CHEMOSTRATIGRAPHY AND CLIMATOSTRATIGRAPHY OF THE PALEOPROTEROZOIC SNOWY PASS SUPergroup, WYOMING AND ITS APPLICATION FOR CORRELATION WITH OTHER SEQUENCES IN NORTH AMERICA

A THESIS

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA

BY

ANDREY BEKKER

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

FEBRUARY 1998
ABSTRACT

The early Paleoproterozoic ocean and atmosphere experienced significant changes in climate and chemical composition. A global glaciation was followed by climatic amelioration. Chemical composition of the ocean, namely, carbon isotope values, changed dramatically during this time.

Collected data support a glacial origin for the Headquarters and Vagner and possibly for the Campbell Lake Formations. Stable isotope values of limestones of the Vagner and Espanola Formations are similar, thereby strengthening correlation of the underlying glacial units. The Nash Fork Formation, based on carbon isotope values, was deposited at the end of the carbon isotope excursion.

Study of carbonates of the Chocolay and Cobalt Groups showed similar carbon isotope values of the Gordon Lake Formation and the Kona Dolomite, supporting their correlation. Other carbonate units of the Chocolay Group that were considered correlative with the Kona Dolomite appear to have different carbon isotope systematics and are interpreted to be older.
Paleoproterozoic rocks with ages between 2.3 and 2.1 Ga are poorly amenable for geochronological dating since they were deposited during a time of tectonic quiescence (protracted “failed” rifting of the Kenorland supercontinent). At the same time, the Paleoproterozoic experienced significant climatic changes and changes in chemical composition of the ocean and the atmosphere. A world-wide “Huronian” glaciation was followed by climatic amelioration expressed by paleosols, quartz arenites, and warm and arid climate indicators in the overlying carbonates. Chemical composition of the ocean, namely, carbon isotope values of the ocean, changed dramatically during this time from normal (around 0% PDB) before 2.45 Ga to heavy (up to 15-20% PDB) between 2.22 - 2.06 Ga, and back to normal (slightly depleted) values after 2.06 Ga. It was also a time of transition from an atmosphere with a low content of oxygen to an oxidizing atmosphere.

Greenhouse and icehouse models have been applied to explain these climatic and chemical variations. An icehouse event around 2.4-2.3 Ga led to the Huronian glaciation. It is unknown what processes caused and ended this icehouse event, but it was closely followed by a change to a warm, arid climate. It is speculated that the low latitude position of Kenorland led to the greenhouse event that induced a stratified, stagnant ocean with an anoxic bottom layer. As organic matter was buried in the deeper part of intracratonic basins and in the deeper part of the ocean, carbonates deposited in the shallow zone became progressively heavier isotopically. This led to the release of oxygen into the atmosphere. The change in composition of the atmosphere and the upper part of the ocean led to new mineral deposits typical of oxidizing environments (e.g. copper stratiform deposits). This period ended around 2.06 Ga with the breakup of Kenorland, thus ending the protracted “failed” rifting that started around 2.45 Ga. Opening of new seaways caused transgression, oceanic turnover, and mixing of deep and shallow waters. Deep waters were enriched in $^{12}$CO$_2$ released from organic matter during oxidation and, as the oxygen was exhausted, sulfate reduction and methanogenesis. It led to normal/slightly depleted carbon isotope values of carbonates and light carbon isotope values of organic matter in post-excursion units. This transgression is recorded in several basins by the appearance of black organic-rich shales. A set of markers, not necessarily all present in one place, can be reconstructed for the Paleoproterozoic: regolith on Archean and Paleoproterozoic rocks (~2.4 Ga), Huronian glaciation (2.4 - 2.33 Ga), regolith on glacial and packages of rocks including glacialis, quartz arenites, red beds, and stratiform copper deposits (~2.33 Ga), heavy carbonates with evidence for a warm arid climate, copper stratiform deposits (~2.06 Ga), and black organic-rich shales (~2.06 Ga).

Application of these changes for intracratonic as well as intercontinental correlation was explored in this work. Field, petrographic, and CIA data support a glacial environment of deposition for the Headquarters and Vagner formations and possibly also for the Campbell Lake Formation of the Snowy Pass Supergroup, WY. Carbon and oxygen isotope values of limestone overlying tillites of the Vagner Formation (middle of three glacial units of the Snowy Pass Supergroup) appear to be similar to the Bruce “Limestone” Member of the Espanola Formation overlying the middle of three glacial units in
the Huronian Supergroup, thereby supporting correlation of the underlying glacial units. Carbonates of the Nash Fork Formation, based on carbon isotope values, were deposited at the end of the carbon isotope excursion (~2.06 Ga); the lower part of this formation is $^{13}$C-enriched whereas the upper part has normal carbon isotope values around 0% PDB. This unit is correlative with the Lower Albanel Formation of the Mistassini basin, Quebec, and the Upper Jatuli/Ludikovi Groups of the Fennoscandian Shield.

Carbon isotope studies of carbonates of the Chocolay Group (Marquette Range Supergroup) and the Gordon Lake Formation of the Cobalt Group (Huronian Supergroup) show similar carbon isotope values of the Gordon Lake Formation and the Kona Dolomite, supporting their correlation. These units were deposited at the early stage of the carbon isotope excursion before intrusion of the Nipissing dikes into the Gordon Lake Formation around 2.219 Ga. Other carbonate units of the Chocolay Group (Saunders Formation, Bad River Dolomite, Randville Dolomite, Denham Formation, and Trout Lake Formation) that were traditionally considered correlative with the Kona Dolomite appear to have different carbon isotope systematics and based on this study are interpreted to be older than the Kona Dolomite.

This study shows the usefulness of combined chemostratigraphic and paleoclimatic studies for correlation and dating of Paleoproterozoic units.
ACKNOWLEDGMENTS

First of all, I would like to thank my adviser, R. W. Ojakangas who helped me a lot when I was struggling to set up this project. He was very supportive and was always around to discuss this project at any stage. Since this project evolved from a sedimentologic study of the Paleoproterozoic glacial units into a mostly chemostratigraphic study of the Paleoproterozoic carbonates, I would especially like to thank him for being tolerant of such shifts. He was very supportive when I decided, as an extension to my work in the Medicine Bow Mountains, to sample roughly correlative carbonates in the Lake Superior region, helping at this stage with his knowledge of this region, references, and samples. He led me to the dusty and stuffy basement of the University of Minnesota, Duluth, to find drill core of the Trout Lake Formation left by Dr. Ralph Marsden decades ago. In fact, the first time I saw the Kana Dolomite was when he took me, a prospective graduate student, with graduate student Amy Galarowicz on a two-day field trip to the Marquette Range Supergroup.

Juha Karhu of the Geological Survey of Finland did all stable isotope analytical work for this project. He kindly agreed to process my samples, provided a hospitable stay in Espoo, Finland, and kept me directed on the chemostratigraphic part of this project.

Many Lake Superior geologists shared their time, expertise, and samples as well as provided me with directions to outcrops. I would especially like to mention Gene LaBerge, Daniel K. Holm, and Thomas D. Waggoner of Cliff Mining Services Company. Amy Galarowitz donated her samples of the Kona Dolomite.

My work on the carbonates of the Huronian Supergroup would not be successful without the advice, samples, and help of the following geologists: Gerald Bennett, Darrel Long, Ken Card, and Grant M. Young. Gerald Bennett sent me samples of the Gordon Lake Formation from Fenwick Township early in the Fall of 1995, provided me with references, and took me on a two-day field trip. Darrel Long provided references to the geology of McGregor Bay area and took me in his boat to outcrops there as well as sharing a rainy night when we were stranded there. He and his wife offered hospitality during my stay in Sudbury.

Kevin Chamberlain and Ron Frost of the University of Wyoming, Laramie were very helpful during my field work in the Medicine Bow Mountains. Kevin Chamberlain did U-Pb work on samples I collected. Jack Redden gave me a short tour of the Black Hills, SD, helped to collect carbonate samples there, and directed me to carbonate outcrops in the Hartville Uplift. Paul Sims, Warren Day, and Terry Klein provided useful discussion during a field trip after GSA-96 to the Hartville Uplift as well as the time to collect samples. Paul Graff provided directions to the Slaughterhouse Formation in the Sierra Madre.

Dr. Ken Eriksson of the Virginia Polytechnic Institute & State University pushed me to finish this thesis before getting involved with a Ph.D. research project. Dr. Fred Read of the same institution provided me with insight into carbonate petrology which helped in writing this thesis.
My father provided me with Russian references related to this project as well as lively although expensive discussions over the phone from Russia. Anna Shipilova, Tim, and Ted tried to keep me alive and working during a long winter in Duluth. Dr. Olga M. Haring supported me in every possible way during this project. All my friends and relatives are thanked for being in touch and encouraging me to overcome frustrations. Larry Sundberg and Charlie Mann were able to stand me for two years as a roommate.

The Graduate School of the University of Minnesota provided me with financial support to carry on this study. The Geological Survey of Wyoming donated maps, and Dan Hausel of that survey gave directions to Cooper Hill. Classes by Charles Matsch, Erik Brown, and Tom Johnson were very helpful in providing background on Quaternary climate, glacial geology, and stable isotopes.

Paul Hoffman provided an excellent tour de force introduction into “western” geology during my otherwise unsuccessful work with him in the summer of 1993.
## TABLE OF CONTENTS

**CHAPTER 1. INTRODUCTION**  
1.1 Purpose  
1.2 Location  
1.3 Previous work  
1.4 Present study  
1.5 Regional Geology  
1.6  

**CHAPTER 2. STRATIGRAPHIC DESCRIPTION OF THE STUDIED SECTION**  
2.1 Deep Lake Group  
2.1.1 Lindsey Quarzite  
2.1.2 Campbell Lake Formation  
2.1.3 Cascade Quartzite  
2.1.4 Vagner Formation  
2.2 Lower Libby Creek Group  
2.2.1 Rock Knoll Formation  
2.2.2 Headquarters Formation  
2.2.3 Heart Formation  
2.2.4 Medicine Peak Quartzite  
2.2.5 Lookout Schist  
2.2.6 Sugarloaf Quartzite  
2.3 Upper part of the Libby Creek Group  
2.3.1 Nash Fork Formation  

**CHAPTER 3. PETROGRAPHY OF THE STUDIED ROCKS**  
3.1 Lindsey Quartzite  
3.2 Campbell Lake Formation  
3.3 Cascade Quartzite  
3.4 Vagner Formation  
3.5 Rock Knoll Formation  
3.6 Headquarters Formation  
3.7 Heart Formation  
3.8 Lookout Schist  
3.9 Nash Fork Formation  

**CHAPTER 4. SEDIMENTATION**  

**CHAPTER 5. TECTONIC MODEL FOR THE DEPOSITION OF THE SNOWY PASS SUPERGROUP**  

**CHAPTER 6. MAJOR AND TRACE ELEMENT GEOCHEMISTRY**
AND GEOCHRONOLOGY

6.1 Major and trace element geochemistry of clastic units
6.2 Geochronology of detrital zircons in the Vagner Formation

CHAPTER 7. CARBON ISOTOPIC STUDY OF THE PALEOPROTEROZOIC CARBONATES, WYOMING, MICHIGAN, WISCONSIN, & MINNESOTA

7.1. METHODOLOGY
7.2. PREVIOUS CARBON ISOTOPIC STUDIES OF PALEOPROTEROZOIC CARBONATES

7.3. CARBON ISOTOPIC STUDY OF CARBONATES FROM THE SNOWY PASS SUPERGROUP: DATA AND INTERPRETATION

7.3.1 Vagner Formation
7.3.2 Lookout Schist
7.3.3 Nash Fork Formation

7.4. CARBON ISOTOPIC STUDY OF THE PALEOPROTEROZOIC CARBONATES FROM THE GREAT LAKES AREA

7.4.1. Kona Dolomite, Marquette Trough, Michigan
7.4.2. Bad River Dolomite
7.4.3. Trout Lake and Denham Formations, East-Central Minnesota
7.4.4. Randville Dolomite, Michigan and Saunders Formation, Wisconsin
7.4.5. Gordon Lake Formation of the Huronian Supergroup, Ontario

7.5. APPLICATION OF CHEMOSTRATIGRAPHY FOR CORRELATION OF PALEOPROTEROZOIC CARBONATES

7.5.1. Cold climate carbonates of the Paleoproterozoic
7.5.2. Summary of stable isotope signatures of 2.22 - 2.06 Ga carbonates

CHAPTER 8. COMPARATIVE STUDY OF PALEOPROTEROZOIC CARBONATES WITH AGES BETWEEN 2.22 - 2.06 Ga: EVIDENCE FOR EVAPORITES, SABKHA MINERALIZATION, AND HIGH ORGANIC MATTER CONTENT

