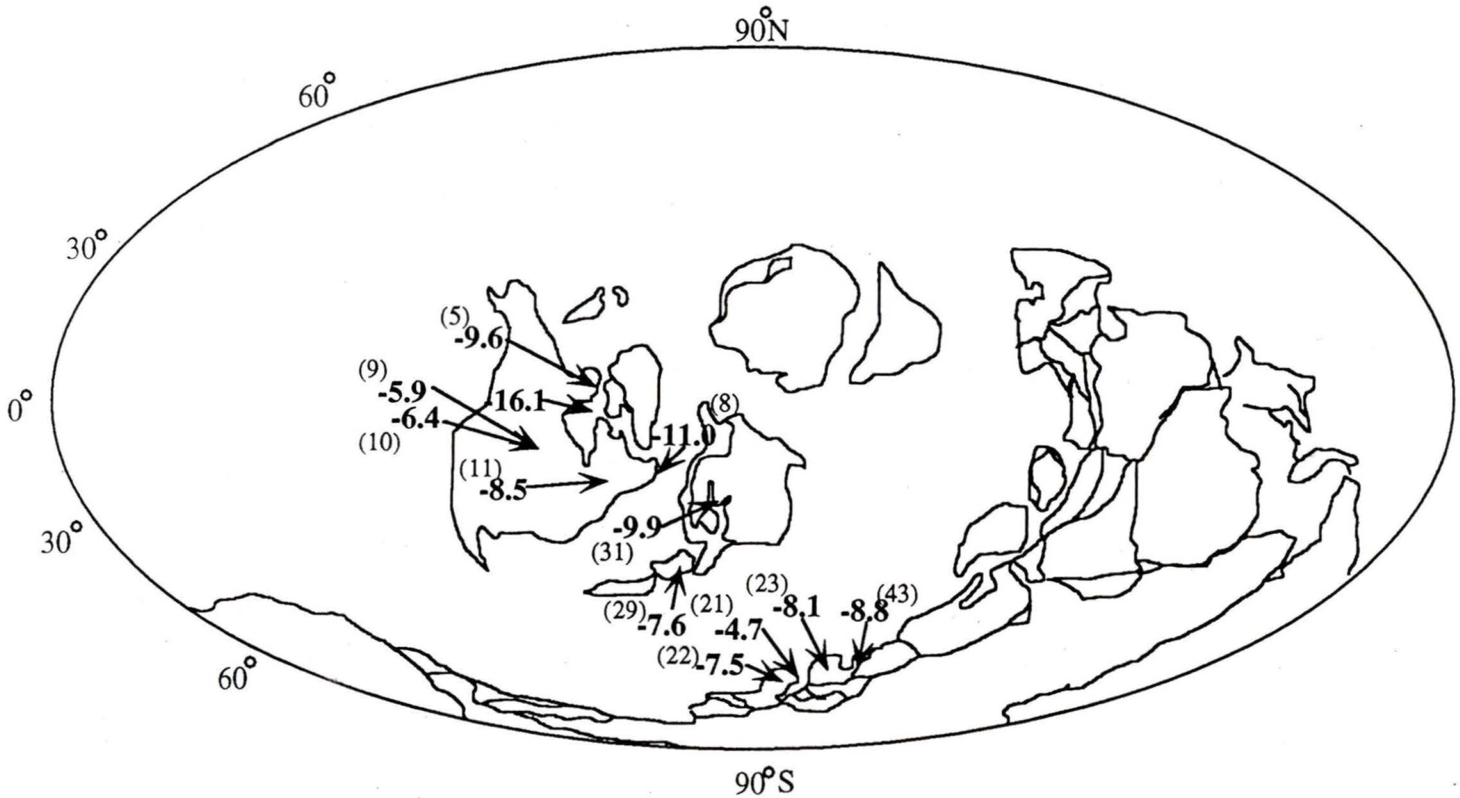


Figure 4.5. Nd isotopic composition of Ashgill interval (443 - 439 Ma) oceans derived from conodont apatite. Paleogeographic reconstruction after Scotese & McKerrow, 1991. Bracketed numbers refer to sample numbers.

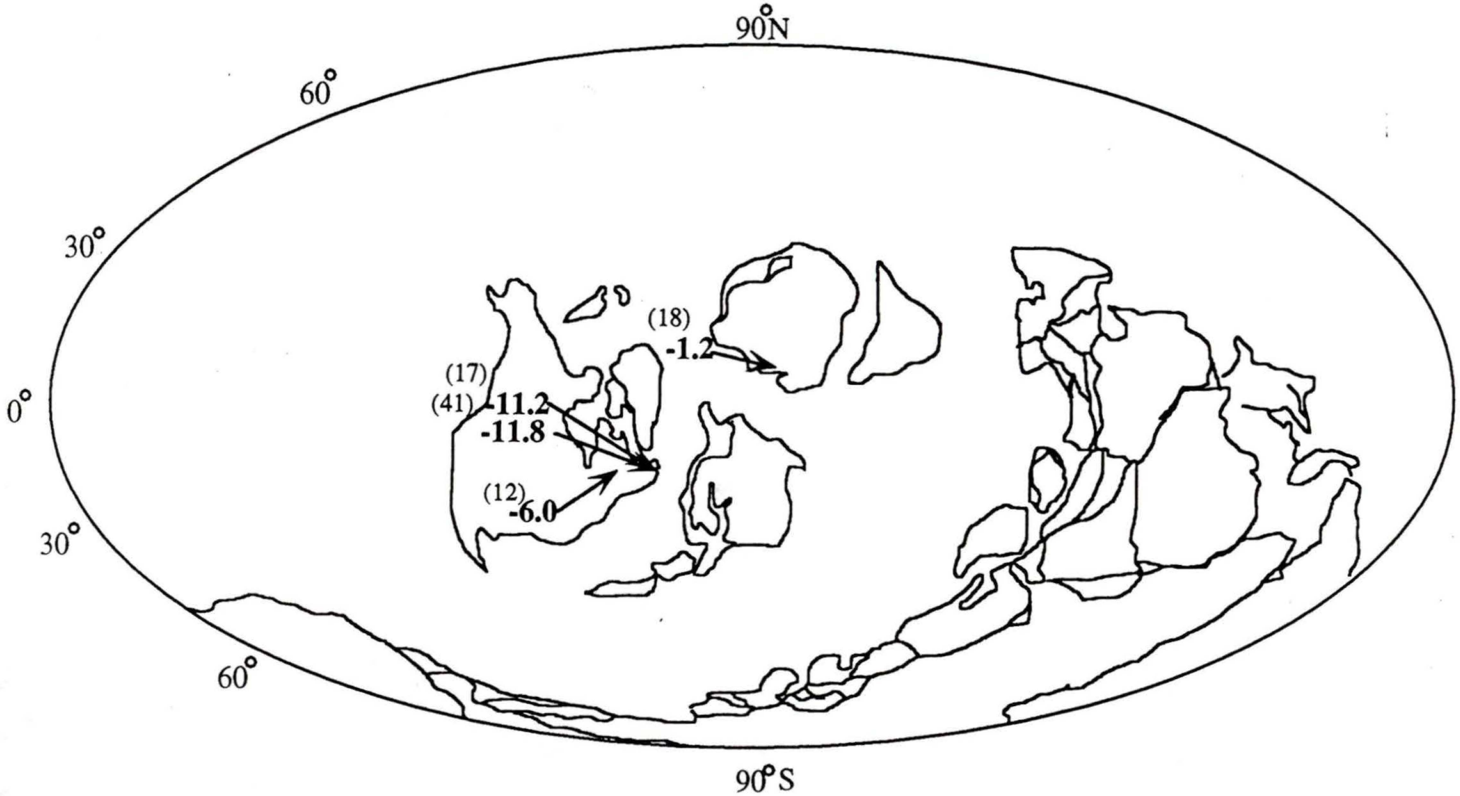


Figure 4.2. Nd isotopic composition of Llandovery interval (438 - 436 Ma) oceans derived from conodont apatite. Paleogeographic reconstruction after Scotese & McKerrow, 1991. Bracketed numbers refer to sample numbers.

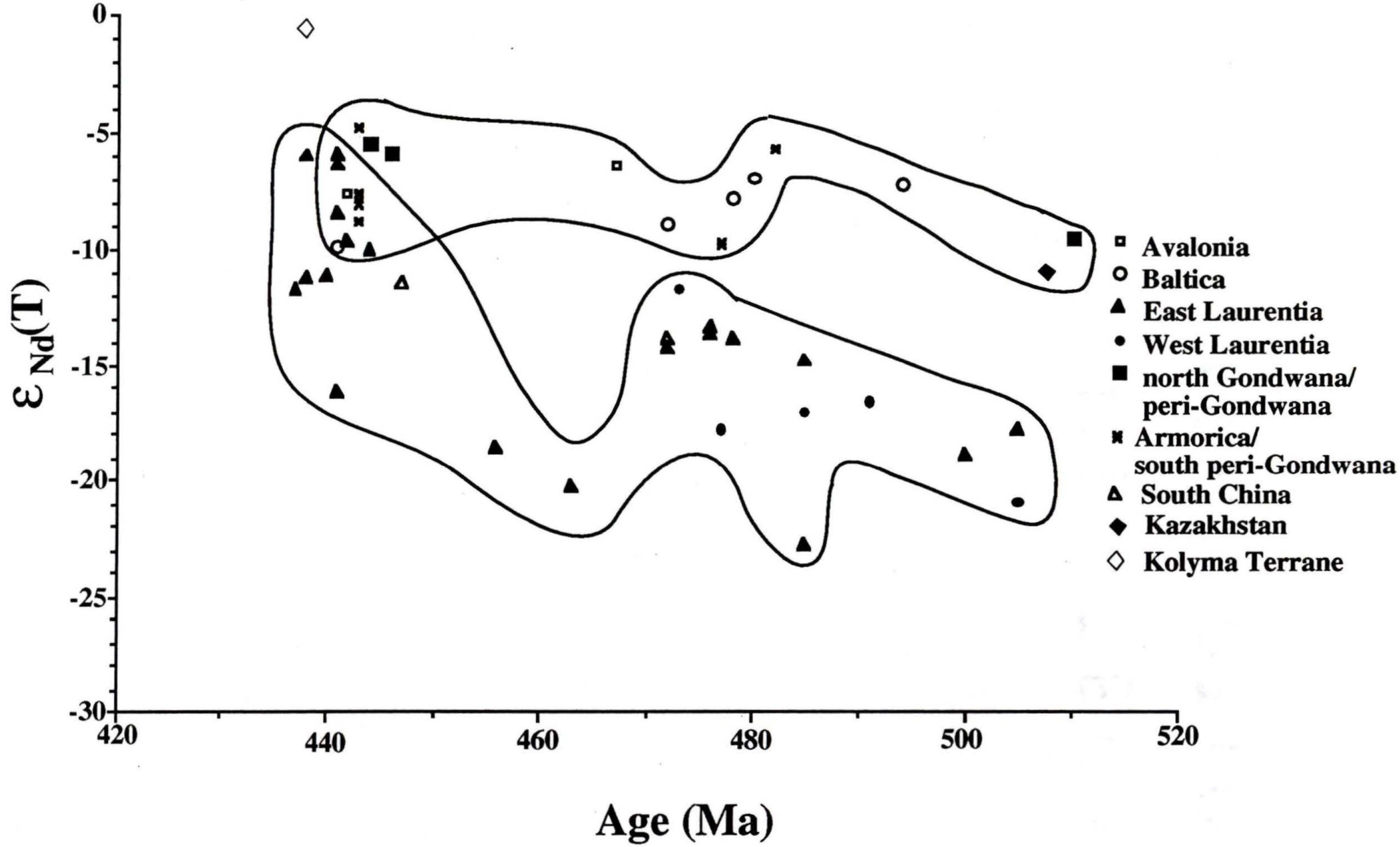


Figure 4.7. Nd isotopic secular variation trend for the Ordovician - Early Silurian oceans as derived from conodont apatite, this study.

4.4 Testing Paleogeography

The ability to test paleogeographic reconstruction models for any period in geologic time is a function of the size and quality of the database. When considering the Nd isotopic dataset, with the exception of Laurentia and Avalonia, the published dataset for the remaining cratons and microplates during the Ordovician - Early Silurian is modest. Further, most of the data for Laurentia and Avalonia are from sediments. Even though these data are a valuable component in developing a more comprehensive picture of the Early Paleozoic, Nd isotope studies are still in their infancy, consequently, testing paleogeographic reconstructions is difficult

4.4.1 Laurentia

The equatorial position for the cratonic core of Laurentia has been widely accepted for many years. Paleopoles are well defined and are in agreement with paleoclimate/lithology and faunal information (Van der Voo, 1988; Li et al., 1993; Kent & Van der Voo, 1990). The Nd isotopic data generated from the eastern and western margins of this craton were not to test the location or configuration of the craton but rather to determine the Nd isotopic composition of its epeiric seas and adjacent oceans and how these change through time while being affected by tectonics, erosional fluxes, and eustasy. The alternative paleogeographic reconstruction of Dalziel et al. (1994) does affect the eastern margin of Laurentia, and will be discussed in part B of section 4.4.2.

4.4.2 Gondwana and peri-Gondwana Terranes

Although there are some apparent discrepancies in the literature (for review see Li et al., 1993), the southern paleopoles of the major blocks of Gondwana generally group around northwest Africa. In the model of Scotese & McKerrow (1991) the orientation of Gondwana is a function of paleoclimate information derived from Scotese & Barrett (1990) rather than paleomagnetics. With the general paucity of carbonates, relatively few samples were analyzed and the majority of these represent peri-Gondwana terranes.