CHAPTER 9. CARBON AND OXYGEN CYCLES DURING THE PALEOPROTEROZOIC AND POSSIBLE MODELS FOR THEIR EVOLUTION

CHAPTER 10. GLOBAL CHANGES DURING DEPOSITION OF THE SNOWY PASS SUPERGROUP

CHAPTER 11. CORRELATION OF THE SNOWY PASS SUPERGROUP WITH THE MARQUETTE RANGE AND HURONIAN SUPERGROUPS

CONCLUSIONS

APPENDICES

APPENDIX 1. PETROGRAPHIC DESCRIPTIONS OF THIN SECTIONS
APPENDIX 2. CARBON AND OXYGEN ISOTOPE RATIOS OF THE STUDIED PALEOPROTEROZOIC CARBONATES
APPENDIX 3. MAJOR AND TRACE ELEMENT ANALYSES OF DIAMICTITES AND OVERLYING UNITS 87
APPENDIX 4. GEOGRAPHIC LOCATION AND LITHOLOGY OF STUDIED SAMPLES 88
REFERENCES 90

LIST OF FIGURES

FIG. 1.1 Generalized geological map of Precambrian rocks of the Medicine Bow Mountains and Sierra Madre, WY 4
FIG. 2.1. Stratigraphic column of the Snowy Pass Supergroup in the Medicine Bow Mountains, WY 8
FIG. 2.1.1 Lindsey Quartzite and Campbell Lake Formation 9
FIG. 2.1.4 Vagner Formation 10
FIG. 2.2.1 Rock Knoll Formation 13
FIG. 2.2.2.1 Headquarters Formation 15
FIG. 2.2.5.1 Medicine Peak Quartzite, Lookout Schist, & Nash Fork Formation 17
FIG. 2.3.1 Nash Fork Formation 19
FIG. 3.1 Photomicrographs 22
FIG. 7.3.1 Scatter diagram of δ¹³C (% PDB) vs. δ¹⁸O (% PDB) for the studied Paleoproterozoic carbonates from the Medicine Bow Mountains, WY 43
FIG. 7.4.1.1 Variations in isotopic composition of carbon in carbonates of the Kona Dolomite, Mount Mesnard, MI 45
FIG. 7.4.1.2 Carbon and oxygen isotope values of carbonates from the Gordon Lake Formation and Kona Dolomite 46
FIG. 7.4.3 Comparison of carbon and oxygen isotope values of carbonates of the Chocolay Group, Lake Superior area 48
FIG. 7.4.4 Geographical position of studied carbonates of the Chocolay Group in the Lake Superior area 49
FIG. 7.5.1 Scatter diagram for Paleoproterozoic carbonates associated with diamictites 53
FIG. 7.5.2 Karhu & Holland (1996) curve of secular variations in isotopic composition of carbon in sedimentary carbonates during Paleoproterozoic time 56
FIG. 9.1 Box model of the global carbon cycle 67
FIG. 11.2 Comparative stratigraphy of metasedimentary rocks of the Sierra Madre, Medicine Bow Mountains, WY; north shore of lake Huron, ON, Canada; and Dickinson County, MI 76

LIST OF TABLES
Table 6.1.1 Inferred environment of deposition based on concentration of Fe, Mn, Cu, V and Ni in studied samples 33
Table 7.1. Excursions of $\delta^{13}C_{\text{carb}}$ in the Phanerozoic and Vendian from Schidlowski & Aharon (1992) compared with the Paleoproterozoic excursion from Karhu (1993) . . 38
Table 7.2. Studies of Paleoproterozoic $^{13}C$-enriched carbonates . . 40
Table 8.1. Characteristic features of Paleoproterozoic $^{13}C$-enriched carbonates . . 64-65
CHAPTER 1.
INTRODUCTION

Purpose

Since most Precambrian rocks are devoid of fossils, the dating of Precambrian sedimentary rocks poses a significant problem. Unless there are dateable volcanic, metamorphic or igneous rocks, dating of sedimentary rocks alone is almost impossible. Recently, U-Pb and Pb-Pb geochronology of carbonate rocks (Jahn & Cuvellier, 1994) and the Sm-Nd method of dating clays (Bros et al., 1992) advanced dating of sedimentary rocks, but in metamorphosed rocks both systems are likely to get reset. Lithostratigraphic correlations seem to be misleading for regional correlations and even so more for interregional correlations. Thus Precambrian stratigraphy is in real need of some extrabasinal time signals that can be correlated worldwide. Oceanic chemistry changes and climatic changes might serve as such signals once we learn the significance of their timing.

Carbonates are the best rocks to study for oceanic composition, since the majority of them were precipitated in situ. Carbon isotope and strontium isotope ratios appear to be useful in correlation and dating of the Neoproterozoic carbonates (Kaufman et al., 1993). There are scarce data available on strontium isotope values in the Paleoproterozoic, but a significant database of carbon isotope measurements was assembled during the last two decades (e.g. Karhu & Holland, 1996). Karhu & Holland’s preliminary curve of secular changes of carbon isotope ratios in Paleoproterozoic time can be used to constrain the age of carbonates. It shows that carbonates with ages between 2.22 - 2.06 Ga were enriched in $^{13}$C above +4 %0 PDB. This departure of carbon isotope ratios in carbonates from normal marine ratios around 0 %0 PDB to high positive values up to +12 %0 PDB and higher was called a “positive excursion” and the duration of this departure was called the excursion time (cf. Baker & Fallick, 1989a; Karhu & Holland, 1996). Carbonates that are younger or older show no enrichment in $^{13}$C. $^{13}$C-enriched carbonates were described in Australia, Zimbabwe (Lomagundi Group), Quebec (New Quebec Trough and Mistassini basin), Scotland (Lewisian complex), and Norway (Lofoten - Vestalen), as well as the Fennoscandian, Ukraine, Voronezh, and Aldan Shields (references are in Table 7.2).

The present study of carbonates has several objectives: to find new localities with $^{13}$C-enriched carbonates in North America in order to confirm their global character and applicability for interregional correlation; to study carbon isotope ratio changes during the Paleoproterozoic glacial event and their potential to become a chemostratigraphic marker; and to improve resolution of Karhu & Holland’s curve of secular changes of carbon isotope ratios during excursion time by collecting stratigraphic sets of samples. A stratigraphic set of samples would provide information on changes of carbon isotope values through time, even though they may not be directly relateable to the geologic time scale. Nevertheless, they might show more complex secular changes of carbon isotope ratios during excursion time than assumed from Karhu & Holland’s curve, and thus they have the potential to become a detailed correlation tool.
I have also attempted to test climatic changes as a correlation tool in the Paleoproterozoic. Climatostratigraphy became a very useful correlation method for rocks of Cenozoic age. "Climatostratigraphy is a system of methods and approaches of paleoclimatic reconstructions used for detailed (interstage) stratigraphic subdivision and interregional correlation of sedimentary units" (Zubakov, 1984, p. 108). This method is applicable only for subdivisions of rocks that were deposited during unstable climatic times such as during glacial cooling and postglacial warming events.

Precambrian climatostratigraphy can be based only on the use of lithologic, geochemical, and isotope methods since usually geomorphologic and paleontologic methods are not applicable to rocks of this age. These methods can give us a crude estimate of paleotemperature and precipitation rate and, what is more important, trends of climatic change. There is a significant difference in level of resolution of climatostratigraphy in Quaternary and Precambrian times. In the Precambrian, only higher level climatic changes such as greenhouse vs. icehouse changes can be recognized and applied in interregional correlations. It was recognized for a long time that diamictites in the Paleoproterozoic supracrustal rocks represent a North American regional glacial event and possibly even a global cooling event (e.g., Young, 1970, Ojakangas, 1985). Evidence for a warming event after glaciation came from geochemical and petrographic studies of paleosols and clastic units above diamictites in Canada, Michigan, Wyoming, Finland, and Russia (Chandler et al., 1969; Young, 1973; Nesbitt & Young, 1982; Marmo, 1992). Additional evidence for warm/hot and arid climates came from clastic and carbonate units higher up in these sections as carbonate or chert pseudomorphs after anhydrite and gypsum (Taylor, 1972; Wood, 1973; Larue, 1981; Chandler, 1986, 1988, 1989; Akhmedov, 1990, 1996; Master, 1991b; this study). Akhmedov et al. (1996) were the first to suggest an "evaporitization epoch" but they relied mostly on lithostratigraphic correlation. In this work all available geochronological and chemostratigraphic data from the literature were compiled to substantiate a greenhouse event following the Paleoproterozoic glaciation.

The final objective of this project is to apply chemostratigraphy and climatostratigraphy along with all other available data to test the correlation of the Snowy Pass Supergroup with the Marquette Range and Huronian Supergroups.

**Location**

The Medicine Bow Mountains are located in southeastern Wyoming, 30 miles west of the city of Laramie on State Highway 130. Most studied outcrops are within walking distance from State Highway 130, Sand Lake Road, Brooklyn Lake Road, Sugarloaf Road, Headquarters Park Road (103 Road), and Road 100. Topographic relief greater than 10,000 feet makes this area accessible only during summer months. The area is uplands with low relief broken by the Snowy Pass Range, with precipitous walls rising 1,000 feet above the adjacent uplands. There are remains of ground moraine, terminal moraines, and outwash aprons around the Snowy Pass Range, especially on its northern side. There is a multitude of small creeks, lakes, and rivers that are fed by the thawing of snow cover during the summer. The area is within the Medicine Bow National Forest, so the forest is unpopulated and is used for watershed control, grazing, recreation, game refuge and control, and winter sports. The highest part of the area is
covered by Arctic tundra. The mountains receive about 20 inches of annual rainfall and are heavily forested with spruce, pine, aspen, and fir.

**Previous work**

Reconnaissance studies in the Medicine Bow Mountains go back to the middle of the last century. The first detailed study was conducted by Blackwelder (1926). Detailed geological mapping was done by R. S. Houston and students of the University of Wyoming at Laramie. The results of these studies were presented in theses, reports, and papers (e.g., Houston et al., 1968; Sylvester, 1973; Lanthier, 1979; Karlstrom, 1977; Karlstrom et al., 1981, 1983). The Medicine Bow Mountains were mapped on the scale of 1:50,000, with some areas mapped at 1:24,000. These studies established the detailed stratigraphy (Houston et al., 1992) and tectonic history of this area (Karlstrom and Houston, 1984).

Diamictites of the Headquarters, Vagner, and Campbell Formations were described by Blackwelder (1926); Houston et al. (1968); Sylvester (1973); Lanthier (1979); Kurtz and Anderson (1979); Kurtz (1980); and Houston et al. (1981). The major element composition of the fine-grained matrix of diamictites was studied by Houston et al. (1968); Young, (1973); Sylvester (1973); and Crichton and Condie (1993).

The Nash Fork Formation was first described by Blackwelder (1926). He also gave the most complete descriptions of several sections of the Nash Fork Formation, but he did not provide their exact locations. Subsequent studies by Fenton and Fenton (1939); Hensley (1955); Knight and Keefer (1966), and Knight (1968) were concerned mostly with the paleontological study of this formation.

**Present study**

No stable isotope (carbon and oxygen) study was done prior to the present study on carbonates of the Snowy Pass Supergroup and carbon isotopes are the main thrust of this study. This project also includes petrography, geochemistry, and sedimentation of glacigenic units of the supergroup.

**Regional Geology**

The Medicine Bow Mountains comprise a north-trending anticline on the southeastern margin of the Wyoming craton; it was thrust eastward during the Laramide orogeny (Houston et al., 1968, see Fig. 1.1 for generalized geological map). The mountain range is bordered on the west by the northwest-trending Saratoga Valley, a graben filled with sedimentary rocks of Tertiary age, and on the east by the north-trending Laramie basin (Houston and Karlstrom, 1992). Glacial deposits of Pleistocene age are widespread in the northern (highest) part of the Medicine Bow Mountains.

The Wyoming craton is a triangular block of Archean crust. It was part of Kenorland, a Late Archean supercontinent (Williams et al., 1991), along with the Superior, Slave, North Atlantic, and North and South Keewatin cratons. The Wyoming craton drifted away in the Paleoproterozoic and is surrounded by Paleoproterozoic mobile belts (Dutch & Nielson, 1990; Roskoe & Card, 1993). These belts are the 1.8-Ga old Trans-Hudson orogen to the east, the 1.8-Ga old Great Falls tectonic zone to the north, and the 1.8-1.6-Ga old Cheyenne belt to the southeast (Wooden & Mueller, 1988). Isotopic
Fig. 1.1. Generalized geological map of Precambrian rocks of the Medicine Bow Mountains and Sierra Madre, Wyoming (after Karlstrom et al., 1983).
studies of Archean rocks which comprise the interior of the Wyoming craton indicate continental crust with an age older than 3.1 Ga (Hoffman, 1989). Part of the Trans-Hudson Orogen is exposed in the Hartville Uplift of southeast Wyoming (Sims et al., 1996). Supracrustal rocks of the Hartville Uplift (Whalen Group: dolomite, quartzite, metabasalts, ferruginous and aluminous schist) are older than 2.0 Ga mafic dikes and could be correlative with the Libby Creek Group of the Medicine Bow Mountains. All except the Cheyenne Belt boundaries of the Wyoming craton are concealed.

The Cheyenne belt is a shear zone as wide as 7 km, interpreted as a south-dipping Proterozoic subduction zone which separates a transgressive continental margin to the north from a volcanic arc complex to the south, with no evidence of the Archean basement (Ball & Farmer, 1991). The Cheyenne belt contains four major mylonite zones (from north to south): Mullen Creek-Nash Fork shear zone, central shear mylonite zone, southern mylonite zone, and the Rambler shear zone (Houston, 1993). The volcanic arc complex to the south of the Cheyenne belt was dated by the U-Pb zircon method at 1,792±15 Ma (Premo & Van Schmus, 1989). It is intruded by a felsic intrusive complex which is 30-50 Ma younger (op. cit.). One massif of this complex, the 1,744±14 Ma Sierra Madre Granite (op. cit.), was intruded along an earlier mylonite zone and was cut by a later mylonite zone. Gravity and seismic studies of the arc-continent boundary show that the crust to the south of the belt is thicker than to the north, being 48-54 km and 37-41 km thick respectively (Houston, 1993).

The oldest rocks of the Archean basement are gneisses and migmatites with a Rb-Sr model age of about 3.2 Ga in the central Laramie Mountains (Houston, 1993). Late Archean metavolcanic rocks of the greenstone belts that overlie crystalline basement were dated at 2,729-2,637 Ma. The Overland Creek Gneiss in the northeastern part of the Medicine Bow Mountains is a possible remnant of a greenstone belt (Houston and Karlstrom, 1992). The overlying >4.7 km thick, isoclinally folded Phantom Lake metamorphic suite of amphibolite grade was subdivided into five units in the Medicine Bow Mountains, as listed below in order of decreasing age: the Stud Creek Metavolcaniclastics, Rock Mountain Conglomerate, Bow Quartzite, Colberg Metavolcanics, Conical Peak Quartzite. There is an unconformity dividing this suite into lower and upper parts (Karlstrom and Houston, 1979b). The suite was intruded by the 2,710-Ma Spring Lake Granodiorite in the central Sierra Madre (Premo & Van Schmus, 1989). Late Archean rocks were deformed before deposition of Paleoproterozoic rocks. This Late Archean deformation caused thickening and melting of the crust and subsequent intrusion of K,0-rich granites with ages from 2,683 to 2,429 Ma (Premo & Van Schmus, 1989).

The Paleoproterozoic passive margin succession in the Sierra Madre and Medicine Bow Mountains consists of the Deep Lake Group and the Upper and Lower Libby Creek Groups, which together constitute the Snowy Pass Supergroup (Fig. 2.1). The least deformed and metamorphosed rocks are in the north-central Medicine Bow Mountains. The degree of metamorphism there is greenschist facies, biotite isograd, and the rocks were folded into broad open folds (Houston et al., 1981).

There is a regional unconformity between the Archean rocks and the Deep Lake Group (Karlstrom et al., 1983). The Deep Lake Group is a fluvial conglomerate and quartzite sequence with diamicitites and laminated phyllites near the middle (Campbell Lake Formation) and the top (Vagner
Formation) (Houston, 1993). The conglomerate member of the 570 m thick Magnolia Formation at the base of the Deep Lake Group is composed of uranium- and thorium-bearing, pyritic quartz-pebble conglomerate and grades up-section into the quartzite member of the same formation (Karlstrom and Houston, 1979b). There are some thin mafic and (?) felsic volcanic rocks in the lower part of the conglomerate member (Karlstrom and Houston, 1979b). The quartzite member of the Magnolia Formation contains subarkosic and arkosic, trough cross-bedded, coarse-grained to granular arenites and was interpreted to be deposited in a fluvial environment (Karlstrom et al., 1983). The upper limit for the age of the deposition of the Deep Lake Group was constrained by dating a pegmatitic metagabbro plug that intruded the Cascade Quartzite of the Deep Lake Group in the Sierra Madre. The U-Pb zircon method yielded an age of 2,092 ± 9 Ma (Premo & Van Schmus, 1989). This age is close to the age of the swarm of mafic to ultramafic dikes in the Laramie Mountains (2,010 +/- 10 Ma, Cox and Chamberlain, 1995), which is considered to be a close estimate for the age of the Paleoproterozoic rifting of the Wyoming Province. The lower age limit of the Deep Lake Group is determined by detrital zircons in the basal conglomerate of the Magnolia Formation (2,451 ± 9 Ma, Premo & Van Schmus, 1989). The upper part of the the Deep Lake Group (Vagner Formation) is in fault contact with the Lower Libby Creek Group.

The Libby Creek Group has glaciomarine deposits at its base (Headquarters and, possibly, Rock Knoll formations), which are overlain by quartzites and arenites of the Heart Formation and Medicine Peak Quartzite, phyllites and arenites of the Lookout Schist, and quartzites of the Sugarloaf Quartzite. There is a major structural discontinuity between the Lower and Upper Libby Creek Group, the Lewis Lake fault. The Lewis Lake fault was likely rotated into its present near-vertical position during the closure of the basin.

The Upper Libby Creek Group includes a thick dolomite unit (Nash Fork Formation), pillow lavas (Towner Greenstone), and black pyritic and graphitic slate (French Slate). It was suggested that the Towner Greenstone and the French Slate were laid down in a foredeep basin caused by the encroachment of the island arc from the south (Houston, 1993). However, study of the trace elements and the REE distributions in the French Slate by Crichton & Condie (1993) and Nd model ages from the Upper Libby Creek Group of Ball & Farmer (1991) indicate no evidence of arc-derived sediments. The Towner Greenstone is a 180 to 490 m thick succession of massive to schistose amphibolite with several small lenses of quartzite, probable chert (Houston and Karlstrom, 1992; Karlstrom et al., 1983), carbonate and BIF. Pillow structures in the amphibolite and associated chert suggest a marine extrusive origin (Houston and Karlstrom, 1992). The French Slate is a 610 m thick succession of laminated ferruginous slate and phyllite with two thick lenses of hematitic iron-formation in the middle and upper parts of the unit (Houston and Karlstrom, 1992, Karlstrom et al., 1983). This formation is truncated by the Mullen Creek-Nash Fork shear zone along its entire upper contact (Houston and Karlstrom, 1992).
CHAPTER 2.

STRATIGRAPHIC DESCRIPTION OF THE STUDIED SECTION

2.1 Deep Lake Group

2.1.1 Lindsey Quartzite

The Lindsey Quartzite gradationally overlies the Quartzite Member of the Magnolia Formation (Fig. 2.1) and includes trough cross-bedded quartzite (Fig. 2.1.1a) and arkosic sandstone (Karlstrom et al., 1983). It is generally a medium-grained unit with scattered pebbles along planar foreset beds and in scours up to tens of cm deep in cross section (Karlstrom and Houston, 1979a). There are thin phyllitic layers and partings. There is a coarser grained, pyritic, quartz-granule conglomerate at the top (Karlstrom and Houston, 1979a and Fig. 2.1.1b). The thickness of the Lindsey Quartzite ranges from zero in the north to 410 m in the central Medicine Bow Mountains (Karlstrom et al., 1983).

2.1.2 Campbell Lake Formation

This formation is a 65 m-thick grey paraconglomerate-phyllite succession. The lowest unit is a diamictite with coarse-grained, arkosic, poorly sorted matrix and rounded to subangular clasts of white granite, gneiss, shale, vein quartz, phyllite, metabasalt and quartzite ranging in size from several mm to 76 cm (Fig. 2.1.1c; d). The paraconglomerate grades into black to dark gray foliated quartz-rich phyllite and gray, fine-grained, cross-bedded phyllitic sandstone (Karlstrom and Houston, 1979b). The Campbell Lake Formation is exposed from the western Sierra Madre to the eastern Medicine Bow Mountains, a distance of ~80 km.

2.1.3 Cascade Quartzite

This unit is the most extensive one in the Deep Lake Group, and it unconformably overlies Archean basement, the Campbell Lake Formation and the Lindsey Quartzite (Karlstrom et al., 1983). It is an 850 m-thick sequence of massive, pebbly, medium-grained quartzite and subarkose with local arkose (Karlstrom et al., 1983). Pebbles have an average size of 2 to 3 cm and are composed largely of quartz, granite, and black chert. There are rounded and euhedral grains of pyrite in the matrix (Karlstrom and Houston, 1979b). This sequence can be divided into three units (from bottom to the top): medium-grained quartzite, pebbly quartz arenite, and pebbly arkose (Karlstrom and Houston, 1979b). There are lenses of orthoconglomerate with normal grading and mudstone stringers in the upper unit.

2.1.4 Vagner Formation

The Vagner Formation is an 800-m thick paraconglomerate-marble-phyllite-quartzite succession that overlies the Cascade Quartzite with a considerable hiatus (Karlstrom et al., 1983 and Fig. 2.1.4a). This succession has been divided into three units: (1) a basal unit as thick as 300 m, comprised of diamictite with angular and subangular clasts of white granite, quartzite, shale, gneiss, vein quartz, and phyllite, and mafic schist with a subarkosic matrix, (2) a middle marble unit with a variable thickness from 5 m to 60 m (Karlstrom, 1977), and (3) an upper quartz-rich phyllite and laminated, fine-grained
Figure 2.1: Stratigraphic column of the Snowy Pass Supergroup in the Medicine Bow Mountains, Wyoming (adopted from Houston et al., 1992).
Fig. 2.1.1. Lindsey Quartzite and Campbell Lake Formation. a - Lindsey Quartzite, trough cross-bedding, 2 ft. hammer for scale; b - Lindsey Quartzite, quartz pebble conglomerate layer, coin for scale; c - Campbell Lake Formation, diamictite, lonestones in grey matrix, pen for scale; d - Campbell Lake Formation, diamictite, lestone in grey-reddish matrix, pen for scale.

Note: Term "lonestone" was used for solitary oversized clast sitting in fine-grained matrix. Term "dropstone" was reserved for isolated oversized clast piercing finely-laminated fine-grained matrix.
Fig. 2.1.4. Vagner Formation. a - erosional contact between the Cascade Formation and the diamictite unit of the overlying Vagner Formation, 2 ft. hammer for scale; b - diamictite unit, 2 ft. hammer for scale; c - rhythmically laminated marble unit, 2 ft. hammer for scale; d - hummocky cross-stratification in the marble unit, pencil for scale; e - flat-pebble conglomerate on bedding plane at the top of the marble unit, pencil for scale.
quartzite unit (Karlstrom and Houston, 1979b).

The diamictite has a greenish and sometimes reddish (due to hematite staining) coarse-grained matrix (Fig. 2.1.4b). Evidence for an erosional contact at the base of the Vagner Formation comes from the presence of the channels, quartzose gritstone and pebbles from the Cascade Formation in the upper phyllite unit, variable thickness of the Cascade Formation, and an angular unconformity east of Reservoir Lake (Fig. 2.1.4a).

The marble unit consists of rhythmically interlayered pure fine-grained carbonates and sand-rich coarse-grained carbonates Fig. 2.1.4c). The arkosic sandy layers are brown whereas the pure limestone has a grey-blue or brown-red color. There is a transition from arkose sandstone with carbonate cement to impure carbonate. Soft-sediment deformation structures, fine lamination, possible hummocky cross-bedding, and lensoidal bedding were observed in Rock Creek (Fig. 2.1.4d), and flat-pebble conglomerate was observed in the same locality at the top of this unit (Fig. 2.1.4e). To the west of Reservoir Lake, marble is present in rhythmites of sandstone-siltstone-marble. There is an interlayering of phyllite containing limestones of granite-granodiorite (from 1 to 5 cm in diameter) and marble to the east of Reservoir Lake.

There are crustose and small columnar stromatolites in the rusty brown-weathering, grey limestone of the Cooper Hill area. Silicified corrugated laminations stand out and make visible the transition from laterally-linked inclined columnar stromatolites (2.5 - 3 cm wide, as high as 3 - 3.5 cm, and with individual relief of about 1 - 1.5 cm) into crustose stromatolites. There are some well-preserved laminations with a high degree of repetition. These stromatolites resemble those described by Hofmann et al. (1980) from the Espanola Formation of the Huronian Supergroup, ON, which they considered similar to "Collenia" kona in the Kona Dolomite of Michigan (Twenhofel, 1919). Clasts of carbonates occur above the marble unit in the overlying phyllite unit at Rock Creek and Trail Creek. Climbing ripples, parallel bedding, and wavy bedding are also present in this unit. No warping or piercing of layering beneath stones was found in the marble or phyllite units. The phyllite is badly deformed and cleaved and contains pyrite crystals.