A) Gondwana

Australia

For the Tremadoc, the sample from the Ninmaroo Formation, Georgina Basin, Northern Territory represents the Nd isotopic composition of seawater residing in an inner cratonic basin and interacting with the northern Paleotethys. This value is also important in the context of the neighbouring microplate, Kazakhstan (discussed in section 4.4.5).

For the Caradoc, the Clearview Limestone, New South Wales, is situated on the stable craton in most reconstructions. However, VandenBerg & Stewart (1992) suggested that the Molong High, of which the Clearview Limestone represents a section of the western flank, was an off-shore volcanic island-arc complex. The signature of the sample suggests significant isotopically juvenile input, but it also detects some mixing with stable continental crust. It is in general agreement with the regional geological reconstruction with the western flank of the Molong High being bordered by volcanics on the east and the stable platform craton on the southwest. The Nd isotopic data can not delimit how far this island was offshore, but it is apparent that continental input was still a contributor to the arc basin. This value is also important because of its similarity to that of the Argentine Precordillera (discussed in part B; peri-Gondwana terranes)

South China

The positioning and orientation of South China has been a considerable problem and paleomagnetic data have not solved this issue (for review see Li et al., 1993). The paleopoles place the Yangtze region in a low paleolatitude and this is in general agreement with the paleoclimate data (Li et al., 1993). Faunal data suggest affinities between the South China and Australian blocks of Gondwana (Young, 1990) supporting the positioning of South China close to Australia in many reconstructions.

There are only two samples from South China, one in the Arenig and the other in the Llandeilo - Caradoc. Both of these sites have Nd isotopic values that are similar to those for Laurentia. Since there are no data from IndoChina, North China or Iran, it is difficult to substantiate the position of South China relative to these other peri-Gondwana blocks. The isotopic values are different from the values of the Armorican and Avalonian microplates in the southern Paleotethys. It is quite possible that South China was in closer proximity to Laurentia than suggested by the Scotese & McKerrow (1991) model.

B) Peri-Gondwana Terranes

Some smaller crustal blocks appear to have been located close to Gondwana during the Ordovician - Early Silurian interval, with several rifting and migrating away during this time.

Avalonia and Armorica

Paleomagnetic results (Johnson et al., 1988; Torsvik et al., 1990; Channel et al., 1992; Trench et al., 1992) are in general agreement that Avalonia was situated at a high southerly latitude during the early Ordovician. It contains a Pan-African basement and was likely adjacent to the northern margin of Africa and the Armorican plate (Scotese & McKerrow, 1990; Van der Voo et al., 1990; Torsvik & Trench, 1990). Avalonia apparently rifted from the margin of North Africa during the Arenig and subsequently traveled north (Van der Voo & Johnson, 1985). One scenario suggests that it came into contact with Baltica, possibly during the late Ashgill and both traveled northwest until their eventual collision with the northern and eastern margins of Laurentia during the Acadian Orogeny in the Late Silurian (Scotese & McKerrow, 1990; Soper et al., 1992; Trench & Torsvik, 1992). Armorica has a similar basement to Avalonia (Van der Voo, 1988) and northeastern Africa (Noblet & Lefort, 1990). Paleomagnetic data suggest a similar high southerly latitude during much of the Ordovician (Perroud & Van der Voo, 1985; Perroud et al., 1984, 1986; Torsvik et al., 1990; Torsvik & Trench, 1991).

No samples represent the northern margin of Africa so it is not possible in this study to compare the positioning of Avalonia against this region of Gondwana and unfortunately, there are no samples until the Llandeilo - Caradoc. However the data for Armorica and Avalonia overlap the Llandeilo - Caradoc, even when Avalonia had supposedly begun its northward drift. It can not therefore, be determined whether there was a separate ocean mass (e.g. initial Rheic Ocean) between them following the rifting of Avalonia. Possibly there was complete circulation in the southern Paleotethys. During the Late Caradoc - Ashgill, it is likely that bottom water formation and invigorated circulation occurred with the growth and progression of the ice sheets across North Africa.

Alternatively, Armorica may have rifted and been in closer proximity to Avalonia and Baltica then previously considered. However this is not supported by the faunal evidence (Section 2.3.1) and there is no paleomagnetic data to support the rifting of Armorica until Late Devonian times (Van der Voo, 1988).

Argentine Precordillera

The timing and evolution of the Precordilleran region are only now becoming understood. Section 2.3.1 describes the alternative interpretations and paleogeographic reconstructions of these displaced terranes. In order to test paleogeographic patterns a few assumptions must be made. The Precordilleran terrane docked with Gondwana at 450 Ma (Taconic & Famatinian orogeny) (Dalla Salda et al. 1992a, b; Dalziel et al. 1994). Unfortunately, the single Nd isotopic analysis from this study can not assist in directly testing the model and in tracking the evolution of the terrane. The sample that from the Precordillera (sample no. 55) has an age of 446 Ma, in the A. superbus zone. This post-dates accretion to Gondwana, hence its would have a typical marginal Gondwana signal. A way to test the reconstruction would be to sample the Famatina terrane through time. For example, to test the Astini et al. (1995) model, samples of the terrane through the Ordovician could be analyzed to see if the terrane initially shows a Laurentian signature with gradual shifts to more radiogenic values associated with the crossing of the Iapetus and eventual collision with Gondwana.

Although this sample represents a post-docking age and shows a typical Gondwana signal, Torsvik et al. (1995) pointed out that in Dalziel et al.'s 1994 model, the distance of separation between eastern Laurentia and the Argentine Precordillera would be small, hence the Iapetus Ocean would have to be narrower than predicted by other models such as Scotese & McKerrow (1991). However, in comparing the Nd data for these two regions, there is a difference of at least five epsilon units. The higher radiogenic signature from this region of Gondwana would not be expected if it was in such close proximity to Laurentia with its more non-radiogenic signature. It is difficult to reconcile two laterally separate ocean masses in such a narrow ocean.

A final consideration are the bentonite ash beds that were deposited during a period of significant volcanic activity. Huff et al. (1992) argued that there is a direct correlation between the deposits in eastern North America and those in Scandinavia. However, Haynes et al. (1995) has recently called this into question, stating that based on biotite phenocryst composition, these beds are not correlative and represent three different magmatic sources. If the correlation of Huff et al. (1992) is correct, then Baltica must have been adjacent to eastern Laurentia. There are bentonite beds in the Argentine Precordillera but they are older than those in eastern North America and Scandinavia (Huff et al., 1995).

In the Scotese & McKerrow (1991) model, the placement of the Argentine margin of the Panthalassa is in general agreement with the more northern value from the Clearview Limestone, Australia. The Argentinean sample is similar in that it records isotopically juvenile material being mixed with stable continental crust. The source of the continental crust is difficult to reconcile as the basement of the region is unknown (Astini et al., 1995), however, it may be derived from Gondwana. Astini et al., (1995) suggested that the prior to accretion to Gondwana, the Precordillera was an island arc complex, the Famatina terrane. If this scenario is correct than the Famatina terrane could be responsible to the more radiogenic signal.

4.4.3 Baltica

Paleomagnetic data for Baltica (Perroud et al., 1992; Torsvik et al., 1992) are reasonably well constrained and the faunal and paleoclimate data are in agreement with an initial southerly high latitude during the early Ordovician with a drift towards more equatorial positions in the Middle and Late Ordovician (Cocks & Fortey, 1982; 1990; Van der Voo, 1988; Scotese & McKerrow, 1990, 1991; Torsvik et al., 1992). Data are also in agreement with a convergence of the paleopoles for Laurentia and Baltica in the Late Silurian (Torsvik et al., 1990). The Nd isotopic values for Baltica determine the range of values for the eastern Iapetus Ocean. There are no significant shifts in epsilon units associated with its northward drift although it does show a slightly more non-radiogenic component during the Ashgill possibly due to increased mixing with the more negative western Iapetus waters.

One of the problems with the Scotese & McKerrow (1991) positioning of Baltica is that they did not have the opportunity to incorporate data published by Perroud et al. (1992) and Torsvik et al. (1992). Based upon their paleomagnetic measurements, Baltica was in a geographically inverted position in the Late Precambrian - Cambrian. By the onset of the Ordovician, the inlet of the present day Baltic Sea faced westwards, an approximately 90° clockwise rotation difference to the Scotese & McKerrow models (1990, 1991). However, this does not affect the interpretation of the Nd isotopic results. Firstly, erosion peneplaned the platform and left it with a westerly slope (Gorbatschev, 1985). This would cause sediments to wash directly into the Iapetus Ocean. Secondly, irrespective of the westerly slope, an extensive epicontinental sea covered much of the Baltic platform. This would likely have caused eroded materials to be transported in other directions as well. Hence, the isotopic values do not simply represent the eastern Iapetus Ocean, they represent the isotopic composition of the circum-Baltic marginal waters.

The reconstruction by Paris & Robardet (1990) is considerably different in its treatment of Gondwana, Avalonia and Baltica. The Armorican plate is rotated into a more easterly position and Avalonia is placed as a southwest tongue of Baltica. In comprehensive reviews, Fortey & Mellish (1992) and Fortey & Cocks (1992) criticized this reconstruction arguing that it used an inappropriate fossil group to constrain the biogeographic patterns and that the authors failed to include critical data that did not support their reconstruction. Unfortunately, the Nd isotopic data from this study does not resolve this conflict. There is a general homogenization of isotopic signals from Avalonia, Armorica and Baltica which could be due to a variety of factors mentioned previously. The data do not show any evidence of a discrete Rheic Ocean or a South

Armorican Ocean that was reported by Paris & Robadet (1990) to have existed as early as the late Tremadoc - Arenig. The Nd isotopic data define similar isotopic values for the southern Paleotethys and do not indicate any other water body during the Ordovician Period. This may be due to strong east - west circulation in this region which would have a homogenizing influence.

The positioning of Baltica proposed by Dalziel et al. (1994) is difficult to reconcile. As discussed previously, the Torsvik et al. (1995) model does not violate the paleomagnetic constraints. However, in the Dalziel et al. (1994) reconstruction at 450 Ma, Baltica is a considerable distance from Laurentia. It does not account for the positioning of Avalonia or Armorica. Even if these microplates are assumed to be in the same position as the Scotese & McKerrow model, the Nd isotopic results from this study can not resolve this debate, at least with respect to the placement of Baltica. If the $\varepsilon(T)$ values are plotted on their reconstruction, they would only resolve the range of values for the Tornquist Sea, rather than the western Iapetus.

Nd analyses could resolve this debate but it would require more extensive sampling. The lack of carbonates for northern Africa and northern South America will make sampling for conodonts difficult.

4.4.4 Siberia

Prior to 1995 there were few published paleopoles for Siberia. Data from Khramov et al. (1981) in cooperation with lithological information placed Siberia in tropical latitudes, adjacent to the northern margin of Laurentia. New paleopole measurements from Torsvik et al. (1995) confirm this and suggest a drift towards more temperate latitudes towards the late Ordovician - early Silurian. However, the sample for Siberia in the early Silurian is from the Kolyma terrane, in the Omulev Mountains. This terrane was not accreted to the Siberian craton until the Mesozoic and its paleoposition is uncertain. Little has been published on the regional or stratigraphic geology of this terrane (see section 4.2.5) but brachiopod evidence suggests that the Kolyma terrane was in close proximity to the northern edge of Laurentia (Rong & Harper, 1988). If Kolyma was part of Siberia during the early Paleozoic there is doubt about its positioning near Laurentia. For this time interval, there are no samples from this region of Laurentia (present day Arctic) but there are in the Ashgill. When these are compared, it is evident that the Kolyma is significantly more radiogenic than the neighbouring values of Laurentia. This indicates that the Kolyma was not influenced by the sediments or the waters encircling Laurentia. If Kolyma was adjacent to the northern margin of Laurentia it should show a more diluted non-radiogenic signal as Laurentia would be a potential non-radiogenic sediment source.

The radiogenic signature of this sample, and that of the brachiopod samples from Siberia published by Keto & Jacobsen (1987) are interesting in that they indicate a strong isotopically juvenile component in the sediment load. This could be a function of the paleogeographic positioning of the Siberian craton and the Kolyma terrane. For most of the Ordovician, the northern hemisphere was devoid of prominent longitudinal barriers to circulation. Most of the major land masses were situated in the southern hemisphere and the northern Panthalassic Ocean had essentially unobstructed circulation above 30° north. This translates into this northern ocean being predominately influenced by younger oceanic crustal material, rather than input from continental crust. Hence, the signal displayed by the Kolyma and possibly the Siberian craton, is the signatures that represents the northern Panthalassic Ocean, which was a distinct water mass due to the globally encircling northern currents. If this is accurate, then the Siberian craton in the Arenig-Llanvirn, and the Kolyma, in the Llandovery, were likely further north than the Scotese & McKerrow (1991) model predicts so that they would not have been influenced by southern circulation processes.

4.4.5 Kazakhstan

There are no systematic paleomagnetic measurements that delineate the position of the Kazakhstan terranes in the early Paleozoic (Li et al., 1993) and the Nd isotopic values from this study provide limited information. The latter data essentially provide a value for the northern Paleotethys in the Tremadoc. It is in good agreement with those from northern Gondwana (Ninmaroo Formation, Australia) supporting the positioning in the Scotese & McKerrow (1991) model. Since Kazakhstan was apparently a series of arcs and exotic terranes future work will need intensive sampling to understand the evolution of this microplate.