This formation extends from the western Sierra Madre to the eastern Medicine Bow Mountains, a distance of ~100 km.

2.2 Lower Libby Creek Group

The Lower Libby Creek Group includes dominantly siliciclastic successions separated by the Reservoir Lake Fault from the Deep Lake Group and by the Lewis Lake Fault from the Nash Fork Formation of the Upper Libby Creek Group (Houston et al., 1992). The Libby Creek Group is divided into two parts based on different lithologies and environments of deposition of these parts (siliciclastics in the lower part, and dolomite, volcanic rocks, and black slate in the upper part) and the structural contact between them (a rotated thrust fault). Therefore, the Upper Libby Creek Group is either allochthonous or para-autochtonous in relation to the Lower Libby Group (Karlstrom et al., 1983).
2.2.1 Rock Knoll Formation

The Rock Knoll Formation is a 380 m-thick arkose unit truncated at the base by the Reservoir Lake Fault (Karlstrom et al., 1983). It consists of a fine- and medium-grained, plagioclase-rich arkose with black phyllitic layers and partings as thick as 30 cm and conglomerates as thick as 1 m (Karlstrom et al., 1983). There are clasts of red and white granite, granodiorite, shale, vein quartz, quartzite, and chlorite schist in the conglomerate. The conglomerates occur mostly in the upper part of this formation.

This formation has symmetrical ripple marks (Fig. 2.2.1a) in the lower part and asymmetrical ripple marks in the upper part), dessication cracks (Fig. 2.2.1b), water-escape structures (Fig. 2.2.1c), clay galls, and planar cross-bedding (Karlstrom et al., 1983). Interference ripples with flat tops, rib and furrow structures, pyrite crystals and hummocky cross-stratification were observed in debris along the eastern flank of the formation at Rock Creek Knoll. There are 20 m long channels of trough cross-bedded arkose sandstone with asymmetrical ripples enclosed in phyllite in the upper part of the formation (same location as above). Graded bedding (conglomerate to sandstone to mudstone) as thick as 1 m occurs at one locality in the swamp of South Brush Creek. Soft-sediment deformation structures were also observed in this unit at Rock Creek Knoll. The top of this formation was eroded prior to the deposition of the Headquarters Formation.

2.2.2 Headquarters Formation

The Headquarters Formation was redefined (Lanthier, 1979) to include a 350 m-thick lower member of diamictite, arkose, and schist and a 300 m-thick upper member of laminated schist and phyllite (Karlstrom et al., 1983). The formation is exposed on the southern limb of a northeastward-plunging anticline (Sylvester, 1973). Beds dip steeply and are locally overturned. The northeast-southwest-trending outcrop extends for 16 km.

The lower member includes several diamictite layers with clasts of granite, gneiss, porphyritic granite, granodiorite, quartzite, shale and grey-green schist. It has a sharp (erosional) boundary with the underlying Rock Knoll Formation. The maximum observed size of clasts is 1.5 m (Fig. 2.2.2.1a, b). The lower member has a very complex stratigraphy with repeated interlayering and lenses of schist, arkose, and diamictite. There are lenses of arkosic sandstone 1 m thick and 15 m long in the diamictite. They have both parallel laminations and large- and medium-scale trough cross-bedding. A 15 m thick coarsening-upward sequence from a pelitic layer with rare dropstones through cross-bedded arkosic sandstone with dropstones to sandstone/gritstone with large trough cross-beds occurs west of North Twin Lake. Reversed and normal grading, slumped and convoluted structures, and cross-bedding are widespread through the lower member (e.g., to the west of South Twin Lakes). There are at least three lensoid reversely graded diamictites (debris flow?) in laminated and cross-bedded arkosic sandstone at Rock Creek Knoll. Mudstone drapes occur along the bedding with quartz pebbles on them.

The Headquarters diamictite occurs to the south of Rock Creek Knoll and continues stratigraphically downward to the change in the angle of the slope at the top of Rock Creek Knoll. Here the lower part of the diamictite is arkosic sandstone with lenses of orthoconglomerate (Fig.2.2.2.1c, f), with scattered 3-5 cm pebbles of granodiorite, granite, gneiss, and coarse sandstone. The combined
Fig. 2.2.1. Rock Knoll Formation. a - symmetrical ripple marks, coin for scale; b - dessication cracks, match box for scale; c - water escape structures, 2 ft. hammer for scale; d - soft-sediment deformation structures, 2 ft. hammer for scale.
thickness of the Headquarters diamictite and arkosic sandstone is about 70-80 m in this area. The following is a measured section on the eastern flank of Rock Creek Knoll, from the top to the bottom:

Diamictite with normal grading, top not exposed------------------------ 5"
Coarse- to medium-grained arkosic sandstone-------------------------- 7'7"
Reversely graded diamictite------------------------------------------ 1'11"
Fine-grained arkosic sandstone-------------------------------------- 1'
Normal and reverse graded diamictite and gritstone with grains up to 2 cm in diameter--1'4"
Fine-grained arkosic sandstone-------------------------------------- 1'
Lens of diamictite (10' wide) in arkosic sandstone---------------------- 2'11"
Lens of diamictite in arkosic sandstone with irregular erosional lower surface-------------------6'8"
Lonestones of quartz and mudstone in argillite that passes locally into sandstone----------1'7"
Fine-grained arkosic sandstone with argillite stringers. There is a small 1" thick lens of orthoconglomerate 1'5" from the base that disappears in one direction and merges with the underlying diamictite in the other direction-------------------11'9"
Reversely graded bed of conglomerate (debris flow ?)-------------------4'3"
Normally graded bed of conglomerate (debris flow ?)-------------------2'8"
Arkosic sandstone with some pebbles in the upper 5'-----------------14'3"

Total thickness: 57'4"

Another section was measured about 50 m southwest along strike from the previous section, from the top to the bottom:

"Phyllite" unit. Top is not exposed but probably continues stratigraphically upward for another 90'--------------------------------------------------------------------------125'
Arkose sandstone with diamictite lenses--------------------------------50'
Diamictite lens 13' wide---------------------------------------------1'4"
Arkosic sandstone, massive-------------------------------------------3'6"
Reversely graded diamictite with pebbles 1-2" in diameter, mostly granite with some mudstone chips. Diamictite disappears to the northeast into cross-bedded sandstone with thin diamictite lenses (1"x2.5"). Size of clasts in the diamictite lenses and lonestones in the arkosic sandstone decreases away from the center of the diamictite lenses------------------------------------------2'5"
Finely laminated arkosic sandstone with thin 2" lag deposits of mud and sand chips 0.5" to 2" in diameter--------------------------------------------------------------------------2'11"
Reversely graded diamictite with 9" thick lenses of planar bedded arkosic sandstone----- 5'3"
Fig. 2.2.1. Headquarters Formation. a - diamicrite unit, 2 ft. hammer for scale parallel to bedding; b - diamicrite unit, 1 ft. hammer for scale; c - debris flow in the diamicrite unit, faint stratification above debris flow in the left corner, pen for scale; d - limestones in the schist unit, pen for scale; e - limestones in the schist unit, coin for scale; f - contact of the arkosic and diamicrite members, 2 ft. hammer for scale.
Reversely graded orthoconglomerate with quartz pebbles up to 6" in diameter—2'8"
Arkose sandstone with 9" thick diamicite included. Base is covered. Granodiorite boulder
24" in diameter is present. Irregular contact with the overlying orthoconglomerate—5'10"
Total thickness: 198'11"

There are dropstones in the laminated phyllite (Fig. 2.2.2.1d,e), small-scale planar and trough
cross-bedding in the arkosic, well-sorted, medium-grained sandstone (Lanthier, 1979), and climbing
ripples at the top of the upper member (Karlstrom et al., 1983). The fine laminations are the result of
interlayering of siltstone and mudstone. The laminated dark-grey schist is badly cleaved, making it
difficult to follow lamination adjacent to clasts.

This formation occurs only in the Medicine Bow Mountains and extends for ~ 14 km in a
southwest to northeast direction.

2.2.3 Heart Formation

The Heart Formation has conformable contacts with the underlying Headquarters Formation and
the overlying Medicine Peak Quartzite. The formation is a 670 m-thick, sericitic, very fine- to medium-
grained quartzite succession with some phyllites (Karlstrom et al., 1983). The Heart Formation was
divided into three members, the lower member consisting of a 400 m-thick sericitic quartzite unit with
some phyllite beds, the middle member consisting of a 90 m-thick laminated phyllite, and the upper
member consisting of a 200 m-thick medium-grained quartzite unit (Lanthier, 1979). There are ball-and-
pillow and water-escape structures at the base of the Heart Formation near North Twin Lake (Lanthier,
1979). Other sedimentary structures in the lower member of this formation include small-scale planar and
trough cross-bedding, climbing ripples, interference and symmetric ripples, and graded bedding
(Karlstrom et al., 1983). There is a gradational contact between the lower and middle members
(Lanthier, 1979). The upper member becomes coarser grained, massive- to plane-bedded, and more
quartzose (Karlstrom et al., 1983). Sedimentary structures in the upper member are ripple marks, small-
scale trough and planar cross-bedding (Lanthier, 1979).

2.2.4 Medicine Peak Quartzite

The Medicine Peak Quartzite is a 1,700 m-thick medium- to very coarse-grained quartzite with
some quartz-pebble conglomerate (Karlstrom et al., 1983). The quartzite has conformable contacts with
the overlying Lookout Schist and underlying Heart Formation. It is a medium- to thick-bedded, massive
to planar cross-bedded unit (Karlstrom et al., 1983). Other sedimentary structures in this formation are
trough cross-bedding, asymmetrical ripples, linear and interference ripples, small shallow channels, small
slump structures, erosional surfaces, herringbone cross-beds, concentrations of hematite and magnetite on
bedding planes, large-scale low-angle cross-beds, and inversely and normally graded conglomeratic beds
(Kauffman and Steidtmann, 1981; Lanthier, 1979; Karlstrom et al., 1983). Kauffman and Steidtmann
(1981) described dubiofossils (sediment-filled tubes) in this formation that they interpreted as burrows of
invertebrate metazoan organisms (Fig. 2.2.5.1a). This interpretation was challenged by Cloud (1983)
who considered them to be water-escape structures. The Medicine Peak Quartzite is rich in
Fig. 2.2.5.1. a - Medicine Peak Quartzite, "gas-escape structures", mature quartzite, 2 ft. hammer for scale; b, c - Lookout Schist, carbonate turbidite, b - 2 ft. hammer for scale, c - soft-sediment deformation structures (highlighted by black line), pen and hand lens for scale; d, e, f - Nash Fork Formation, lower part, d - biostrome, 1 ft. hammer for scale; e - brown ribbon-like rock, 1.5 ft. hammer for scale; f - soft-sediment deformation structures, silty hematite-rich dolomite, 1 ft. hammer for scale.
aluminosilicates (sericite, kaolinite, pyrophyllite, and kyanite) and rarely has feldspar (maximum feldspar content of this formation is 3%, compared to 33% in adjacent formations, according to Flurkey, 1983). This enrichment of aluminosilicates was interpreted as an in situ alteration product of feldspar (Young, 1973; Flurkey, 1983).

2.2.5 Lookout Schist

The Lookout Schist is a 400 m-thick succession of laminated phyllites and quartzites lying conformably between the overlying Sugarloaf Quartzite and the underlying Medicine Peak Quartzite (Karlstrom et al., 1983). Several thin metadolomite beds were observed to the north of Sugarloaf Peak and to the northwest of Big Telephone Lake (Blackwelder, 1926; Karlstrom et al., 1983; Fig. 2.2.5.1b, c).

Graded beds of silt-mud-dolomite (up to 1.5 m thick) occur in the western corner of Big Telephone Lake. There are holes after dissolved carbonate concretions in rhythmites (Fig. 2.2.5.1b). Fine-grained dolomite occurs in layers 5 cm thick.

Sedimentary structures observed in the Lookout Schist include: small-scale planar cross-bedding, hummocky cross-stratification, climbing ripples, flat-pebble conglomerate, symmetrical ripples, graded bedding, partial and complete Bouma beds, convolute bedding, syndepositional deformation (Fig. 2.2.5.1c), clastic dikes, flame structures, and sole marks at the bases of graded beds (Houston and Karlstrom, 1992, Karlstrom et al., 1983).

2.2.6 Sugarloaf Quartzite

This formation has a gradational contact with the underlying Lookout Schist and is in fault contact with the Nash Fork Formation. The Sugarloaf Quartzite is a 580 m-thick, fine- to medium-grained quartzite sequence (Karlstrom and others, 1983). Sedimentary structures of this formation include medium- to thin-plane beds, small-scale planar and trough cross-beds, larger-scale planar cross-beds, and symmetrical, interference, and climbing ripples (Karlstrom et al., 1983).

2.3 Upper part of the Libby Creek Group

The upper part of the Libby Creek Group includes three formations: Nash Fork Formation, Towner Greenstone, and French Slate. This study was concerned only with the Nash Fork Formation.