4.4.6 Testing Displaced Terranes

Nd data exist from the sediments of the Southern Uplands of Scotland, the Dalradian sediments of Scotland, and the Eastern Central Mobile Belt of western Newfoundland. Since these regions were not sampled for this study, they were not integrated into the discussion of the time slices. However, the Nd isotopic data from these microplates can help constraint their paleogeographic positions.

The Dalradian (Late Precambrian - early Paleozoic) sediments of Scotland are a thick sequence of unfossiliferous metasediments, sandwiched between the Highland

Border Complex and the Durness Limestone, both of which have Ordovician strata that contain faunas with Laurentian or Appalachian affinities (Curry & Williams, 1984; Curry et al., 1984). Presently the Dalradian sediments span across Scotland to western Ireland. Deposition of the Dalradian initiated during the rifting to the Proterozoic supercontinent (Piper, 1983), developing on the northwest margin between the rifting and dispersing plates, Laurentia and Baltica. The upper Dalradian is suggested to have formed on the continental margin of Laurentia (Anderton, 1982). O'Nions et al. (1983) report $\varepsilon(T)$ values of -19 to -18 for Tremadoc Dalradian slates, indicating that these sediments were influenced predominately by Archean continental crust. These values fall into the $\varepsilon(T)$ curve of Laurentia for that time and supports the idea that the Dalradian was deposited on the margin of Laurentia along the Iapetus Ocean.

The Southern Uplands (SU) of Scotland is thought to represent an accretionary prism deposited on the northwest margin of the Iapetus Ocean (Leggett et al., 1979). Other interpretations suggest a thrust stack transitional from a back arc to foreland basin on the Laurentian margin (Stone et al., 1987). Stone & Evans (1995) presented a thorough Nd isotopic analysis of greywacke samples from the SU, including previously published values of O'Nions et al. (1983). The data suggested that the SU in the Ordovician had two provenances; a volcanic arc and a basement provenance. The arc shows a characteristic radiogenic signal of -3 to -2 whereas the basement has a range of -12 to -8. By the Ashgill and Llandovery, these provenances were indistinguishable with a range of values from -8 to -5. The authors suggested that these data are compatible with a foreland basin transition. Assuming that there is good agreement between sediment and seawater values, the Nd isotopic data support the SU being placed in the northwest region of the Iapetus Ocean off the northeast (present day) margin of Laurentia.

The Eastern Central Mobile Belt (ECMB) of Newfoundland includes the Gander Zone, parts of the Exploits Subzone and the Avalon Zone. The rocks consist of granitoid suites and metasediments underlain by Gondwana basement (for review of the tectonostratigraphy see Williams et al., 1988). As mentioned above, faunal affinities imply a close position to Avalonia/peri-Gondwana in the early Ordovician (Williams et al., 1992). Nd isotopic values for metasediments with a minimum age of 470 Ma have a range of $\varepsilon(T)$ values from -8 to -6.5 and the granitoid suites show a range of -8 to -2. The T_{DM} values for the metasediments are 1.6 to 1.54 Ga (Kerr et al., 1995. Both the epsilon values and the depleted mantle ages indicate that the affinities for the ECMB in the Arenig are with the eastern Iapetus waters, those off Avalonia and Baltica . This is supported by faunal evidence from the Arenig of the Exploits Subzone where graptolites and trilobites show Avalonia/peri-Gondwana affinities (Williams et al., 1992).

Summary

In the Early Ordovician, distinct ocean masses and the dispersion of the cratons and microplates is borne out by the Nd isotopic values that support the presence of distinct water masses. As Laurentia was separated from other land masses, its east and west margins show different isotopic values associated with the western Iapetus and the Panthalassa Ocean, respectively. These values are distinct from those representing Baltica, Gondwana and peri-Gondwana terranes. These samples delineate the Nd isotopic composition of the eastern Iapetus Ocean, southern and northern Paleotethys Ocean. Changing paleogeographic configurations and the Taconic Orogeny are reflected in the changing isotopic values as the signatures for Baltica/Avalonia and eastern Laurentia become increasingly similar as the former drifts northwards after closure of the Tornquist Sea. By the Late Ordovician there is complete overlap in the values from both sides of the Iapetus as these two formerly distinct water masses mix and the southern hemispheric oceans become isotopically homogenous, perhaps signaling enhanced circulation as a result of converging land masses.

On a finer scale, there are some microplate configurations that can be called into question in the Scotese & McKerrow (1991) model. The Nd isotopic composition of South China is closest to that of Laurentia rather than Gondwana or the other peri-Gondwana terranes, suggesting that perhaps this microplate is misplaced in the reconstruction. Additionally, it is suggested here that the Kolyma terrane, and perhaps the Siberian craton, represent the isotopic value for the northern Panthalassic Ocean . This can be verified by further sampling, however if it continues to be true, then to maintain such a distinct value, these land masses must have been located farther north than indicated by Scotese & McKerrow (1991) in order for this water mass to have not been influenced by southern hemispheric circulatory processes.

Finally, as the Nd database grows, the range of values for each ocean mass will become more defined. As the global ocean values are delineated, it will become easier to model the relative position of displaced terranes by placing them in the appropriate ocean mass.

4.5 Relationships between Nd Isotopic Data and Conodont Paleobiogeography

By the end of the Tremadoc and into the Arenig, marked faunal provincialism of conodonts, graptolites, and trilobites had developed (Sweet et al., 1959; Sweet & Bergström, 1962, 1974; Barnes et al., 1973b, in press; Bergström, 1971, 1973, 1990). For conodonts, two realms were present: the Midcontinent Realm and the North Atlantic

Realm. There is general agreement that provincialism developed in response to continental dispersion and latitudinal constraints that controlled physical conditions such as temperature and salinity (Miller, 1984; Sweet & Bergström, 1984; Bergström, 1990). The Midcontinent Realm includes tropical, warm water faunas (Sweet & Bergström, 1974), highly diversified and adapted to low latitudes and relatively shallow water conditions (Barnes & Fårhæus, 1975). The North Atlantic Realm includes faunas that are indicative of a more temperate, cool water environment (Sweet & Bergström, 1974) and the conodonts are viewed as a more normal marine fauna with a wide spectrum of shallow and deep environments (Barnes & Fårhæus, 1975).

By the Arenig, the realms were quite distinct (for review see Charpentier, 1984). Conodonts from the Laurentian Province (Midcontinent Realm) are discrete from those of the Baltic Province (North Atlantic Realm) (Miller, 1984; Bergström, 1990). Faunas (e.g. trilobites, brachiopods) of the Gondwana inner shelf and Avalonia are more endemic compared to those of Laurentia or Baltica (Cocks & Fortey, 1982; 1990; Fortey & Cocks, 1992; Fortey & Mellish, 1992). Although in some regions of Gondwana (e.g. Iran), there are trilobites and shelly faunas of mixed affinities (Cocks & Fortey, 1990). The Mediterranean Province (Dzik, 1983; Gutiérrez Marco & Rábano, 1987; Bergström, 1990; Cocks & Fortey, 1990), led Cocks & Fortey (1982) to deduce that there must have been oceanic separation between Gondwana and Baltica which they termed the Tornquist Sea.

Correlating the Nd isotopic signatures of the samples with patterns of conodont faunal provincialism is tenuous. Within a single realm, Nd isotopes have a varying correlation. For the Midcontinent Realm, Nd isotopic differences between the Laurentian and Australian Province in the Early Ordovician are easy to reconcile as the Kazakhstan microterranes and the Siberian craton likely acted as barriers to east - west circulation. As a result, there are two distinct water masses associated with these regions, and their faunas are also distinct since it is unlikely that they could have circumvented these barriers and cross into the Laurentian Province.

Faunal provincial regions of the North Atlantic Realm are, however, not correlative with the Nd isotopic data. Conodont faunal differences between Avalonia, Armorica, and Baltica are not apparently the result of distinct water masses that are not mixing. The Nd isotopic signals of these regions are overlapping, hence a distinct southern Paleotethys mass can not be distinguished from the eastern Iapetus mass. This holds true for the Late Ordovician as well, where the Iapetus Ocean becomes isotopically indistinguishable from the southern Paleotethys, although the faunas do retain some provincialism (Barnes & Bergström, 1988). Some other factor was likely controlling conodont provincialism in this region.

Even correlation within a realm can be problematic. In the Tremadoc, the Midcontinent Faunas of the Boat Harbour Formation showed a similar isotopic signal to that of Green Point Formation which has North Atlantic affinities. However, the differences between the faunas of the Laurentian Province and the Baltica Province, even though some genera are shared, are mirrored by the isotopically distinct water masses associated with the two cratons. Latitudinal separation probably led to sufficient differences in temperature and salinity resulting in distinct water masses that did not interact. As a result, it was unlikely that faunal or circulatory excursions from between the two masses could have occurred. As Baltica, and Avalonia, moved into more equatorial latitudes and drifted closer to eastern Laurentia, faunal excursions between the two realms occurred and this pattern of exchange is supported by the increasing isotopic homogeniety between Laurentia and Baltica.

In the Ordovician, the controls on provincialism in the southern Paleotethys are hard to determine since Avalonia, Armorica, and Baltica were all positioned in high southerly latitudes, ≥60° south (Torsvik et al., 1992). Possibly the faunas of Avalonia are distinct in the early and early-middle Ordovician because of heightened endemism associated with island communities. Additionally, the Mediterranean Province during the middle - late Ordovician likely retained endemic characteristics because of temperature gradients associated with the onset and progression of glacial conditions.

Additionally, correlations between the Nd isotopic values and provincialism will probably vary depending on the fauna. For example, Cocks & Fortey (1990) stated by the mid-Caradoc there was mixing of trilobite faunas between Baltica and some regions of peri-Gondwana. As well, in the Mediterranean Province, there are trilobites that are typical of Shropshire (Avalonia) faunas. This would indicate that trilobites were mixing in and around the margins of the southern Paleotethys, and this is reconcilable with a well mixed water mass as indicated by the Nd isotopic signatures. The differences in the degree of correlation between Nd isotopes and faunal types may be the result of differences in reproductive strategies, dispersal mechanisms, and life history strategies that are employed by the different organisms, which is beyond the scope of this study.

It is apparent that some correlations between Nd isotopic signatures of ancient water masses and faunal provincialism is possible. Where correlations are supported they are related to paleocirculation and the degree of mixing between water masses. However, where correlations are unsupported, other factors driving provincialism that are independent of circulation must be considered, including the biology of the organism.

Summary

Correlations of conodont biogeographic patterns with the Nd isotopic values from ancient oceans is tenuous. Correlations within and between the realms are variable and some patterns of provincialism are not supported with Nd isotopic values. There is some correlation between the isotopic signals and the patterns associated with some individual provinces (e.g. Laurentia and Baltica), while not with others (e.g. Baltica and Armorica). Faunal exchanges between the realms can be correlated with increasing homogeneity between the eastern and western Iapetus waters. There are also differences in the degree of correlation depending on the fauna, and this is likely related to biotic rather than abiotic factors such as ocean circulation.

4.6 Testing Paleoceanographic Patterns

Although temperature differences and distance between continental shelves are considered as the principal barriers to migration or dispersal, the role of ocean circulation is important. Modeling paleoceanographic circulation is difficult . Many assumptions are involved, including planetary conditions (for review see Wilde et al., 1991) also the positioning of the major land masses. The purpose of making these primary assumptions is to develop a basic model of oceanographic conditions.

Today's ocean circulation is a function of two major processes: wind driven stress and thermohaline circulation. Wind stress generally controls the upper mixed layer while thermohaline processes, in general, control bottom water circulation. It is difficult to assess the extent of thermohaline circulation in paleoceans in the geologic past. From the latitudinal position of the continents and lithofacies distribution it is possible to postulate where sinking saline waters may have initiated bottom water formation. The extent of deep water circulation is difficult to determine from lithologic, geochemical or paleontological data as most deep sea deposits were subducted or deformed in accretionary wedges and also were normally below the carbonate compensation depth.

These limitations have led paleoceanographers to reconstruct their models to largely the pattern of circulation in the upper surface waters. Information on these can be supported by such lithological, geochemical and paleontological data. The major currents can be modeled using Ekman transport parameters and assuming that present day atmospheric conditions prevailed in the past. The only principal studies to model Ordovician to early Silurian ocean circulation were those of Wilde (1991) and Wilde et al. (1991). These studies were concerned with only the upper mixed layer, to 100 metres depth, and involved platform and shelf deposits. Some of the lower shelf deposits may not be within this 100 m limit, but the depth of this upper mixed layer can vary and wind driven effects can be transported by geostrophic flow down to depths of 1000 m in present day oceans (Pond & Pickard, 1991). Therefore, it is reasonable to suggest that all shelf deposits, even during the Caradoc, would have been affected by wind-driven ocean circulation. Wilde (1991) used an older paleogeographic reconstruction than Scotese & McKerrow (1991), involving differences in the configuration of Gondwana and the proximity of Siberia, Baltica and Laurentia. These differences do not substantially affect the ability to study and evaluate the gross trends in circulation and their comparison with the Nd isotopic data.