2.3.1 Nash Fork Formation

The Nash Fork Formation is in fault contact with the underlying Sugarloaf Quartzite along the Lewis Lake Thrust. The upper contact of this formation is not exposed but is considered structurally conformable with the overlying Towner Greenstone (Karlstrom et al., 1983). The Nash Fork Formation is a 1,980 m-thick, tan siliceous metadolomite with thick lenses of black (graphitic), pyritic phyllite (Fig. 2.3.1a) and thin beds of quartzite, metachert, and sulfide iron-formation (Houston and Karlstrom, 1992; Karlstrom et al., 1983). The dolomite displays stromatolites (Fig. 2.2.5.1d), cross-bedding, scours, and flat-pebble conglomerates. The chert is mostly white, but some is gray to black. Blackwelder (1926)
Fig. 2.3.1. Nash Fork Formation. a - middle part: organic-rich shale with pyrite crystals (Py); b, c - lower part, b - evaporite with dissolved gypsum crystals (Gy); c - imbricated oncolites; d - upper part, rare branching stromatolites; pen was used for scale on all pictures.
described polygonal cracks in clayey slate filled with gritty slate and interpreted them as mudcracks. Pseudomorphs after gypsum occur on several levels in this unit (Fig. 2.3.1b). Knight and Keefer (1966) and Knight (1968) described stromatolite-bearing bioherms enclosed in a phyllite in the lower part of this formation. Some digital stromatolites shown in Knight (1968) have an inclination applicable for the study of possible heliotropism and comparison with similar data for stromatolites of the Kona Dolomite. Micro-oncolites similar to the genus Osagia were also described by Knight (1968) and imbricated oncolites were observed in this study (Fig. 2.3.1c). Walcott (referenced in Blackwelder, 1926) identified stromatolites as the genus Collenia, but Fenton and Fenton (referenced in Knight, 1968) described them as new species - *Hadrophycus immanis* sp. nov. Stromatolites are widespread in the lower part of this unit below black graphitic shale; above it they are rare and have small-scale domal/conical shape (Fig. 2.3.1d). At the very base of the lower part of this unit there are ribbon-like (Fig. 2.2.5.1e) and soft-sediment deformation structures (Fig. 2.2.5.1f) possibly indicating a periodical deeper subtidal environment of deposition.

A possible correlative unit in the Sierra Madre (Karstrom et al., 1983) is the Slaughterhouse Formation that is composed of 1,160 m of metacarbonate, quartzite, phyllite and metachert (Houston and Karstrom, 1992; Houston and Graff, 1995).
CHAPTER 3.

PETROGRAPHY OF THE STUDIED ROCKS

Twenty-nine thin sections were studied for this work. Detailed petrography was already done in previous studies (e.g., Karlstrom et al., 1981). Since point counting and visual estimates were done by previous workers and are not critical for this study, these methods have not been applied. Petrographic descriptions of individual thin sections are given in Appendix 1.

3.1 Lindsey Quartzite

The Lindsey Quartzite is composed mostly of common quartz with the following minor minerals: perthite, plagioclase, muscovite, biotite, chlorite, zircon, and apatite. It is a mature quartzite. Grain boundaries have been sutured and interlocked during metamorphism (Fig. 3.1a).

3.2 Campbell Lake Formation

The matrix of the diamictite consists of sand-sized grains of common and polycrystalline quartz (most abundant); feldspar (second in abundance) including plagioclase, microcline, and perthite; amphibole; rutile; apatite; and felsic igneous and volcanic rock fragments (less than 5% of grains) in a matrix of chlorite, muscovite, and biotite (Fig. 3.1b). Some grains have been stained by hematite and limonite.

3.3 Cascade Quartzite

The Cascade Quartzite contains the following minerals: quartz, K-feldspar, plagioclase, muscovite, biotite, and chlorite. It is also mature quartzite.

3.4 Vagner Formation

The matrix of the diamictite consists of sand-sized grains of feldspar (plagioclase is more abundant than microcline, and both are altered); porphyritic felsic volcanic, plutonic (mostly granite), and schist rock fragments; amphibole; and common, undulatory and polycrystalline quartz in a matrix of chlorite, calcite, epidote, muscovite, and biotite. The marble of the Vagner Formation is impure limestone and includes common quartz, perthite, plagioclase, and where more metamorphosed (e.g., the Cooper Hill area on the northeastern flank of the Medicine Bow Mountains) includes garnet, idocrase, epidote (clinozoisite), and muscovite. Quartz grain boundaries were corroded by carbonate and carbonate was recrystallized into calcite mosaic (Fig. 3.1c). Columnar and crustose stromatolites are present in the Cooper Hill area and show a faintly banded microstructure in thin section BE-95-C-3. The stromatolites are composed of a silicified xenotopic uniform granular mosaic of limestone.

3.5 Rock Knoll Formation

Lithologically, the Rock Knoll Formation is different from the quartzites of the underlying Deep Lake Group in the predominance of plagioclase over other feldspars, ranging from 2:1 to 5:1 plagioclase over potash feldspar (Houston and Karlstrom, 1992). This predominance was observed in the Vagner Formation as well as in the Lower Libby Creek Group (see above). The Rock Knoll Formation contains the following minerals: common, undulatory, and polycrystalline quartz; microcline; orthoclase; perthite; muscovite; biotite; chlorite; felsic plutonic rock fragments; chert rock fragments; quartzite rock fragments;
Fig. 3.1. Photomicrographs. a - Lindsey Quartzite, mature quartzite with sutured quartz grains and sericite; b - Campbell Lake Formation, diamicite, plutonic rock fragment (P. R. F.) in a matrix of sericite and quartz; c - Vagner Formation, marble member, recrystallized limestone (R. Lm.) and quartz (Q.); d - Headquarters Formation, diamicite unit, plutonic rock fragment (P. R. F.) and quartz grains in a matrix of sericite, muscovite, and quartz; e - Lookout Schist, recrystallized limestone (R. Lm.), corrugated grains of quartz (Q.), and muscovite (Mus.); f - Nash Fork Formation, recrystallized dolomite grain (R. Dlm.) in fine-grained dolomite; each field of view is 2.5 mm wide, all pictures were taken under crossed polars.
and schist rock fragments. Some grains of quartz show staining by iron oxides.

3.6 Headquarters Formation

The matrix of the diamictite consists of sand-sized grains of feldspar ((plagioclase is more abundant than microcline and perthite), rock fragments (mostly granite (Fig. 3.1d) but also quartzite, volcanics, mudstone/schist); common, undulatory, and polycrystalline quartz; and pyrite, zircon, and magnetite in a matrix of chlorite, muscovite, and biotite. Quartzites of the Headquarters Formation are plagioclase-rich. One thin section (BE-95-34) has fine laminations produced by interlayering of silt- and sand-sized grains.

3.7 Heart Formation

Quartzite of the Heart Formation usually contains the following minerals: quartz, plagioclase, chlorite, biotite, muscovite, sericite, zircon, tourmaline, sphene, rutile, and apatite (Karlstrom et al., 1983).

3.8 Lookout Schist

The Lookout Schist consists of these minerals: quartz, sericite, plagioclase, K-feldspar, chlorite, biotite, zircon, sphene, apatite, epidote, garnet, tourmaline, calcite, iron oxides (Houston and Karlstrom, 1992; Karlstrom et al., 1983), tremolite and siderite (Houston et al., 1968). Thin section (BE-95-16) of a thin dolomite layer showed that it is comprised of recrystallized dolomite with some muscovite, and some corroded grains of common and recrystallized quartz (Fig. 3.1e).

3.9 Nash Fork Formation

The unit contains, in addition to recrystallized dolomite (Fig. 3.1f), corroded grains of common quartz, plagioclase, and muscovite, phlogopite, tremolite, talc, apatite, and opaque minerals (Karlstrom et al., 1983). Petrographic studies showed that it also includes grains of perthite and felsic plutonic rock fragments.
Chapter 4.

SEDIMENTATION

The following is a discussion of the environments of deposition of the studied succession, mostly based on literature review. Since this information is relevant to climatic interpretation and stable isotope studies, data from the literature and some field observations were combined in this chapter.

The Lindsey Quartzite is interpreted as a fluvial deposit (Karlstrom et al., 1983). Thin phyllite layers and partings are interpreted as overbank deposits (Karlstrom et al., 1983). Trough cross-bedding (Fig. 2.1.a) shows a unimodal paleocurrent direction towards the southwest, as do ripple marks.

The Campbell Lake Formation is comprised of debris flows (Fig. 2.1.1 c, d), and, based on association with interpreted glacial units stratigraphically higher in the section, possibly of glacial origin (Karlstrom & Houston, 1979a; Houston et al., 1981; Karlstrom et al., 1983).

The Cascade Quartzite extends over 19mi in the Medicine Bow Mountains and a correlative unit is exposed in the Sierra Madre Mountains to the west (Houston et al., 1992). Trough and planar cross-bedding with a unimodal west-southwest directed mean paleocurrent is interpreted as an indication of a fluvial (Karlstrom and Houston, 1979a) or an alluvial plain or deltaic environment (Karlstrom et al., 1981; Karlstrom et al., 1983).

The Vagner Formation is interpreted as a deposit of a retreating dry-based glacier with the lower unit (diamictite) deposited in the floating shelf-ice and iceberg zone, the middle (marble) unit being precipitated in the iceberg zone from carbonate brines caused by freezing of marine water onto the base of a glacier (the model of Carey and Ahmad, 1961), and the upper (phyllite) unit being deposited seaward of the glacier (Sylvester, 1973; Houston et al., 1981). This model for carbonate precipitation in a glacial environment has not been confirmed by studies in modern glaciomarine environments (Fairchild, 1993). Another possible environment of deposition is in a deeper subtidal part of the basin during glacioeustatic transgression, as has been suggested for Neoproterozoic cap dolomites by Kennedy (1996) and Kennedy et al. (1996). If the latter interpretation is accepted, the time of deposition would be constrained to ~ 15 - 35 kyrs, the time lapse between glacioeustatic sea level rise and the following glacioisostatic rebound in the Holocene. There are scarce cross-beds and ripple marks in the quartzite of the upper unit, which indicate west-directed paleocurrents (Karlstrom and Houston, 1979b). The basal diamictite is interpreted to have been deposited in a glaciomarine environment, based on the presence of dropstone clasts in laminated phyllite, faint stratification in some conglomerates, and major element analyses of sand-sized matrix of the diamictite (Young, 1970, 1973; Houston et al., 1981; Sylvester, 1973). Hummocky cross-stratification, fine rhythmical lamination, and absence of indicators of high energy environment of deposition in the middle (marble) unit except at its very top suggests subtidal and, likely, deeper-water environment of deposition. Pyrite crystals in the phyllite unit might indicate a deeper-water reducing environment of deposition. All these sedimentary features suggest a subtidal environment of deposition for the marble unit similar to one postulated for the Neoproterozoic cap dolomites of Australia (Kennedy,
This unit probably was deposited during a transgression caused by eustatic sea level rise and it underlies mudstones of the prograding highstand system tract.

The Lower Libby Creek Group is interpreted as a marine deltaic deposit in a subsiding rift basin, with the lowest two units (the Rock Knoll and Headquarters Formations) being glaciomarine successions (Karlstrom et al., 1983).

The Rock Knoll Formation is interpreted as a glacial retreat fluviual and deltaic sequence based on its stratigraphic position between two glaciomarine sequences and its lithological similarity with them (Karlstrom et al., 1983). Blackwelder (1926) interpreted conglomerate in the upper part of this unit as a fluvial deposit. The predominance of plagioclase over potash feldspar, along with west-directed paleocurrents, is interpreted as either an indication of a different source area for the Vagner, Rock Knoll, and Headquarters formations, or an indication of climate deterioration (Karlstrom et al., 1983; Houston and Karlstrom, 1992). Fedo et al. (1997) interpreted predominance of plagioclase over potassium feldspar in the correlative Serpent Formation of the Huronian Supergroup, ON as being related to less intense (in comparison with other Huronian arenites) paleoweathering conditions due to approaching continental glaciation. Similar paleocurrent direction and predominance of plagioclase over potassium feldspar in the Rock Knoll Formation as well as in the Vagner and Headquarters formations also suggests that the difference in weathering rate due to cooling preceding the continental glaciation, rather than different source areas, led to compositional variations in the Snowy Pass Supergroup.

The Headquarters Formation was first interpreted as a glacial unit by Blackwelder (1926) and this interpretation was accepted in following studies (Houston et al., 1968; Sylvester, 1973; Karlstrom, 1977; Lanthier, 1979; Kurtz and Anderson, 1979; Houston et al., 1981). Studies of glaciomarine sedimentation on the continental slope of Antarctica led to the reinterpretation of this sequence as a glaciomarine deposit (Kurtz and Anderson, 1979; Houston et al., 1981; Karlstrom et al., 1983). This interpretation is supported by several lines of evidence: dropstones in the laminated phyllites, rapid lateral facies changes in the lower diamicite member, debris flows, and turbidites. It was inferred even further that deposition occurred on the continental slope (Kurtz and Anderson, 1979). Houston et al. (1981) applied the wet-based glacier model and suggested that the diamicite member was till deposited in either the terrestrial or grounded shelf-ice zone and includes till, fluvioglacial deposits and normal marine deposits. Later, Karlstrom et al. (1983) suggested that this formation was deposited in a prodelta and delta-front setting based on similarity with the underlying and overlying formations that were interpreted to be deposited in fluvial/deltaic, and prodelta/delta-front environments, respectively. It was also suggested that the upper member was deposited in either a large lake or a marine environment (Karlstrom and Houston, 1979b).

The lower member of the Heart Formation was interpreted by Lanthier (1979) as a transition from glaciomarine to shallow marine and, later, to a deltaic environment of deposition. It seems reasonable that the upper part of the Headquarters Formation (phyllite member) was deposited in a deep water environment following sea level rise after climatic amelioration. Subsequent isostatic rebound could have shifted the shoreline position and the environment of deposition to shallow marine/deltaic.
The middle (phyllite) member of the Heart Formation was interpreted as deeper marine deposits based on lithology and fine laminations (Lanthier, 1979). The upper member of the Heart Formation was deposited in a high energy environment and thus was interpreted to indicate shallowing (Lanthier, 1979). Karlstrom et al. (1983) interpreted this formation as prodelta and delta-front sediments associated with a prograding tide-dominated delta. Paleocurrents indicate a paleoslope to the southwest (Karlstrom et al., 1983).

The Medicine Peak Quartzite was interpreted as having been deposited on the fluvial to subtidal part of a tidally dominated delta plain (Karlstrom et al., 1983). Kauffman and Steidtmann (1981) suggested that the environment of deposition of this formation was an intertidal to shallow subtidal beach, sand flat and emergent bar environment. Unusual enrichment in aluminosilicates was interpreted as an in situ alteration of feldspar in a warm (subtropical or tropical) wet climate during or shortly before the deposition of the Medicine Peak Quartzite (Flurkey, 1983). This would require subaerial exposure and nondeposition, but poor outcrop at the boundary of the Heart Formation and Medicine Peak Quartzite does not provide field evidence for an unconformity. Paleocurrents indicate a paleoslope to the southwest (Karlstrom et al., 1983).

The Lookout Schist was interpreted to have been deposited in a prodelta-delta front environment that was affected by storm events (Karlstrom et al., 1983). These authors interpreted carbonates in the Lookout Schist as chemical precipitates in the prodelta basin. Houston and Karlstrom (1992) proposed that Bouma beds and soft-sediment deformation of this unit indicate turbidites on the delta-front slope. Hummocky cross-stratification along with sole marks, wave ripples, and graded bedding could suggest the interpretation of these deposits as storm events in areas below fair weather wave base (Collinson and Thompson, 1992, p. 104). Paleocurrents show a bimodal-bipolar, northeast-southwest trend (Karlstrom et al., 1983).

The Sugarloaf Quartzite is a shallow-marine sediment deposited in shallower water than the Lookout Schist, as a result of delta progradation. This is based on the maturity of the sediments and sedimentary structures (Karlstrom et al., 1983). Paleocurrents indicate a paleoslope to the west-southwest.

The Nash Fork Formation was interpreted as intertidal flat deposits of the shallow marine platform (Karlstrom et al., 1983) with a reducing environment producing graphitic and pyritic phyllite of the middle part of this unit in adjacent restricted subtidal bays (Houston and Karlstrom, 1992). The following observations were used in support of an intertidal environment: abundance of siliciclastic particles, cross-bedding, flat-pebble conglomerate, erosional scour.s on bioherms, dessication cracks and sulphate pseudomorphs. Knight and Keefer (1966) presented the following evidence of contemporary erosion of bioherms: 1) angular pieces of dolomite at the base of bioherms, 2) intraformational conglomerate, 3) some stromatolites with nuclei of angular blocks of phyllite and dolomite, and 4) erosional contacts between stromatolites. Alternatively, it was suggested that the Nash Fork Formation was deposited in both intertidal and subtidal environments (Houston and Karlstrom, 1992). This association of intertidal indicators and surrounding black graphitic shales could be explained as deposition on a drowned platform with stromatolite reefs keeping up with the sea level rise and projecting...
above the bottom as pinnacles. Similar associations are widespread on Phanerozoic drowned carbonate platforms (Read, 1980). There are some indications of deepening above two black graphitic shale layers in the middle part of this unit including the disappearance of stromatolites, and the presence of monotonous thick-bedded locally rhythmical sequences with sea-floor precipitates of carbonate.
CHAPTER 5.
TECTONIC MODEL FOR THE DEPOSITION OF THE SNOWY PASS
SUPergroup

Tectonic models for the southern margin of the Wyoming Province were presented in several papers (Hills and Houston, 1979; Karlstrom et al., 1981; Karlstrom and Houston, 1984; Duebendorfer and Houston, 1987; Houston et al., 1989; Duebendorfer and Houston, 1990; Houston et al., 1993). This short review is intended to clarify the background of deposition during the rifting and passive margin stages.

The Wyoming Province was assembled and intruded by Late Archean granites during the Kenoran orogeny. This event was followed by deep erosion and weathering before fluvial deposition of the Deep Lake Group started. Thin volcanic rocks and conglomerates of the lower part of the Magnolia Formation are probably related to the early rifting event. The Magnolia and Lindsey formations represent a fining-upward sequence which is the first of four cycles in deposition in the Snowy Pass Supergroup. These two formations consist of debris flows of alluvial fans and braided river deposits. The rift basin had a NE-SW orientation (similar to the present margin of the Wyoming Province) and served as a focus of fluvial and deltaic sedimentation of the Deep Lake Group and the Lower Libby Creek Group, respectively. Paleocurrents of these formations are parallel in general to the inferred continental margin (NE-SW). The parallelism of paleocurrents in the Magnolia and Lindsey formations to paleocurrents in the marine Lower Libby Creek Group was interpreted by Karlstrom et al. (1983) as evidence for an elongated intracratonic basin.

The following three cycles were influenced by the Paleoproterozoic glaciation. They start with diamicite (Campbell Lake, Vagner, Headquarters formations) followed by finer clastic units (Cascade, Rock Knoll, and the upper Headquarters formations), respectively. Paleocurrents in the Vagner and Rock Knoll formations were to the west; this was interpreted along with the predominance of plagioclase over K-feldspar in these formations as an indication of a different provenance, with a mafic to intermediate rather than felsic composition of volcanic and plutonic rocks (Karlstrom et al., 1983). Another interpretation of the same phenomenon suggests that a climate deterioration slowed chemical disintegration of plagioclase rather than the provenance shift to the later rifted-away part of the craton with a different composition of igneous rocks (Houston and Karlstrom, 1992; Fedo et al., 1997).

The end of the Paleoproterozoic glaciation was marked by sea level rise during the deposition of the laminated schist of the Headquarters Formation. Glacial rebound returned the area to the deltaic environment that may have existed during Cascade time (Karlstrom et al., 1983). This deltaic environment of deposition with a southwest-directed paleoslope persisted during deposition of the Lower Libby Creek Group (Karlstrom et al., 1983).

Evidence for another rifting event is widespread dikes and sills with an age about 2.0-2.1 Ga cutting the Deep Lake Group and the Lower Libby Creek Group (Premo & Van Schmus, 1989; Cox and Chamberlain, 1995; Houston et al., 1993). At this time the rifting event succeeded, and passive margin
deposition started with carbonates of the Nash Fork Formation. Changes in carbon isotope values of carbonates (see below) in the middle part of the Nash Fork Formation suggest that the passive margin was formed some time before 2.06 Ga. This is the time of transition from heavy to “normal” carbon isotope values, as constrained on the Fennoscandian Shield (Karhu, 1993). The overlying Towner and French Creek formations were deposited in the foredeep axial zone as an island arc approached the passive continental margin from the south, inducing crustal thinning and normal faulting favorable for mafic volcanism (Hoffman, 1987; Houston, 1993). It is unclear why magmatism occurred in many Paleoproterozoic foreland basins, but Hoffman (1987) suggested a higher thermal regime in the Paleoproterozoic and faster oceanic plate recycling as possible causes.
CHAPTER 6. MAJOR AND TRACE ELEMENT GEOCHEMISTRY AND GEOCHRONOLOGY

6.1 MAJOR AND TRACE ELEMENT GEOCHEMISTRY OF CLASTIC UNITS

Twelve samples were analyzed for major and trace element concentration (Appendix 3). Samples were collected from the Campbell Lake, Vagner, Headquarters, and Heart formations, and the Medicine Peak Quartzite. Both matrix from diamictites and fine-grained rocks (argillites, schists) were analysed. In all the analysed samples, care was taken to exclude the coarse-grained fraction. Young (1969) noted that there is little change in composition of the matrix of the Gowganda Formation with an increase in degree of metamorphism. Results of major element analyses were reported by previous workers for some of these units (Sylvester, 1973; Young, 1970; Crichton & Condie, 1993).

Young (1969) noted the enrichment in Na$_2$O of the Gowganda tillites in comparison with argillites and the average Archean crust composition of the Superior Shield (Shaw et al., 1967). Our data show that the samples of the schist and diamicrite member of the Headquarters Formation have higher Na$_2$O concentrations than other samples. The Na$_2$O concentration in these samples is also higher than the average Archean crustal composition of the Superior Shield (Shaw et al., 1967). Somewhat smaller Na$_2$O concentrations were found in the lower part of the Heart Formation (95-WY-88b), and the diamicrite (BE-95-8) and schist (BE-95-28a) units of the Vagner Formation. Na$_2$O/K$_2$O ratios were used to estimate Na$_2$O-enrichment (Young, 1969). Only one sample from the schist member of the Headquarters Formation (BE-96-26) has a ratio above 2. Another sample of the same member (95-WY-88a), sample BE-95-34 of the diamicrite member of the same formation, and sample 95-WY-88b from the lower part of the Heart Formation have Na$_2$O/K$_2$O ratios between 2 and 1. Therefore, all studied samples of the diamicrite and schist members of the Headquarters Formation show significant enrichment in Na$_2$O above the average for sedimentary rocks, and are comparable with those recorded by Young (1969, 1970) from matrix of the tillites and argillites of the Gowganda Formation and matrix of the diamicrite and schist members of the Headquarters Formation. Young (1969) explained this enrichment by the absence of chemical weathering during deposition in a frigid climate. We adopt his interpretation for the Headquarters Formation.

All analysed samples are CaO-depleted in comparison with the average Archean crust composition of the Superior Shield (Shaw et al., 1967). Only samples from the diamicrite unit and the schist unit of the Vagner Formation, and the sample of the diamicrite member of the Headquarters Formation, show slightly higher values, although they are below the average Archean crust composition of the Superior Shield (Shaw et al., 1967). In connection with these values, it should be noted that the middle member of the Vagner Formation is composed of limestone and some amount of it could have been incorporated into these samples during or after deposition. Nevertheless, petrographic analysis did not indicate the presence of carbonates (Appendix 1). The average CaO/Na$_2$O ratio (Young & Nesbitt, 1986) for matrices of the tillites of the Gowganda Formation is 0.328 (average of 105 analyses) and for the argillites of the same formation it is 0.29 (average of 119 analyses). Our data (Appendix 3) indicate
similar ratios for the Headquarters Formation but higher ratios for the Vagner and Campbell Lake formations. The Heart Formation shows a mixture of CaO/Na₂O ratios, from those that are similar to the Headquarters Formation to others that are significantly higher, indicating a recurrent influx of glacier-derived material during its deposition. CaO-depletion was also noted in the Gowganda tillites and was explained by the absence of abundant Archean limestones, susceptibility of Ca-rich plagioclase, clinopyroxene, and amphibole to comminution and postdepositional alteration/chloritization (Young, 1969), and by albitionization (Young & Nesbitt, 1986).

All studied samples from the diamictite units and some from the Heart Formation are enriched in iron and/or magnesium compared with the average Archean crust composition of the Superior Province. Shaw et al., (1967) reported that the average Archean crust has about 2.05 weight percent of MgO and 4.11 weight percent of FeO plus Fe₂O₃. Young (1969) described similar enrichment in iron and magnesium in the matrices of tillites of the Gowganda Formation and explained it by preferential comminution of mafic minerals and their concentration in the fine matrix. Crichton & Condie (1993) also observed enrichment in Fe and Mg of the Headquarters diamictites in comparison with pelites from the Libby Creek Group.