Comparing the $\varepsilon(T)$ values with the relevant current patterns of Wilde (1991) for individual time slices, it is apparent that the Nd isotopic data are compatible with ocean circulation reconstructions (Figures 4.8-4.12). In the Tremadoc, the model of Wilde (1991) predicted a strong flow down the western margin of the Iapetus (eastern Laurentia) with weak northerly flow along the eastern margin. The model does not predict a strong oceanic gyre for the Iapetus Ocean. The north equatorial currents are deflected to the north by the margins of Siberia, Laurentia, and Gondwana. Off Australia, this current is deflected counter-clockwise. At tropical latitudes, approximately 30 ° south, there is a counter-clockwise gyre in the Paleotethys (Figure 4.8A).

The general trend for the Iapetus Ocean is likewise supported by the Nd isotopic analyses. There are two distinct water masses associated with the northeast and southeast margins of Laurentia and this supports the model of a south tropical current being deflected by the Gondwana margin and not continuing up the western margins of Laurentia to be mixed with the Panthalassic Ocean. Additionally, isotopically distinct water masses on either side of Iapetus (Figure 4.8B) support the patterns of flow in this region as modeled by Wilde (1991). Although Wilde's (1991) model did predict some Iapetus water leakage in the westward flowing south polar currents, the flow along Baltica was possibly weak and may have had limited influence on the isotopic composition. Similar Nd isotopic values between the Australian platform and Kazakhstan suggest that there was strong circulation across the northern Paleotethys. This does not support Wilde's model as the north tropical current is deflected away from interaction with the Paleotethys gyre. However, there could have been deflected currents and meridianal leakage that is not accounted for in the reconstruction. It is also possible that Kazakhstan was at a different paleolatitude and placing it at a higher northerly position would not conflict with either faunal or lithological data.

In the model for the Arenig and Llanvirn interval (Figure 4.9A), the western north equatorial current is maintained and the south tropical current, hugging the Iapetus margin of Laurentia, is modeled to be strongly deflected away from the south with the south subpolar current deflected north along the margin of Baltica. At 60° south a clockwise gyre connects the Iapetus with the Paleotethys via the Tornquist Sea. The model predicts some transport of cool water from the Paleotethys across Siberia and Kazakhstan to the warmer Iapetus waters (4.9A). Separation between east and west Iapetus Ocean is predicted by Wilde (1991) and supported by the Nd isotopic data (Figure 4.9B). The gyre circulation at the high southern latitude would have resulted in these waters being well mixed. This prediction is borne out by the Nd isotopic values that show overlapping signatures for Armorica and Baltica. In predicting the transport of waters across Siberia/Kazakhstan from the Paleotethys Ocean to the Iapetus Ocean, our data do not substantiate this flow. Although there are similarities between the Laurentian and South China values, the flow is westward such that sediment influence from Laurentia would be unlikely.

In Wilde's (1991) reconstruction of circulation for the Llandeilo - Caradoc (Figure 4.10A), slight variations occur in the placement of cratons compared to those of Scotese & McKerrow (1991) (e.g. Laurentia - Siberia and Siberia - Baltica). With this major north - south barrier, the Iapetus Ocean and the Paleotethys Ocean were isolated from each another but Wilde (1991) predicted a small seaway between them for the passage of the south equatorial current. At mid- latitudes an anticyclonic gyre circulated the waters of the Iapetus and at 60° south there is a cyclonic gyre in the region of the southern Paleotethys and the Rheic Ocean.

The increasing circulation between the water masses of the Iapetus is also reflected in increasing similarities between the Nd isotopic values of Laurentia and Baltica, although the values still suggest distinct water masses. Similarly, the Nd isotopic homogeneity in the seas at 60° south is also supported the cyclonic gyre. Perhaps the inability of the Nd isotopes to resolve the presence of the Rheic Ocean is because the circulation between it and the southern Paleotethys is relatively complete (Figure 4.10B).

In the Ashgill (Figure 4.11A & B), with the narrowing of the Iapetus, the Wilde (1991) model predicted a significant meridianal current on both sides of this ocean which is supported by the overlapping Nd isotopic values. This model places a second gyre at 60° south between the southern Paleotethys and the Rheic. This, too, is supported by the general overlap of Nd isotopic values from Amorica, Avalonia and Baltica. Wilde (1991) suggested that before the Ashgill, the tropical regions experienced most of the convergence as warm, salty water sank. However, he stated this would likely only extend into the lower regions of the upper mixed layer. He cited the presence of anoxic sediments as proof that intrusions of surface waters into the deeper waters did not generally occur. However, by the Ashgill, bottom water formation likely occurred in response to the growing southern icesheet and the transition to an icehouse state. He suggested that this would have ventilated the mid to deeper depths, using the presence of more oxic sediments as evidence. This ventilation would have resulted in a more complete mixing of oceans and the divergence and convergence zones would have intensified. This more complete mixing can be supported by the general overlapping of Nd isotopic values for the oceans sampled at the end of the Ordovician.

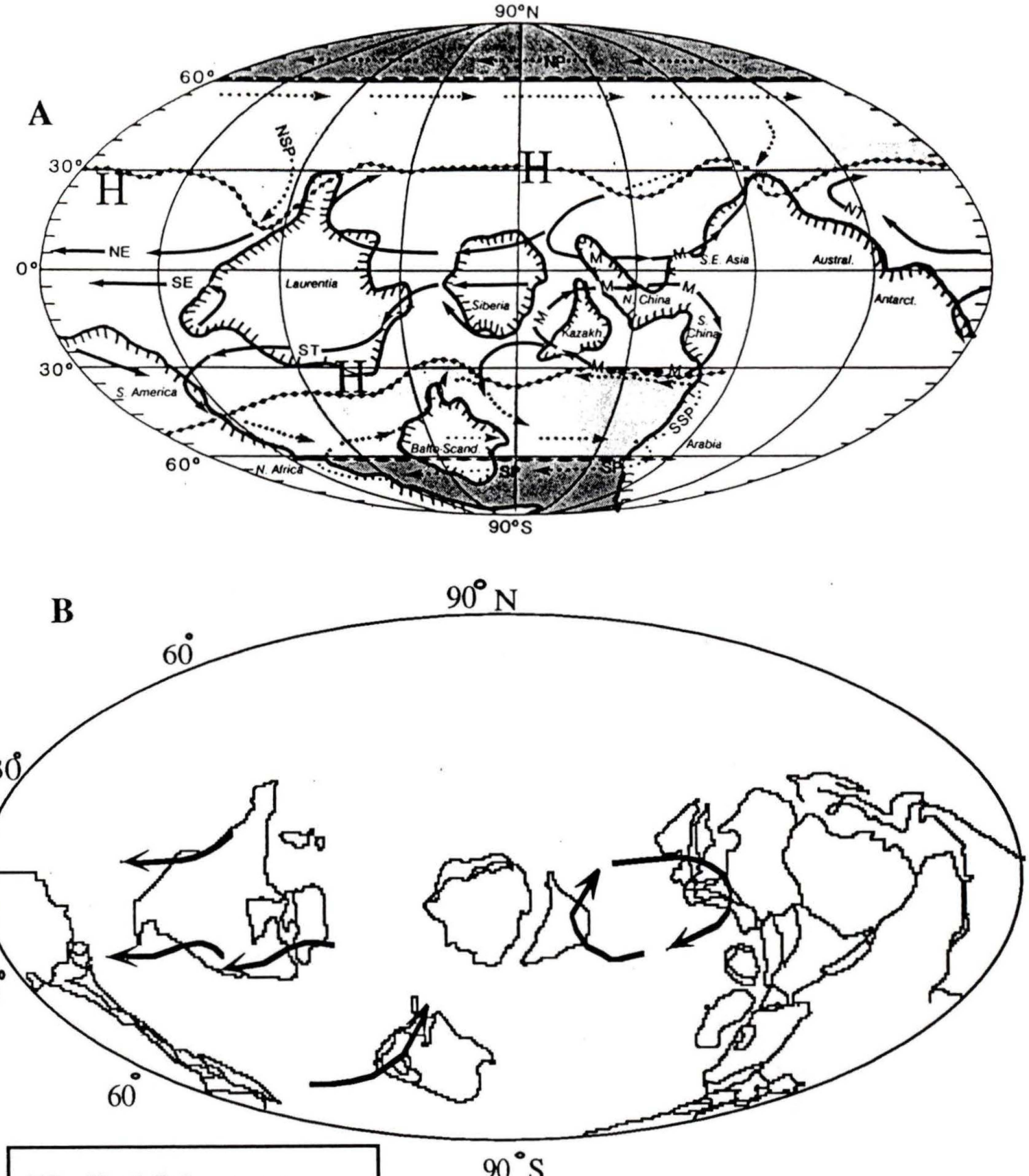
It is difficult to confirm Wilde's (1991) model for the Llandovery (4.12A & B) due to the small number of samples. This model predicts a strong south tropical current along the Iapetus margin of Laurentia and a counter-clockwise gyre in the southern Paleotethys and Rheic. Due to the undetermined position of the Kolyma terrane, it is not possible to substantiate the extent of hydrographic mixing between this land mass and Laurentia. If the Kolyma was positioned farther to the north, at greater than 30° N latitude, then the distinctness of this value would be easy to reconcile, as the signature would be carried by the global encircling north polar current that is not influenced by ciruclation processes to the south.

Summary

It is apparent that on a gross scale, the paleocirculation reconstruction, derived from Ekman modeling, by Wilde (1991) is supported by the Nd isotopic data from this study. However, finer scale circulation or minor currents are either unsupported or not detetectable. These conclusions should provide incentive to modelers that the reconstructions presented to date have merit and should be updated in the light of increasing information and refined paleogeographic reconstructions.

A

B



NP = North Polar current
NSP = North Subpolar current
NT = North Tropical current
NE = North Equatorial current
M = Monsoonal Counter-current
SE = South Equatorial current
ST = South Tropical current
SSP = South Subpolar current
SP = South Polar Current

Legend for A

Warm Currents
Cool Currents
Polar Convergence
Subtropical Convergence
H Center of Oceanic High Pressure

Figure 4.8: Tremadoc surface circulation patterns. (A) Wilde (1991) model, (northern hemisphere winter). (B) Major currents that are supported by Nd isotopic values derived from this study. Reconstruction is after Scotese & McKerrow, 1991.

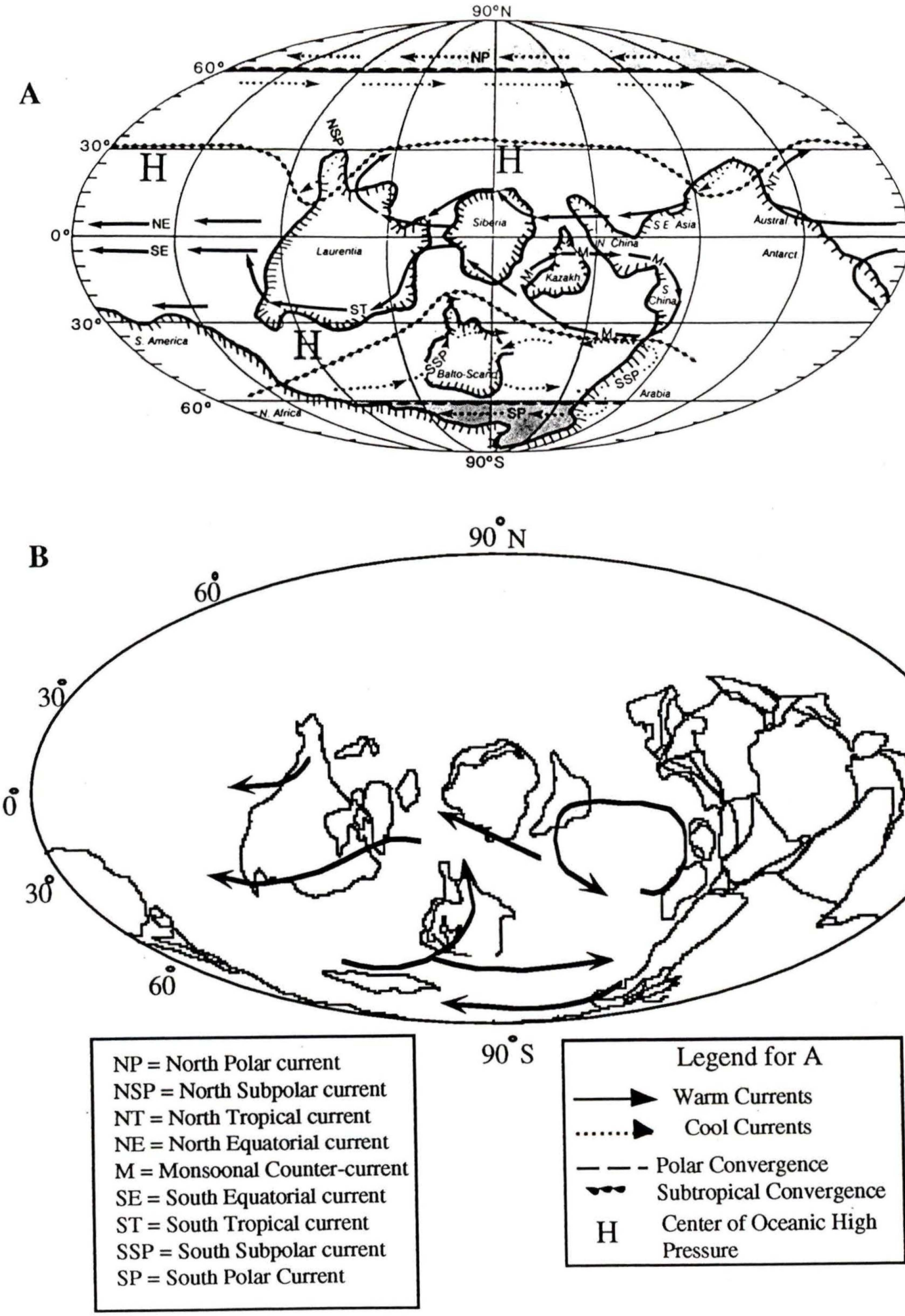
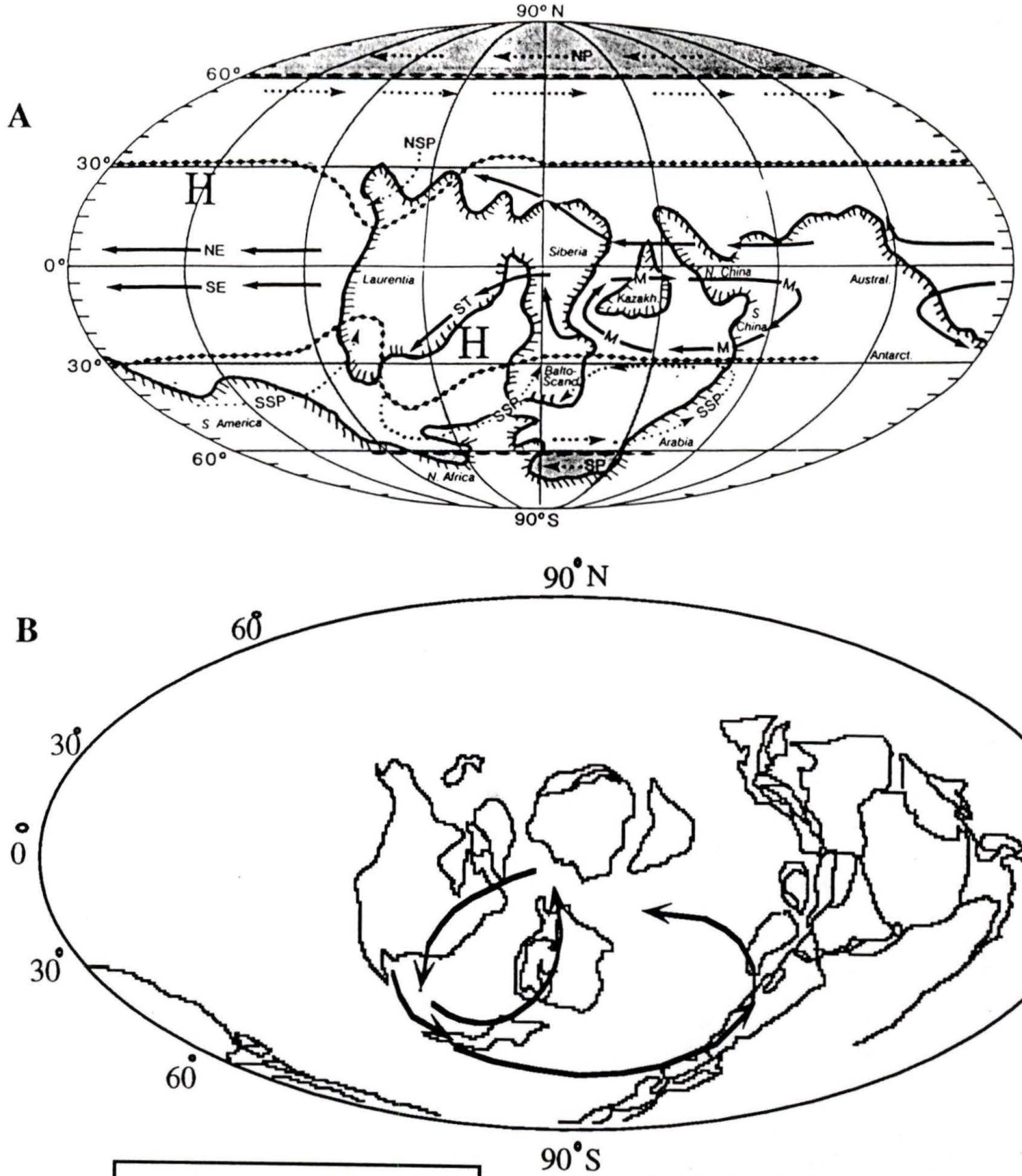


Figure 4.9: Arenig - Llanvirn surface circulation patterns. (A) Wilde (1991) model, (northern hemisphere winter). (B) Major currents that are supported by Nd isotopic values derived from this study. Reconstruction is after Scotese & McKerrow, 1991.



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SSP = South Subpolar current
SP = South Polar Current

Legend for A
Warm Currents
Cool Currents
Polar Convergence
Subtropical Convergence
H Center of Oceanic High Pressure

Figure 4.10: Llandeilo - Caradoc surface circulation patterns. (A) Wilde (1991) model, (northern hemisphere winter). (B) Major currents that are supported by Nd isotopic values derived from this study. Reconstruction is after Scotese & McKerrow, 1991.

A

B

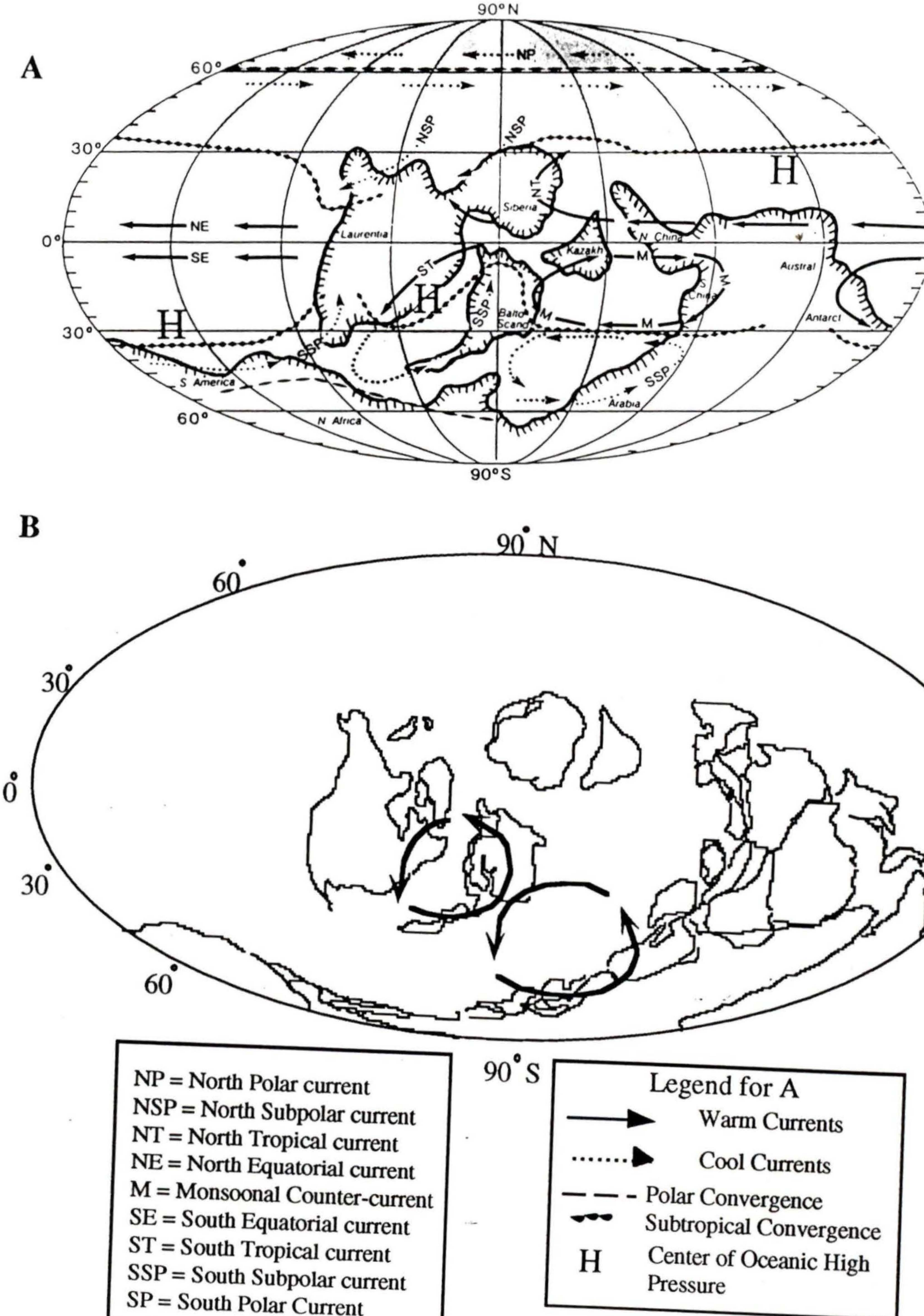
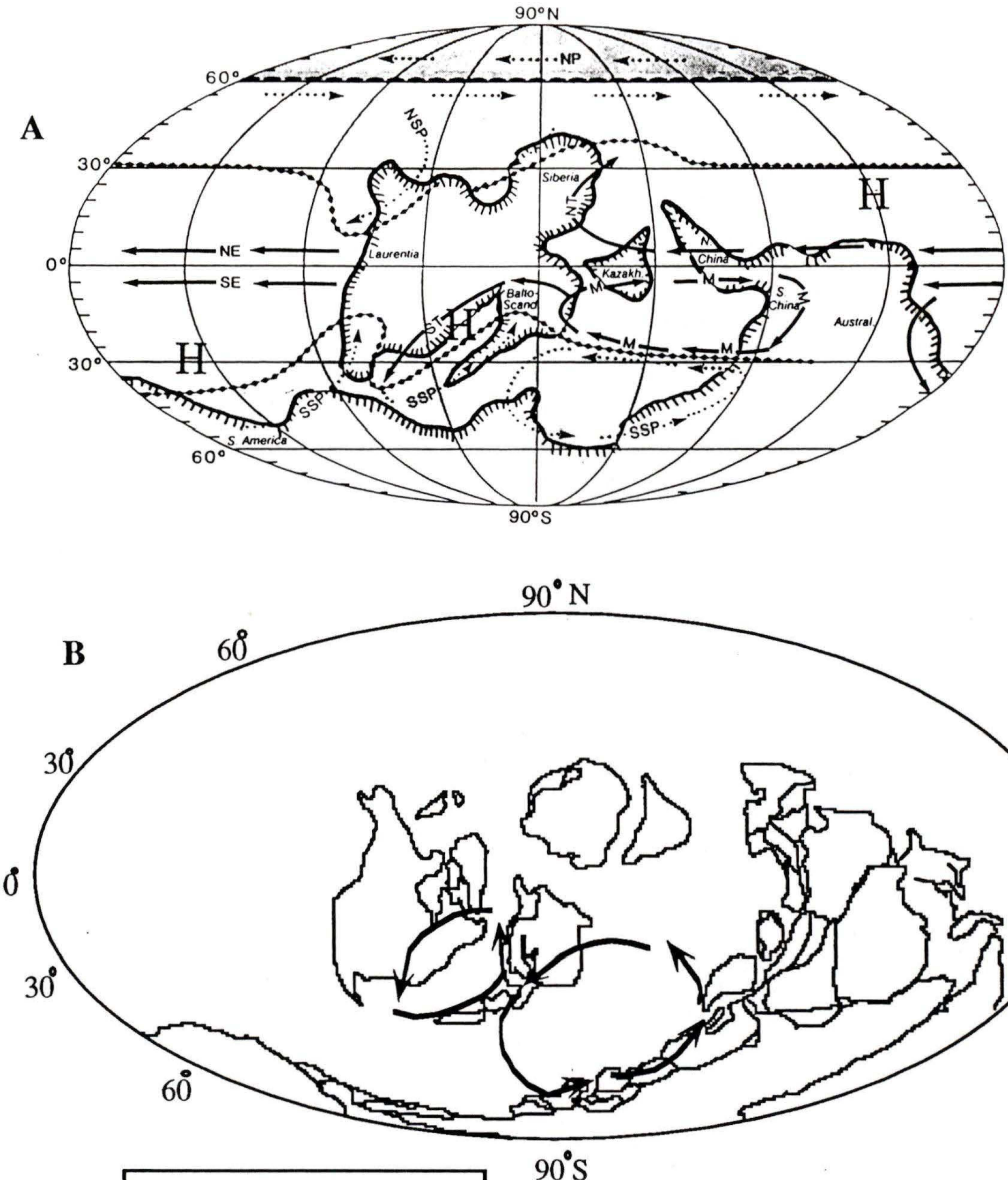


Figure 4.11: Ashgill surface circulation patterns. (A) Wilde (1991) model, (northern hemisphere winter). (B) Major currents that are supported by Nd isotopic values derived from this study. Reconstruction is after Scotese & McKerrow, 1991.



NP = North Polar current
NSP = North Subpolar current
NT = North Tropical current
NE = North Equatorial current
M = Monsoonal Counter-current
SE = South Equatorial current
ST = South Tropical current
SSP = South Subpolar current
SP = South Polar Current

Legend for A

Warm Currents
Cool Currents
Polar Convergence
Subtropical Convergence
H Center of Oceanic High Pressure

Figure 4.12: Llandovery surface circulation patterns. (A) Wilde (1991) model, (northern hemisphere winter). (B) Major currents that are supported by Nd isotopic values derived from this study. Reconstruction is after Scotese & McKerrow, 1991.