Based on our analyses (Appendix 3), the CIA (chemical index of alteration) was calculated using the following equation (Nesbitt & Young, 1982):

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100
\]

where Na₂O, K₂O, Al₂O₃, and CaO^* are weight percents of oxides. Molar proportions used in calculating CaO^* should be corrected for the amount used in apatite and carbonate (Nesbitt & Young, 1982). Petrographic analyses did not show any significant amount of apatite and carbonate in studied samples. Nevertheless, corrections were made for the measured concentration of CaO, assuming all phosphorus is used in apatite. Calculated CIA indices are listed in Appendix 3. Comparison of these indices with those of Nesbitt & Young (1982) for average shale (70-75), glacial clay (60-65), and Pleistocene till (52, average of 9 samples) indicate that the Vagner and Headquarters formations have indices typical for tills and glacial clays. The only sample of the Campbell Lake Formation that was analysed in this study has a CIA index of 72 which indicates a high weathering rate and does not agree with previous suggestions of a glacial origin (Houston et al., 1981). Nevertheless, more analyses are needed before discarding their interpretation. Another possible explanation for the presence of highly weathered material within the Campbell Lake Formation is that it was deposited during the first glacial episode when the glacier scooped highly weathered regolith that was formed on the Archean and Paleoproterozoic crust. The lower part of the Heart Formation (samples 95-WY-88b, c) has a composition indicating unweathered source rocks. It might be explained by redeposition of glacier-derived material. The middle and upper parts of the Heart Formation show a definite trend to higher CIA indices (samples 95-WY-88a-k were collected in stratigraphic order from the base to the top) which indicates climatic amelioration during their deposition. No remains of paleosols were observed during traverses in which studied samples were collected.
Another possible application of major element analyses is to evaluate whether preserved diamicrites were deposited in terrestrial or glacial-marine environments. Elements such as Fe and Mn are less soluble in oxygenated environments and will concentrate in terrestrial deposits (tills). Elements that are less soluble in reducing environments, such as Cu, Pb, Zn and V, will concentrate in glacial-marine deposits (Frakes, 1985). Concentrations of Fe, Ni, V, Mn, and Cu measured in our samples (Appendix 3) were compared with average crustal abundances of Taylor (1964) as cited in Frakes (1985): Fe - 5.63 weight %, Mn - 0.095 weight %, Ni - 75 ppm, V - 135 ppm. Concentrations of Fe, Ni, and Mn above the average crustal abundances should indicate an oxygenated environment, and concentrations of Cu, and V above the average crustal abundancies should indicate a reducing environment. This comparison did not show any consistency. V data indicate an oxygenated environment for all except BE-95-8 (Vagner Formation, Diamicite Member), Ni data indicate a reducing environment for all samples, Mn measurements indicate an oxygenated environment only for samples 95-WY-87a (Heart Formation) and BE-95-26 (Headquarters Formation, Schist Member), and Fe measurements show significant variation in the environment of deposition even within the same formation (e.g. Heart Formation). These obvious discrepancies can be explained by several factors, including significant metamorphic, diagenetic, and authigenic changes that might have occurred after deposition. No petrographic or mineral separation study was undertaken to analyse in which minerals (detrital, metamorphic or authigenic) these elements are concentrated, and there is a lack of information about average crustal composition of the source area (Wyoming craton). The sequence under study was deposited during a transition to an oxygenated atmosphere and therefore it might be misleading to compare concentrations of elements sensitive to the oxygen level in their depositional environment in studied samples and samples deposited after this transition. Also pH affects the concentration of Fe in water; for example, the pH might have been different in Paleoproterozoic time due to a higher concentration of CO₂ in the atmosphere. At any rate, this study indicates that the method suggested by Frakes (1985) does not work to discriminate tills and glacial-marine sediments of Paleoproterozoic age. Similar conclusions have been made based on work on the Huronian Supergroup (G. M. Young, pers. com., 1995). The data for the current study are summarized in Table 6.1.1.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Name of formation/member</th>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>V</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE-95-8</td>
<td>Vagner Fm., Diamictite Mbr.</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>BE-95-26</td>
<td>Headquarters Fm., Schist Mbr.</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>BE-95-28A</td>
<td>Vagner Fm., Schist Mbr.</td>
<td>R</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>BE-95-34</td>
<td>Headquarters Fm., Diamictite Mbr.</td>
<td>O</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>BE-95-35</td>
<td>Campbell Lake Fm.</td>
<td>O</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-87A</td>
<td>Heart Fm.</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88A</td>
<td>Headquarters Fm., Schist Mbr.</td>
<td>O</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88B</td>
<td>Heart Fm., lower part</td>
<td>R</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88C</td>
<td>Heart Fm.</td>
<td>R</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88D</td>
<td>Heart Fm.</td>
<td>O</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88G</td>
<td>Heart Fm.</td>
<td>O</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
<tr>
<td>95-WY-88K</td>
<td>Medicine Peak Fm.</td>
<td>R</td>
<td>R</td>
<td>O</td>
<td>O</td>
<td>R</td>
</tr>
</tbody>
</table>

Table 6.1.1. Inferred environments of deposition based on concentration of Fe, Mn, Cu, V, and Ni in studied samples. R stands for a reducing environment, and O stands for an oxygenated environment of deposition. Note obvious discrepancies in environment inferred from these measurements.
6.2 GEOCHRONOLOGY OF DETRITAL ZIRCONS IN THE VAGNER FORMATION

A siliciclastic layer in the marble unit of the Vagner Formation was sampled in Rock Creek Valley (SE1/4, SE1/4, T. 17 N., R. 78 W.) for geochronological study of detrital zircons. The layer is a 0.7 m thick recessive bed in the middle part of the 40 m thick marble unit. This layer is composed of altered siliceous beds rich in an undetermined fine-grained dark-green mineral (biotite, pyroxene, or amphibole) and lighter gray-green siliceous layers. Some siliceous layers pass along strike into calcisilicates.

Two bags of collected material yielded a variety of euhedral and rounded zircons. U-Pb single zircon dating was done by Dr. Kevin Chamberlain of the University of Wyoming at Laramie. A single yellow rounded grain was dated at 2,469 ± 2 Ma, a single colourless slightly rounded grain was dated at 2,627 ± 4 Ma, two small euhedral grains yielded an age of 2,577 ± 3 Ma, and two euhedral fragments were dated at 2,676.6 ± 1.2 Ma (Fig. 6.3.1). It is evident that all grains yielded Late Archean or very old Paleoproterozoic ages that have no significance for the depositional age of the Vagner Formation. The variety of ages and the roundness of zircons fits well a glacial environment of deposition of the Vagner Formation since continental glaciation collects materials from large areas and sample different levels of crust. The absence of younger zircons can be explained by the absence of magmatic activity in this area between about 2.47 Ga and the time of deposition of the Vagner Formation.

It is interesting to compare these ages with other provenance ages for Proterozoic rocks of Wyoming and Colorado. Walter et al. (1993) reported $^{207}$Pb/$^{206}$Pb ages of single detrital zircons for a paragneiss in the Barber Lake Block of the Cheyenne Belt; two of them at 2,539 and 2,466 Ma come close to our ages. Premo and Van Schmus (1989) reported some Archean and Paleoproterozoic U-Pb zircon ages from the Sierra Madre; the age of detrital zircons from the Magnolia Formation (the basal unit of the Deep Lake Group) is 2,451 ± 9 Ma and comes close to the youngest age we obtained from detrital zircons of the Vagner Formation (2,469 ± 2 Ma) suggesting that probably no magmatic activity occurred in the basin during deposition of the Deep Lake Group. Quartzfeldspathic orthogneiss from the Sierra Madre was dated by Premo and Van Schmus (1989) at 2,683 ± 6 Ma. Our two euhedral fragments appear to have the similar age within the limits of accuracy (2,676.6 ± 1.2 Ma).
CHAPTER 7.
CARBON ISOTOPIC STUDY OF THE PALEOPROTEROZOIC CARBONATES, WYOMING, MICHIGAN, WISCONSIN, & MINNESOTA

7.1 METHODOLOGY

There are several isotopes of carbon (\( ^{12}\text{C}, ^{13}\text{C}, ^{14}\text{C} \)) but \(^{14}\text{C} \) is unstable and should not be considered in studies of Precambrian carbonates. There is a predominance of the \(^{12}\text{C} \) isotope over \(^{13}\text{C} \) in nature: 98.9\% of carbon is \(^{12}\text{C} \) and only 1.1\% of it is \(^{13}\text{C} \). Organic matter discriminates against \(^{13}\text{C} \) during photosynthesis as a result of a kinetic isotope effect involved in the first carbon-fixing reaction (Schidlowski and Aharon, 1992); thus organic matter is usually depleted in \(^{13}\text{C} \). Oxygen also has three isotopes (\( ^{16}\text{O}, ^{17}\text{O}, ^{18}\text{O} \)) but \(^{17}\text{O} \) is less abundant, close in mass to more abundant \(^{16}\text{O} \), and in terrestrial systems \(^{18}\text{O}/^{16}\text{O} \) and \(^{17}\text{O}/^{16}\text{O} \) are linearly related.

In geochemistry, the difference in absolute isotopic ratios can be measured more precisely than absolute ratios (O'Neil, 1986). Consequently, only the relative difference is measured on isotope ratio mass spectrometers and this is reported as the \( \delta \) value. A belemnite from the Cretaceous Peedee Formation of North Carolina was accepted at the University of Chicago as a standard. It has \( \delta^{13}\text{C} = 0\% \) PDB and \( ^{13}\text{C}/^{12}\text{C} = 88.99. \) \( \delta^{13}\text{C} \) and \( \delta^{18}\text{O} \) values are given in parts per thousand or permil (\( \% \)) relative to PDB (the Peedee Belemnite):

\[
\delta^{13}\text{C} = \left[ \frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right]_{\text{st}} - 1 \right] \times 1000 \text{, } (\%o, \text{PDB [Peedee Belemnite]})
\]

\[
\delta^{18}\text{O} = \left[ \frac{^{18}\text{O}/^{16}\text{O}}{^{18}\text{O}/^{16}\text{O}} \right]_{\text{st}} - 1 \right] \times 1000 \text{, } (\%o, \text{PDB [Peedee Belemnite]})
\]

\( \text{st} \) - standard, \( \text{sa} \) - sample.

A sample with a positive value of \( \delta^{13}\text{C} \) is enriched in \(^{13}\text{C} \) relative to the standard and a sample with a negative value of \( \delta^{13}\text{C} \) is depleted in \(^{13}\text{C} \) relative to the standard. What is more important in chemostratigraphy is the carbon isotope value of a sample relative to what is considered average for the particular time interval being studied. Veizer et al. (1992a, b) reported an average value of \( \delta^{13}\text{C} \) for Paleoproterozoic carbonates around \( 0 \pm 2 \% \) PDB and an average value of \( \delta^{18}\text{O} \) around -5 to -7\% PDB. The present study is concerned about positive and negative departures of \( \delta^{13}\text{C} \) from the Paleoproterozoic normal marine water values of \( 0 \pm 2 \% \) PDB. In this study, a positive departure of \( \delta^{13}\text{C} \) above 4 \% PDB, was defined as an excursion, following Baker & Fallick (1989a) and Karhu (1993). A departure of -2 \% PDB or more from the Paleoproterozoic normal marine water values is considered here as a depletion in carbon isotope values.

All samples were analyzed using the traditional phosphoric acid reaction method at the laboratory of the Finnish Geological Survey according to the methods described by Karhu (1993). The
yield is given in micromoles of released CO$_2$ per 1 mg of sample. It gives the carbonate content of the sample. Pure dolomite has a yield about 10.8 µmol/mg and pure calcite would have a yield of about 10 µmol/mg. Based on semiquantitative XRF, the carbonates of the Vagner Formation are pure calcites and the carbonates of the Nash Fork Formation are pure or nearly pure dolomites. The oxygen and carbon isotope composition of carbonates was determined by the analysis of CO$_2$ generated from the carbonates by reaction with 100 percent phosphoric acid.

Carbon isotope ratios of carbonates formed as a result of the exchange in the following equilibrium system:

$$\text{CO}_2(\text{gas}) \leftrightarrow \text{CO}_2(\text{aq}) \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$$

Carbon dioxide supplied to the atmosphere from the mantle has a -5% PDB carbon isotope ratio (Schidlowski & Aharon, 1992). It is divided between sedimentary carbonate and organic matter. There is a preferential use of the light carbon isotope in photosynthesis by organisms. The relationship between organic carbon, carbonate carbon and primordial mantle carbon is expressed by the following equation:

$$\delta^{13}C_{\text{prim}} = R \delta^{13}C_{\text{org}} + (1-R) \delta^{13}C_{\text{carb}}$$

where $\delta^{13}C_{\text{prim}}$ = -5% PDB is primordial mantle carbon, carb is carbonate, org is organic matter, x is the multiplication sign, and $R = C_{\text{org}}/(C_{\text{org}} + C_{\text{carb}})$ is a fraction of the total carbon flux buried as organic matter. For the present ocean, $\delta^{13}C_{\text{org}} = -25\%$, $\delta^{13}C_{\text{carb}} = 0\%$, $C_{\text{org}}/C_{\text{carb}} = 1/4$, and $R = 0.2$.