4.7 Comments on Colour Alteration Index and Element Size

4.7.1 Colour Alteration Index

The effects of increased temperatures due to burial and diagenesis could lead to isotopic fractionation or elemental loss. Since it is not certain to what extent burial and temperature affect the isotopic patterns in biogenic apatites, a knowledge of the burial history of the sample may help explain anomalies. Conodont colour alteration index (CAI) values provide a quantitative estimate of the burial temperatures and can be useful in choosing samples. Bertram et al. (1993) did a systematic analysis of $^{87}Sr/^{86}Sr$ and varying CAI values. They suggested that conodont elements with a CAI $\geq$ 2.5 should be regarded as suspect. They also suggested that the same criterion may apply to Nd isotopes but no comprehensive testing was provided. Unfortunately, this study (Wright, M.Sc. Thesis) did not pursue the CAI issue in detail. When the samples for the present study were chosen, the Bertram et al. (1993) paper had not been published and the samples were selected based upon the work of Keto & Jacobsen (1987) that CAI values up to and including 5 were acceptable for Nd analysis.

However, therein considerating the CAI values of the conodonts in this study, there is clear reason to suspect that CAI values had an affect on the Nd isotopic compositions. It is true that some samples with high CAI values (e.g sample 25) were low in total Nd and did not warrant further analysis, there were low CAI conodonts (e.g. samples 4, 24) that were also rejected. Additionally, some samples with high CAI values , those from Armorica in the Ashgill (samples 21, 22, 23, 43) show remarkably consistent Nd isotopic values, not only between themselves but in comparison to earlier samples from Armorica with lower CAI values.

Testing the effects of CAI changes on Sr isotopes is easier since Sr ratios are assumed to be the same throughout the ocean waters. Hence, testing a shelf-slope transect which contained variable CAI is possible with Sr as the isotopic values between the environments should not be different. However, this is not the case with Nd where different water masses can be encountered in such a transect. It would be difficult to prove whether changes in the Nd ratios were associated with variable CAI or with different water masses. Testing requires a sedimentary basin that is known to be a homogenous water mass and to have been affected by tectonic processes to induce a sufficient range of CAI values. Another way to test the influence of CAI would be to choose a sample with a CAI of 1, split the sample into replicates and artificially induce color alteration, and then analyze the relevant ratios. Although this is not a natural situation, it would eliminate the possibility of post deposition flux from outside sources and would test only the effects of the thermal maturation process.

4.7.2 Element Size

It is interesting to note that the samples that did not qualify for further analysis (those with less than 4 ng of total Nd) fell predominately into the small size category. The range of total Nd for each size class overlap and was as follows: small elements had a range of 0.3 ng to 34.4 ng; medium sized elements, a range of 0.2 ng to 150.6 ng; while elements categorized as long had a range of 1.5 ng to 228.6 ng. There was a general trend that as the elements increased in size, the amount of total Nd increased. It may be that surface area or volume is a more stringent requirement for analysis than CAI at least from an analytical perspective. As the 'size' of the conodont elements increases, there are more potentially available calcium sites to host Nd and Sm. However, in this study the size categorization was subjective and used only to attain rough estimates of total Nd for the purposes of spiking. Measuring surface area or volume on individual conodonts would be extremely difficult due not only to their microscopic size but also because the elements are not simple geometric shapes. Conodonts have variable basal cavities, striations, and fluid inclusions that would make such measurements a complex task.

4.8 Comments on the Effect of Taxonomy

Bertram et al. (1993) published analysis of Sr and Nd isotopes and REE patterns from Silurian conodonts. Based upon the variations in the $^{87}Sr/^{86}Sr$ ratios they suggested that using a different taxon was a possible source of error and that since there is a linear relationship between Nd abundance and $^{87}Sr/^{86}Sr$ ratios, then Nd isotopes from different taxa should also be treated as suspect. However, for the conodonts from one locality they found $\varepsilon(T)$ values of -6.13, -5.89, and -7.08 for Ozarkodina, Panderodus, and Dentacodina respectively. These are tightly constrained values for which the authors did not include associated errors , therefore, it is possible that within statistical error, these values are identical.

The results from the present study do not support the claim that taxonomic variability is a factor when studying Nd isotopes. Samples 9 and 10 are from the upper Stony Mountain Formation, are from the same whole rock sample, and represent Panderodus gracilis and Drepanoistodus suberectus respectively. Although there were some variations in the ^{144}Nd and ^{147}Sm abundance, they had similar $^{143}Nd/^{144}Nd$ ratios and statistically, their $\varepsilon(0)$ and $\varepsilon(T)$ values are not different. Similarly, Shaw & Wasserburg (1985) found that abundance between taxa did differ but this did not affect he isotopic signal. With respect to intra-taxon variation, samples 17 and 41 are from the Lower Silurian Ellis Bay and Bescie Formations. Although the Bescie is slightly younger, they essentially represent similar environments. Both are represented by Panderodus gracilis and again, although there are abundance variations the $\varepsilon(0)$ values are similar and the $\varepsilon(T)$ are almost identical.

Intra or inter-taxon isotopic variation is generally not expected. Since the signal is picked up from the contemporaneous surrounding water mass, then the elements should record this value true. Variation in abundance is likely to occur, possibly due to the availability of calcium sites, but overall there is little or no effect on the epsilon signal. As well, isotopic signature is picked up during post-mortem processes so biological fractionation during life is not an issue.

CHAPTER 5 CONCLUSIONS

Ordovician - Early Silurian conodont samples were chosen for Nd isotopic analysis to attain a proxy signal for ancient oceans contemporaneous with the timing of deposition. Once delimited, the Nd isotopic signature of these ancient oceans can be related to regional and global geological processes and be used to test models of proposed paleogeography. By association, other models which rely on paleogeographic reconstructions (e.g. paleobiogeography, paleoceanography) can be assessed. It is apparent that the Nd isotopic composition of Ordovician to Early Silurian oceans is a function of tectonic forces that affect and alter the sedimentary load and ocean circulation patterns.

The show conclude that there are isotopically distinct ocean masses in the Ordovician and Early Silurian. Overall, the Iapetus Ocean has $\varepsilon Nd(T)$ values of approximately -20 to -5, the southern Paleotethys, -10 to -5, northern Paleotethys, -13 to -9, and the Panthalassic Ocean has a range of values from -18 to -1. The craton of Laurentia shows the most nonradiogenic values and these are in the Tremadoc interval. The most radiogenic value is from the Kolyma terrane in the Early Silurian. In the early Ordovician there were two isotopically distinct water masses associated with the Iapetus Ocean; one with eastern Laurentia and the other with Baltica. Laurentian waters, especially those of the eastern sea-board, show a trend towards increasing radiogenic input over time until the eastern and western Iapetus waters masses are isotopically homogenous. Additionally, there is overlap between the signals displayed by Baltica, Avalonia and the Armorican microplate throughout the interval.

In almost all cases, the Nd isotopic signal can be correlated with the regional geology of the area. Additionally, changes in the isotopic signal can be correlated with tectonic processes such as eustacy, plate tectonic drift, and orogenic events. Additionally, with the range of Nd isotopic values for the oceans delimited, it will become less difficult to position a lost or displaced terrane within a relevant water mass by determining its Nd isotopic signature from either biogenic minerals or from metasediments.

Testing paleogeographic reconstructions, both regional and global are discussed. Unfortunately, the Nd isotopic results can not resolve the reconstructions of Paris & Robardet (1990) nor that of Dalziel et al. (1994). There is generalized broad scale support for the reconstruction as modeled by Scotese & McKerrow (1991) with respect to the major craton configurations. There are some possible discrepancies concerning the positioning of the South China microplate and the Kolyma terrane.

There is some degree of correlation between the Nd isotopic signatures and conodont faunal provincialism patterns. However, the correlations are variable within a particular realm indicating the provincialism in conodonts is not a simple function of water mass inhabitability. Additionally, the ability to correlate isotopic signatures with patterns of biogeography will vary with the fauna in question.

The Nd isotopic results show broad scale support for the paleoceanographic circulation reconstruction of Wilde (1991). The major currents are supported whereas minor currents are either unsupported or undetectable by the isotopic values. Although not rigorously tested, it appears that colour alteration index does not have a direct affect on the isotopic constraints.

This study has shown that conodonts can be used to determine the Nd isotopic signature of ancient oceans. This is valuable since it provides a method for testing paleogeographic reconstruction models that are independent of the methods (e.g. paleomagnetism) used to establish such models. This is critical since it provides a means of dealing with plate configurations without dealing with the potential errors involved in paleomagnetism. The Nd isotopic data can be used to integrate the various paleoenvironmental models and yield a more comprehensive picture of the early Paleozoic world.

This study is a foundation for future research. The basic ranges of these early Paleozoic oceans are delimited and further sampling and analysis could tighten the ranges and increase the resolution of the different ocean masses. This would be beneficial because it would reveal finer scale patterns, not detectable in this study, for testing paleogeographic reconstructions. Finally, conodonts provide a valuable proxy tool for this independent method of examination. In a small number of elements, there are analytically acceptable amounts is Sm and Nd, and up until their extinction in the Triassic, they were abundant in marine waters. Hence, employing conodont Nd isotopic values to delimit ocean masses and test paleogeographic reconstruction models can be performed for other periods of the Paleozoic.

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APPENDICES

Appendix A

Major Ion Exchange Chromatographic Microcolumns

The major element chromatography microcolumns used at Harvard University's Isotope Laboratory are not commercially available. They are hand-blown and each column is unique. The columns are approximately 15 cm long with an internal diameter of approximately 0.5 cm. The exit neck of the column is plugged with a porous quartz frit (Figure A1). The columns were packed with ultraclean BIO-RAD AG50W-X8 resin. All acids used were ultraclean. Caution was taken to avoid contamination (e.g. using new pipettes for each step in the elution) and to avoid sample loss (i.e. spillage, loading sample onto glass, etc.). Glass 9 inch pasteur pipettes were thoroughly cleaned in warm 50% reagent strength HCl. The resin was cleaned with approximately 200 ml with 4N HCl.

The elution scheme was as follows:

a)	2 ml	ultrapure H_2O
b)	3 ml	1.5N HCl
c)	1 ml	sample in 1.5N HCl
d)	1 ml	1.5N HCl
e)	1 ml	1.5N HCl
f)	10 ml	2.5N HCl
g)	7 ml	2.5N HCl
h)	3 ml	4N HCl
i)	17 ml	4N HCl

In step (c), 500 μl of 1.5N HCl was added to the dried sample and centrifuge to sediment any debris. This volume was added to the resin and then a second 500 μl of 1.5N HCl was added, centrifuged again, and then added to the column resin. In steps (g) and (h), strontium fractions were collected. These fractions were dried down under heat and pure N_2 gas and stored for future work. In step (i), the rare earth element fraction was collected, dried down under heat and pure N_2 gas. This fraction was then loaded onto a rare earth ion exchange microcolumn.

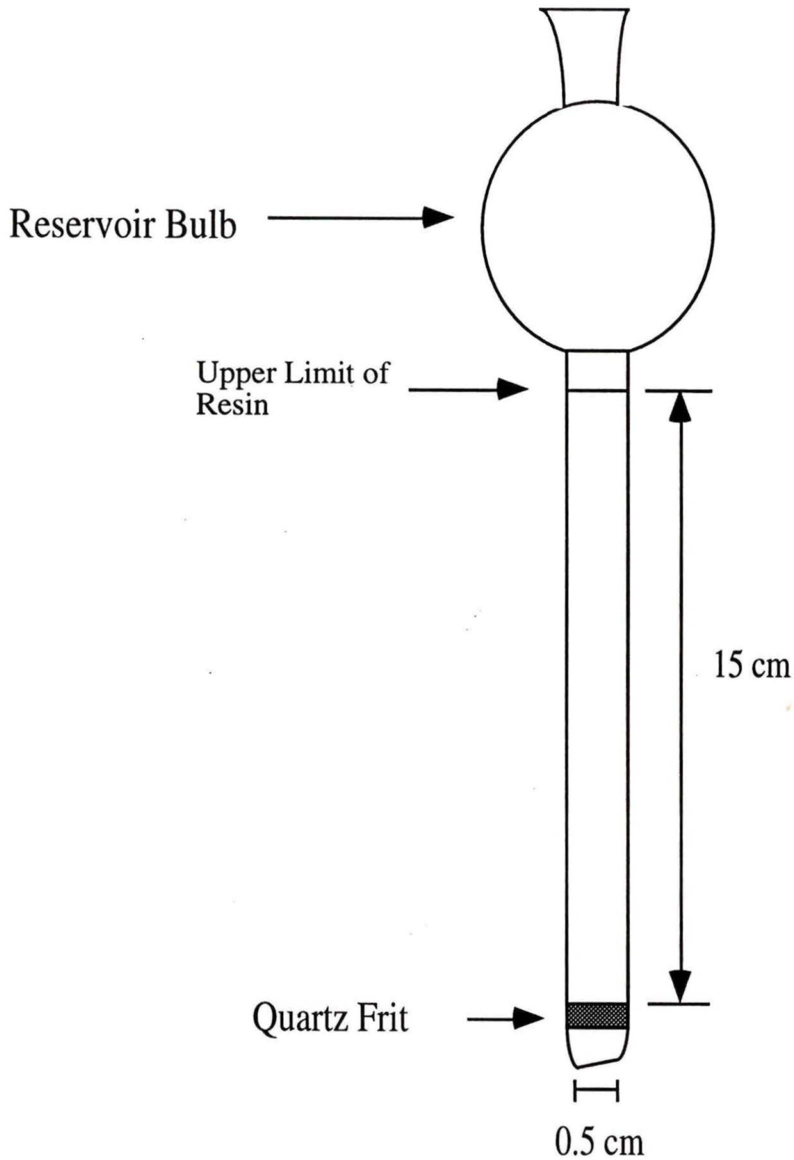

Figure A1 Diagrammatic representation of the major ion exchange chromatographic columns used at the Harvard Isotope Laboratories.

Appendix B

Rare Earth Element Separation Microcolumn

The rare earth element (REE) chromatographic columns used at the Harvard facility were hand designed and hand blown, like the major element columns and each one is unique. There were five columns with a length of approximately 32.5 cm. The exit end of the column was fitted to a Teflon microspout lined with a 0.8 mm diameter Whatman 40 ashless filter paper (Figure B1). The columns were packed with BIO-RAD AG50W-X8 (<400 mesh) cation resin and the acid used for elution was 0.2M methyl-lactic acid (pH 4.65). The rare earth elements differ only slightly in atomic weight. These minute difference assist in the separation of the rare earths from lightest to heaviest. The columns are equipped with pressurized air connections that pushed the liquid through the columns, and also with automatic drip counters. Since the elements are separated by minute differences in weight the point at which an element is extracted is calibrated with drop numbers. The columns were each calibrated individually to ensure that fractionation and extraction was carefully coordinated with specific drop numbers.

Care was taken to avoid contamination and sample loss. Additionally, the liquid levels in the column were monitored to prevent the column from running dry. For each run, the column was loaded with new clean resin that was carefully loaded and conditioned. To ensure that the column was clean and free of debris, it was filled with ultrapure H_2O and all air bubbles were removed by pushing them through with pressurized air. With a clean 9 inch pasteur pipetter, resin was injected into the column and allow to gravitationally settle. Once the settled excess resin and water were removed and the column reservoir bulb was filled with 0.2M methy-lactic acid (MLA) (pH 4.65) and 100-150 drops were allowed to pass through the resin.

Once this was complete, the excess acid was removed from the bulb and to the resin ultrapure H_2O was added and allowed to pass through the resin. Care was taken not to allow the meniscus to drop below the top of the resin as this would create air pockets in the resin, dry it out, and result in poor separation. The dried REE fraction was dissolved with 2 drops of 0.75N HCl. With a clean micropipette, the sample was carefully added to the resin by touching the tip of the pipette to the neck of the column's capillary tube and letting the liquid flow down onto the resin. Caution was taken to release the liquid slowly to prevent bubbles from forming. With pressurized air, the sample was blown onto the resin. A second 2 drops of 0.75N HCl was added to the sample container and the last step repeated. Care was taken to set the drop counter prior to adding any MLA. The drop counter was set by observing the next drop. If it was small, the counter was immediately set, if large, then the counter was set after it was released.

Once the sample was loaded, any remaining sample adhering to the sides of the glass was washed down into the capillary tube onto the resin using a micropipette and slowly releasing MLA. This wash procedure was done 2-3 times and once complete the columns and its reservoir bulb were filled with MLA and connected to the pressurized air. Individual Nd and Sm fractions were collected as well as intermediate drops (safety cuts) and all fractions were dried down under heat and pure N_2 gas.

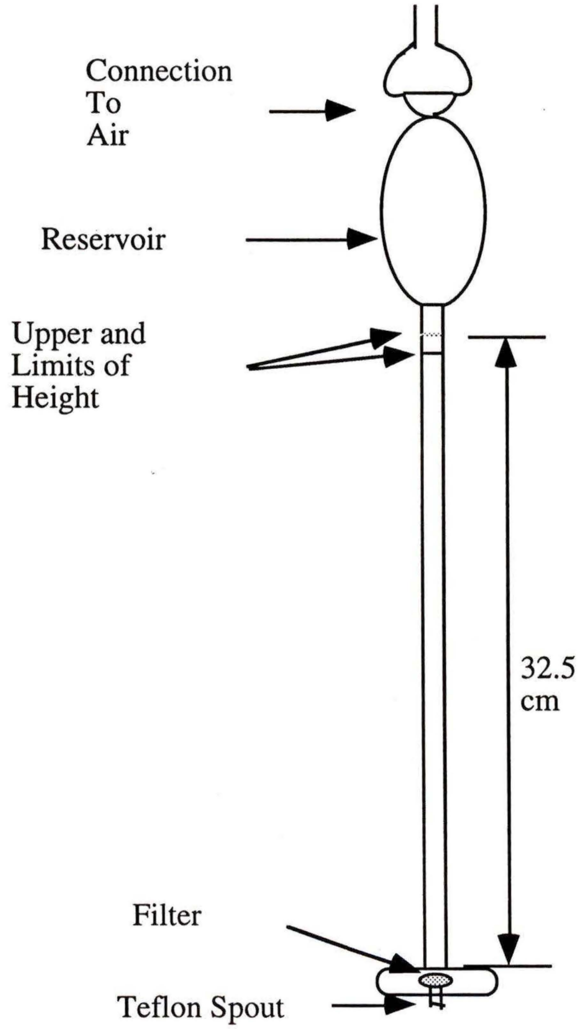

Figure B1 Diagrammatic representation of the rare earth element ion exchange chromatographic columns used at Harvard Isotope Laboratories.

Appendix C Sample Information

Sample No: 1
Lab. I.D. No.: 5650 TC 1360
Location: Threadgill Creek, Llano Uplift, Texas
Loc. Ref.: Miller et al., 1982
Unit: San Saba Limestone Member, Wilberns Formation, 414.5 m below the base of the C. lindstromi Biozone
Taxon: Eoconodontus notchpeakensis (Miller)
CAI: 1

Sample No: 2
Lab. I.D. No.: JC7
Location: Dry Creek, Johnny Creek Anticline, Amadeus Basin, Australia, (Lat 24°15'S: Long 131°44'E)
Loc. Ref.: Laurie et al., 1991
Unit: Stokes Formation, Larapinta Group, 200 m from the top
Taxon: Bryantodina sp.
CAI: 2

Sample No: 3
Lab. I.D. No.: 35187
Location: N.E. Ny Friesland, Spitsbergen
Loc. Ref.: Fortey, 1975
Unit: Olenidsletter Member, Valhallfonna Formation, 92 m above the base of the member
Taxon: Oepikodus communis (Ethington & Clark)
CAI: 1

Sample No: 4
Lab. I.D. No.: 8312 127 03-27 (or 8312 A27 of Carson, 1980)
Location: Dundas Harbour, Devon Island (largest gorge on the northern bank of the Mingo River), N.W.T
Loc. Ref.: Carson, 1980
Unit: Bay Fiord Formation, Cornwallis Group, 159.6 m above the base of the formation
Taxon: Striatodontus gracilis (Ethington & Clark)
CAI: 1½

Sample No: 5
Lab. I.D. No.: 9618 (Field No. W.06.31)
Location: west side of Maxwell Bay, Devon Island, N.W.T.
Loc. Ref.: Carson, 1980
Unit: Irene Bay Foramtion, Cornwallis Group, sample taken from top of formation
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 2.½ - 3

Sample No: 6
Lab. I.D. No.: CC4
Location: Cañon City, Colorado, southeast corner of Nonas Peak, 0.55 km north of Branson & Mehl's 1933 locality
Loc. Ref.: Branson & Mehl, 1933; site 6 of Sweet, 1955
Unit: Harding Sandstone Formation, 15.5 m above the base of the formation
Taxon: Chirognathus sp.
CAI: 1

Sample No: 7
Lab. I.D. No.: H77/401
Location: U.S. Highway 77, south side of Arbuckle Mountain, Oklahoma,
Loc. Ref.: Harris, 1962; Lewis & Yochelson, 1978
Unit: Oil Creek Formation, Simpson Group, 13.4 m above the base of the formation
Taxon: Eoneoprioniodus sp.
CAI: 1

Sample No: 8
Lab. I.D. No.: A088/6092
Location: Anticosti Island, Québec, near Ruisseau Barbarin on east side of Cape Henry
Loc. Ref.: McCracken & Barnes, 1981
Unit: Ellis Bay Formation, middle of member 3, 12 m above the base of the section
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 1 $\frac{1}{2}$

Sample No: 9
Lab. I.D. No.: 79146 0138
Location: Southern Manitoba, Standard Limestone Quarry, 2.4 km north of Highway 67
Loc. Ref.: Elias, 1982
Unit: Gunton Member, Stony Mountain Formation
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 1. $\frac{1}{2}$

Sample No: 10
Lab. I.D. No.: 79146 0138
Location: Southern Manitoba, Standard Limestone Quarry, 2.4 km north of Highway 67
Loc. Ref.: Elias, 1982
Unit: Gunton Member, Stony Mountain Formation
Taxon: Drepanoistodus suberectus (Branson & Mehl)
CAI: 1

Sample No: 11
Lab. I.D. No.: 039-5454
Location: Manitoulin Island, Ontario, Highway 540, 3 km west of Kagawong, Kagawong West Quarry
Loc. Ref.: Section 5 of Tarrant, 1977

Unit: 15.5 m above the Upper Member, 15.6 m above the base of the Georgian Bay Formation, Nottawasaga Group,
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 2

Sample No: 12
Lab. I.D. No.: 046 5467
Location: Manitoulin Island, Ontario, Highway 540 3 km west of Kagawong, Kagawong West Quarry
Loc. Ref.: Section 5 of Tarrant, 1977
Unit: 0.3 m above the base of the Manitoulin Formation, Nottawasaga Group, 30 cm above the recessive interval
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 2

Sample No: 13
Lab. I.D. No.: 102.5608
Location: Craigleith, Grey County, Ontario, Lot 21, Concession II
Loc. Ref: Section 6 of Tarrant, 1977
Unit: 2.15 m above the base of the lower member of the Whitby Formation,
Taxon: Drepanoistodus suberectus (Branson & Mehl)
CAI: $1\frac{1}{2}$ - 2

Sample No: 14
Lab. I.D. No.: E0033
Location: West Bay Quarry, Port au Port Peninsula, Newfoundland, south side of Highway 49, 1.75 km west of Picadilly Head
Loc. Ref: James et al., 1988
Unit: Table Head Formation, south face of quarry, 40 cm above the bentonite layer
Taxon: Erraticodon sp.
CAI: 2. $\frac{1}{2}$

Sample No: 15
Lab. I.D. No.: E0033
Location: West Bay Quarry, Port au Port Peninsula, Newfoundland, south side of Highway 49, 1.75 km west of Picadilly Head
Loc. Ref.: James et al., 1988
Unit: Table Head Formation, south face of quarry, 40 cm above the bentonite
Taxon: unidentified inarticulate brachiopod

Sample No: 16
Lab. I.D. No.: 91.WW.4
Location: Whitland, Wales, roadcut 4 km west of Whitland on A40
Loc. Ref.: Fortey & Owens, 1987
Unit: 67 m above the base of the roadcut section, 5.7 m above the base of the Shaolshook Formation
Taxon: Amorphognathus ordovicicus (Branson & Mehl)
CAI: 5

Sample No: 17
Lab. I.D. No.: E0054 A79-C13
Location: Baie Ellis, Pointe Laframboise cliff section, Anticosti Island, Québec
Loc. Ref.: Section A-2A of Duffield, 1982
Unit: Ellis Bay Formation, Member 6, 2.75 m above the base
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 1. $\frac{1}{2}$

Sample No: 18
Lab. I.D. No.: E11875 Sib 79.45
Location: Mirny Creek Section, Kolyma, Siberia, Kolyma River Basin, upstream Kravchun Creek
Loc. Ref.: Field Guide, 1979
Unit: Chalmak Horizon, member 74, 2 m above the base of Unit R
Taxon: Panderodus gracilis (Brason & Mehl)
CAI: 4. $\frac{1}{2}$

Sample No: 19
Lab. I.D. No.: E1158 Sib79.16
Location: Mirny Creek Section, Kolyma, Siberia, Kolyma River Basin, ~7 km from the mouth of the river
Loc. Ref.: Field Guide, 1979
Unit: Konyon Formation, top bed of Unit A
Taxon: Periodon grandis (Hadding)
CAI: 4

Sample No: 20
Lab. I.D. No.: E1144 Sib79.2
Location: Inya River, Kolyma, Siberia, 1.5 - 2.5 km upstream from the mouth of Mirny Creek and 200 m from the mouth of Kravchun Creek
Loc. Ref.: Field Guide, 1979
Unit: Tirekytyakh Formation, Bed 60, 5 m above the base of Unit O
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 2 $\frac{1}{2}$ - 3

Sample No: 21
Lab. I.D. No.: CDACA4/also CDACA5
Location: Cannemenda, Sardinia
Loc. Ref.: Ferretti, 1992
Unit: Domunsnovas Formation, Punta S'Argiola Member, thin calcareous lens
Taxon: Scabbardella altipes (Henningsmoen)
CAI: 4 $\frac{1}{2}$ - 5

Sample No: 22
Lab. I.D. No.: FO(B)
Location: Eastern Sierra Morena, Fontanosa, Spain
Loc. Ref.: Ferretti, 1992
Unit: N/A; 1 m below the contact with the Chavera Formation
Taxon: Scabbardella altipes (Henningsmoen)
CAI: 3 - 4

Sample No: 23
Lab. I.D. No.: 1428
Location: Carnic Alps, Italy
Loc. Ref.: Serpagli, 1967
Unit: Tonflaserkalk Limestone, Rifugio Nordio,
Taxon: Scabbardella altipes (Henningsmoen)
CAI: 5

Sample No: 24
Lab. I.D. No.: SC1
Location: Napanee, Ontario, 2.2 km north of the Napanee type section
Loc. Ref.: Schopf, 1966
Unit: Selby Foramtion, Simcoe Group, from the basal 1 m
Taxon: Phragmodus undatus (Branson & Mehl)
CAI: $1\frac{1}{2}$ - 2

Sample No: 25
Lab. I.D. No.: 85240C
Location: Camel Back Mountain, New Brunswick
Loc. Ref.: Kennedy et al., 1979
Unit: Metabasalt Unit, Tetagouche Group
Taxon: Periodon aculeatus, Hadding
CAI: $4\frac{1}{2}$

Sample No: 26
Lab. I.D. No.: LeF1
Location: Lévis, Québec, near Québec City
Loc. Ref.: Uyeno & Barnes, 1970, GSC Locality 82740
Unit: Lévis Formation, ~ 2 m from the base of the Côte Fréchette section
Taxon: Periodon aculeatus (Hadding)
CAI: 2 - $2\frac{1}{2}$

Sample No: 27
Lab. I.D. No.: GSC 83213
Location: Southampton Island, 64°04'55", 83°34', nothern Hudson Bay
Unit: Churchill River Group
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 1

Sample No: 28
Lab. I.D. No.: HS4
Location: Highgate Springs, Lake Champlain, Vermont, section on south side of Phelps Bay
Loc. Ref: Kay, 1953
Unit: Isle la Motte Formation, sample taken from the middle of the 70 ft thick formation
Taxon: Phragmodus undatus Branson & Mehl
CAI: 4

Sample No: 29
Lab. I.D. No.: CR1
Location: Crûg Farm Quarry, 1 km north of Crûg, Wales, SE of farm house
Loc. Ref.: Lindström, 1959; location 8 of Bergstöm & Orchard, 1985
Unit: Crûg Formation
Taxon: Amorphognathus superbus Rhodes
CAI: $4\frac{1}{2}$ - 5

Sample No: 30
Lab. I.D. No.: F4
Location: Ffairfach, Wales, Gennen Valley railway cutting
Loc. Ref.: locations 11 & 12 Bergström & Orchard, 1985
Unit: Ffairfach Group
Taxon: Eoplacognathus lindstroemi (Hamar)
CAI: 4 - $4\frac{1}{2}$

Sample No: 31
Lab. I.D. No.: 76/1D
Location: Tønnerudodden, east side of Randsfjord, Hadeland, North Oslo Region, Norway
Loc. Ref.: Bruton & Williams, 1982
Unit: lower part of Gamme Formation (Gagnum Limestone), ~ 15 - 15.5 m above the base of the formation
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 5

Sample No: 32
Lab. I.D. No.: BP6
Location: Broom Point, Western Newfoundland
Loc. Ref.: James & Stevens, 1986
Unit: Unit 92, Broom Point Member, Green Point Formation, 12.5 m above the seaward base of the Broom Point North Section
Taxon: Cordylodus primitivus Bagnoli, Barnes & Stevens
CAI: 1

Sample No: 33
Lab. I.D. No.: 313
Location: Horns Udde, Öland, Sweden
Loc. Ref.: Stop 4 of Lindström, 1971
Unit: Lanna (Limbata) Limestone, top of cliff section
Taxon: Drepanoistodus basiovalis (Sergeeva)
CAI: 1 - $1\frac{1}{2}$

Sample No: 34
Lab. I.D. No.: 321
Location: Gullhögen Quarry, southern Sweden
Loc. Ref.: Stop 10 of Lindström, 1971
Unit: Segerstad Limestone, ~ 14 m from the base
Taxon: Protopanderodus varicostatus Sweet & Bergström
CAI: 2

Sample No: 35
Lab. I.D. No.: 324
Location: Stora Bakor, quarry on NW slope of Mt. Mosseberg, Sweden
Loc. Ref.: Stop 12 of Lindström, 1971
Unit: Ceratopyge Limestone, 1 m above the base
Taxon: Cordylodus intermedius (Furnish)
CAI: 1 - 1 $\frac{1}{2}$

Sample No: 36
Lab. I.D. No.: Cl2
Location: Cloche Island near Manitoulin Island, roadcut on Highway 68, Ontario
Loc. Ref.: Barnes et al., 1978
Unit: Gull River Formation, 2 m above the base of the section within a 5.5 m unit of maroon shales
Taxon: Trucherognathus sinuosa Branson & Mehl
CAI: 2

Sample No: 37
Lab. I.D. No.: Stop179
Location: Black Mountain, Northern Territory, Australia
Loc. Ref.: Shergold et al., 1976; Shergold et al., 1991
Unit: Ninmaroo Formation, Corrie Member, 575 m above the base of the formation
Taxon: Chosodina herfurthi Müller
CAI: 1

Sample No: 38
Lab. I.D. No.: Stop132
Location: Black Mountain, Northern Territory, Australia
Loc. Ref.: Shergold et al., 1976; Shergold et al., 1991
Unit: Ninmaroo Formation, Jiggamore Member, upper part of the varigated limestone member, 310 m above the base of the formation
Taxon: Cordylodus proavus Müller
CAI: 1

Sample No: 39
Lab. I.D. No.: B.4.7 R 2057
Location: Central New South Wales, Australia, Bowen Park, Malachi's Hill
Loc. Ref.: Wyborn et al., 1991
Unit: Clearview Limestone Member, Ballingoole Formation
Taxon: Protopanderodus liripipus Kennedy, Barnes & Uyeno
CAI: 4

4Sample No: 40
Lab. I.D. No.: B 515 E 2082
Location: New South Wales, Australia, East Fossil Hill, Cliefden Caves
Loc. Ref.: Wyborn et al., 1991
Unit: Boonderoo Limestone, Belubula Formation (Limestone), 1 m above the base of the Boonderoo Limestone member
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 3 - 4

Sample No: 41
Lab. I.D. No.: 9725 A79 P89
Location: 9 Mile Pool, Salmon River, Anticosti Island, Québec
Loc. Ref.: Duffield, 1982
Unit: Becscie Formation
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 1

Sample No: 42
Lab. I.D. No.: 8049
Location: Crystal Peak, Wah Wah Range, Utah
Loc. Ref.: Miller & Ethington, 1978
Unit: Crystal Peak Dolomite, 6.1 m above the base
Taxon: Belodella jemtlandica Löfgren
CAI: $3\frac{1}{2}$ - 4

Sample No: 43
Lab. I.D. No.: Ferretti
Location: Thuringia, Germany
Loc. Ref.: Ferretti, 1992; Ferretti & Barnes, in press
Unit: Kalkbank Limestone
Taxon: Scabbardella altipes (Henningsmoen)
CAI: 4

Sample No: 44
Lab. I.D. No.: St PI 81
Location: St. Pauls Inlet, North Tickle, Western Newfoundland
Loc. Ref.: Johnson, 1986
Unit: St. Pauls Member, Green Point Formation, middle of Bed 11
Taxon: Periodon aculeatus Hadding
CAI: 1 - $1\frac{1}{2}$

Sample No: 45
Lab. I.D. No.: St PI 94
Location: St. Pauls Inlet, North Tickle, Western Newfoundland
Loc. Ref.: Johnson, 1986
Unit: St. Pauls Member, Green Point Formation, lower part of Bed 13
Taxon: Periodon aculeatus Hadding
CAI: 1 - $1\frac{1}{2}$

Sample No: 46
Lab. I.D. No.: St PI 120
Location: St. Pauls Inlet, North Tickle, Western Newfoundland
Loc. Ref.: Johnson, 1986
Unit: St. Pauls Member, Green Point Formation, Bed 14
Taxon: Periodon aculeatus Hadding
CAI: 1 - $1\frac{1}{2}$

Sample No: 47
Lab. I.D. No.: 1.4.2
Location: Maekalda Road, roadcut section, Tallinn, Estonia
Loc. Ref.: Kaljo, D. & H. Nestor, 1990
Unit: Leetse Formation, 10 cm from the top of the Maekola Member
Taxon: Oistodus lanceolatus (Pander)
CAI: 1

Sample No: 48
Lab. I.D. No.: R-90.6
Location: Radium, British Columbia, St. Clair Canyon, north side of Highway 93, inside Kootenay National Park
Loc. Ref.: Aitken et al., 1972
Unit: McKay Group, 110 m above the base of the section
Taxon: Rossodus manitouensis (Repetski & Ethington)
CAI: 4

Sample No: 49
Lab. I.D. No.: Wp90-13
Location: Wilcox Pass, Jasper National Park, Alberta
Loc. Ref.: Dean, 1989
Unit: Putty Shale Member, Survey Peak Formation, 6.5 m above the base of the member
Taxon: Cordylodus angulatus Pander
CAI: 5 - 5 $\frac{1}{2}$

Sample No: 50
Lab. I.D. No.: Wp90-125
Location: Wilcox Pass, Jasper National Park, Alberta
Loc. Ref.: Dean, 1989
Unit: Outram Formation, 181 m above the base of the formation
Taxon: Oepikodus communis Ethington & Clark
CAI: 5 - 5 $\frac{1}{2}$

Sample No: 51
Lab. I.D. No.: Wp90-154
Location: Wilcox Pass, Jasper National Park, Alberta
Loc. Ref.: Dean, 1989
Unit: Skoki Formation, 111 m above the base of the formation
Taxon: Drepanoistodus suberectus (Branson & Mehl)
CAI: 5 - 5 $\frac{1}{2}$

Sample No: 52
Lab. I.D. No.: Z4-32
Location: Port au Port Peninsula, Western Newfoundland
Loc. Ref.: Section 4 of Ji & Barnes, 1994
Unit: Boat Harbour Formation, St. George Group, Jerry's Nose Section, 30.1 m above the base of the formation
Taxon: Acanthodus lineatus Furnish
CAI: 1

Sample No: 53
Lab. I.D. No.: Z6-32
Location: Port au Port Peninsula, Western Newfoundland
Loc. Ref.: Section 6 Ji & Barnes, 1994
Unit: Catoche Formation, St. George Group, Pigeon Head Section, 21 m above the base of the formation
Taxon: Drepanoistodus concavus (Branson & Mehl)
CAI: 1
Sample No: 54
Lab. I.D. No.: Z6-44
Location: Port au Port Peninsula, Western Newfoundland
Loc. Ref.: section 6 of Ji & Barnes, 1994
Unit: Catoche Formation, St. George Group, Pigeon Head Section, 55.4 m above the base of the formation
Taxon: Oepikodus communis Ethington & Clark
CAI: 1 - 2

Sample No: 55
Lab. I.D. No.: A.9 Trip E
Location: Mendoza, Argentina, north side of creek, section along rio San Isidro, San Isidro, Mendoza Province
Loc. Ref.: Heredia et al., 1990
Unit: Empozada Formation
Taxon: Amorphognathus superbus (Rhodes)
CAI: 4

Sample No: 56
Lab. I.D. No.: B651
Location: Sobova Valley, 7 miles south of Beyshir, Turkey
Loc. Ref.: Dean & Monad, 1970
Unit: Sobova Limestone, Sobova Section
Taxon: Drepanoistodus cf. D. basiovalis (Sergeeva)
CAI: 2 1/2 - 3

Sample No: 57
Lab. I.D. No.: E804 4142
Location: Sobova Valley, 7 miles south of Beyshir, Turkey
Loc. Ref.: Dean & Monad, 1970
Unit: Seydisehir Foramtion, Sobova Section
Taxon: Cordylodus proavus Müller
CAI: 2 1/2 - 3

Sample No: 58
Lab. I.D. No.: CC3 AC562/E4655
Location: Huanghuachang, Little Yangtze Gorge, Central China
Loc. Ref.: Xi-Ping, 1984
Unit: Nanjinguan (Nantsinkwan) Foramtion, lowest 25 cm of the formation
Taxon: Rossodus manitouensis Repetski & Ethington
CAI: 4 1/2 - 5

Sample No: 59
Lab. I.D. No.: CC10 ACC657
Location: Huanghuachang, Little Yangtze Gorge, Central China
Loc. Ref.: Xi-Ping, 1984
Unit: Fenhsiang Foramtion, topmost bed
Taxon: Drepanodus arcuatus Pander
CAI:5

Sample No: 60
Lab. I.D. No.: CC21 E4678
Location: Huanghuachang, Little Yangtze Gorge, Central China
Loc. Ref.: Xi-Ping, 1984
Unit: Kunitan Formation, 40 cm below the top
Taxon: Periodon aculeatus Hadding
CAI: 3 - 4

Sample No: 61
Lab. I.D. No.: CC26 E4678
Location: Huanghuachang, Little Yangtze Gorge, Central China
Loc. Ref.: Xi-Ping, 1984
Unit: Pagoda (Baota) Formation, taken from the middle of the formation
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 2

Sample No: 62
Lab. I.D. No.: Ck129.5
Location: Batrybasai, Malyi Karatau, Kazakhstan
Loc. Ref.: Chugaeva & Apollonov, 1982; Apollonov et al., 1988
Unit: Shabakty Formation, Tamdy Group, Batrybasai Section, 129.5 m above the base of the formation
Taxon: Cordylodus proavus Müller
CAI: 1 - 1 $\frac{1}{2}$

Sample No: 63
Lab. I.D. No.: SIB79.25 E1167
Location: Kolyma River Basin, Kolyma, Siberia
Loc. Ref.: Field Guide, 1979
Unit: Padun Horizon, 1 m above the base of Unit L
Taxon: Panderodus gracilis (Branson & Mehl)
CAI: 3 $\frac{1}{2}$ - 4

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