“Normal” values for $\delta^{13}C$ of carbonates are around 0% and for organic matter around -26% (e.g. Schidlowski & Aharon, 1992) and the difference in value of carbon isotope ratios of organic matter and coeval carbonates is usually around 26%. The residence time of carbon in the oceans is around 200,000 years (Schidlowski & Aharon, 1992), significantly longer than the mixing time of sea water, making it a good proxy for the isotopic composition of the oceanic HCO$_3^-$. Recent studies show that the carbon isotope value of the oceans has deviated from “normal” values during geological history (Table 7.1). These secular variations can be used to correlate sedimentary rocks from different basins. For example, secular variations of the carbon isotope ratio were used for the worldwide correlation of Late Proterozoic carbonate sequences (Aharon et al., 1987).

The effects of diagenetic and metamorphic processes on isotopic composition of carbonates tends to enrich them in $^{12}C$. This depletion in $^{13}C$ appears to be minor, especially for pure carbonates (Schidlowski & Aharon, 1992). It has been shown that even in the amphibolite facies of metamorphism, marbles preserved their original carbon isotope compositions (Baker and Fallick, 1989a). Oxygen isotope composition is more susceptible to postdepositional processes, and thus a significant depletion of $\delta^{18}O$ might indicate that $\delta^{13}C$ values have been altered as well. It was observed that during metamorphism, de-carbonation of mixed carbonates and silicates leads to covariance between $\delta^{18}O$ and $\delta^{13}C$ (Valley, 1986). Our samples were collected from relatively pure carbonates and do not show any covariance between $\delta^{18}O$ and $\delta^{13}C$. Major elements can also be used to check whether the original compositions of carbonates were strongly affected. Major element analysis of studied carbonates were still in process and were not available at the time this thesis was being written.
Most of the samples analyzed for this study are pure dolomites with the exception of the Vagner Formation that is composed of relatively pure limestone. Limestones are generally less affected by postdepositional alteration than dolostones, but nevertheless dolostones have been widely used in studies of carbon isotopic variations during Late Proterozoic time (Kaufman et al., 1993). The amount of oxygen and strontium carried by water are much higher than the amount of carbon; therefore oxygen and strontium isotopic ratios would be affected first, and only in rare cases would carbon isotopic values be altered.
### Direction of excursion

<table>
<thead>
<tr>
<th>Direction of excursion</th>
<th>$\delta^{13}$C shift (%)</th>
<th>Stratigraphic age</th>
<th>Duration (10$^6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative</td>
<td>1.5</td>
<td>Pliocene to Recent</td>
<td>7</td>
</tr>
<tr>
<td>Negative</td>
<td>0.8</td>
<td>Late Miocene</td>
<td>0.2</td>
</tr>
<tr>
<td>Positive</td>
<td>1.0</td>
<td>Mid-Miocene</td>
<td>3</td>
</tr>
<tr>
<td>Negative</td>
<td>1.2</td>
<td>Paleocene/ Eocene</td>
<td>3</td>
</tr>
<tr>
<td>Positive</td>
<td>2</td>
<td>Late Paleocene</td>
<td>5.5</td>
</tr>
<tr>
<td>Negative</td>
<td>1.5</td>
<td>Cretaceous/Tertiary</td>
<td>0.2</td>
</tr>
<tr>
<td>Positive</td>
<td>2</td>
<td>Santonian/ Campanian</td>
<td>5.7</td>
</tr>
<tr>
<td>Positive</td>
<td>3</td>
<td>Cenomanian/ Turonian</td>
<td>3</td>
</tr>
<tr>
<td>Positive</td>
<td>3</td>
<td>Aptian/Albian</td>
<td>9.7</td>
</tr>
<tr>
<td>Positive</td>
<td>3</td>
<td>Toarcian</td>
<td>0.5</td>
</tr>
<tr>
<td>Negative</td>
<td>4.5</td>
<td>Pernian/Triassic</td>
<td>1</td>
</tr>
<tr>
<td>Positive</td>
<td>3.5</td>
<td>Late Pernian</td>
<td>1</td>
</tr>
<tr>
<td>Positive</td>
<td>3</td>
<td>Mid-Carboniferous</td>
<td>?</td>
</tr>
<tr>
<td>Negative</td>
<td>8 (?</td>
<td>Devonian/Carboniferous</td>
<td>0.5 (?)</td>
</tr>
<tr>
<td>Positive</td>
<td>2</td>
<td>Devonian/Carboniferous</td>
<td>7 to 15</td>
</tr>
<tr>
<td>Negative</td>
<td>1.5</td>
<td>Frasnian/ Famennian</td>
<td>1</td>
</tr>
<tr>
<td>Negative</td>
<td>1</td>
<td>Ordovician/Silurian</td>
<td>?</td>
</tr>
<tr>
<td>Negative</td>
<td>4</td>
<td>Tommotian</td>
<td>?</td>
</tr>
<tr>
<td>Positive</td>
<td>4 to 6</td>
<td>Latest Vendian</td>
<td>3 (?</td>
</tr>
<tr>
<td>Positive</td>
<td>up to 12</td>
<td>Paleoproterozoic</td>
<td>160 (?</td>
</tr>
</tbody>
</table>

Table 7.1. Excursions of $\delta^{13}$C$_{carb}$ in the Phanerozoic and Vendian from Schidlowski & Aharon (1992) compared with the Paleoproterozoic excursion from Karhu (1993). Note that the excursions are arranged from youngest to oldest.
7.2 PREVIOUS CARBON ISOTOPIC STUDIES OF PALEOPROTEROZOIC CARBONATES

In the last twenty years, carbon isotope values of Precambrian carbonates have been measured extensively worldwide and, as a result, a significant database has been assembled. Schidlowski et al. (1975) in their extensive study of Precambrian carbonates found that most of them are similar in carbon isotope values to modern marine carbonates, with δ¹³C = 0 ± 2 % PDB. They were the first to discover the Lomagundi event (enrichment in δ¹³C up to +12 to +13 % PDB in carbonates of the Paleoproterozoic Lomagundi Group, Zimbabwe) but the absence of isotope data from other basins and poor time resolution for the Precambrian precluded them from recognition of the global significance of this event (Schidlowski et al., 1975, 1976). Subsequent studies in various Paleoproterozoic basins (see Table 7.2) made it obvious that the δ¹³C-enriched carbonates with ages between 2.06 - 2.22 Ga record a global event and are not local in origin as was originally suggested by Schidlowski et al. (1976). Table 7.2 is a tabulation of references of the geochemical work done on these carbonates, with their age constraints and the shifts in carbon isotope values.

In North America, carbonates enriched in δ¹³C were described from Labrador (New Quebec Orogen: Melezhik & Fallick, 1994; Rosenbaum, Cuney, & Sheppard, 1995; Melezhik et al., 1997) and were noted in Quebec (unit 1 of the Lower Albanel Formation, Mistassini basin: Schidlowski et al., 1983). Studies by Melezhik & Fallick (1994) and Melezhik et al. (1997) showed that carbonates of the Uve, Alder, and Dunphy formations of the New Quebec Orogen have high carbon isotope ratios. Studies by Mirota and Veizer (1994) in the Mistassini basin showed that the overlying carbonate units of the Lower Albanel Formation fall within the "normal" sea water range. This might indicate that the transition to normal values from the δ¹³C-enriched levels is between unit 1 and 2 of the Lower Albanel Formation. This suggestion is further enforced by the lithologic and geochemical similarities of the Ludikovi sequence in Karelia, Russia and Finland, and units 2-5 of the Lower Albanel Formation. They lie above δ¹³C-enriched carbonates which contain evidence of a warm, arid climate (gypsum, anhydrite, and halite casts; dessication cracks; tepee structures; boron-enrichment; sabkha environment of deposition; and redbeds) and copper mineralization; have δ¹³C values varying within a wide range around 0%; are composed of argillaceous dolomite with black graphitic shale ("shungites" in Karelia) and pyrite; show some evidence of warm and arid climates such as dessication cracks, tepees, and evaporite molds; and they are overlain by carbonates with "normal" marine stable isotopic signatures. It is interesting to note that, based on studies in Finland, the carbon isotope excursion ended around 2.06 Ga (Karhu, 1993), whereas the Lower Albanel Formation was dated using diagenetic galena at 2.07-2.13 Ga (Pb/Pb model age, Roscoe, 1984). This supports the previous interpretation based on the carbon isotope data that the unit 1 of the Lower Albanel Formation records the transition from the enriched to normal carbon isotope values.
<table>
<thead>
<tr>
<th>Area</th>
<th>Age</th>
<th>$\delta^{13}$C shift</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scottish Lewisian, Norway</td>
<td>2.1-1.83 Ga</td>
<td>12% PDB</td>
<td>Baker &amp; Fallick, 1989a</td>
</tr>
<tr>
<td>Lofoten-Vestenalen, Norway</td>
<td>~2.0 Ga</td>
<td>&gt;10% PDB</td>
<td>Baker &amp; Fallick, 1989b</td>
</tr>
<tr>
<td>Georgetown Inlier, Northern Queensland,</td>
<td>&gt;1570 Ma</td>
<td>5.1 - 5.9% PDB</td>
<td>McNaughton &amp; Wilson, 1983</td>
</tr>
<tr>
<td>Australia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deweras and Lonagundi Groups, Zimbabwe</td>
<td>2.07 ± 0.1 Ga</td>
<td>&gt;10% PDB</td>
<td>Schidlowski, Eichman, &amp; Junge, 1975, 1976; Master et al., 1990</td>
</tr>
<tr>
<td>Lofoten-Vesteralen, Norway</td>
<td>&gt;2.07 ± 0.9 Ga</td>
<td>10.78% PDB</td>
<td>Master et al., 1993</td>
</tr>
<tr>
<td>Mistassini basin, Quebec, Canada</td>
<td>2.07 - 2.13 Ga</td>
<td>6.38% PDB</td>
<td>Schidlowski et al., 1983; Bekker et al., 1997c</td>
</tr>
<tr>
<td>Dunphy, Portage, Uve, &amp; Alder fms., Labrador Trough, Canada</td>
<td>2.14 - 2.17 Ga</td>
<td>+5.3 to +15.4% PDB</td>
<td>Melezhik &amp; Fallick, 1994; Rosenbaum, Cuney, &amp; Sheppard, 1995; Melezhik, Fallick, &amp; Clark, 1997</td>
</tr>
<tr>
<td>Jhamarkotra Formation, Aravalli Group, India</td>
<td>2.075 Ga (Pb age for galena)</td>
<td>-1 to +11.1% PDB</td>
<td>Sreenivas et al., 1996</td>
</tr>
<tr>
<td>Franceville basin, Gabon</td>
<td>2.14 - 2.05 Ga</td>
<td>2.6 - 6.3% PDB</td>
<td>Gauthier-Lafaye &amp; Weber, 1989</td>
</tr>
<tr>
<td>Pechenga Complex, Imandra-Varzuga Complex, Ust'-Ponoi zone, Keivy series, Pasvik zone, Kola Peninsula, Russia</td>
<td>&gt;1990 Ma, &lt;2328 Ma</td>
<td>4.6 - 9.6% PDB</td>
<td>Galimov et al., 1968, 1975; Karhu &amp; Melezhik, 1992; Pokrovsky &amp; Melezhik, 1995; Melezhik &amp; Fallick, 1996</td>
</tr>
<tr>
<td>Gdantzevskaya, Rodionovskaya, Sachkinskaya suites, Ukraine</td>
<td>&gt;1.85 - 2.15 - 2.32 Ga</td>
<td>7.2-6.3% PDB &amp; 5.7% PDB &amp; 8.2% PDB</td>
<td>Zagnitko &amp; Lugovaya, 1985; Prilutsky et al., 1992</td>
</tr>
<tr>
<td>Fennoscandia</td>
<td>2.06 - &gt;2.22 Ga</td>
<td>10±3% PDB</td>
<td>Schidlowski et al., 1975; Karhu, 1993</td>
</tr>
<tr>
<td>Ontario</td>
<td>&lt;2.45 - &gt;2.219 Ga</td>
<td>4.95-8.18% PDB</td>
<td>Bekker et al., 1996; Bekker et al., 1997</td>
</tr>
<tr>
<td>Michigan</td>
<td>&gt;1.91Ga</td>
<td>4.6 - 7.8% PDB</td>
<td>Feng, 1986; Bekker et al., 1996</td>
</tr>
<tr>
<td>Yakovlevskaya, Rogovskaya suites, and Stoylenksaya suite, Voronezh Massif</td>
<td>2.009 ± 0.1 - 2.3 Ga</td>
<td>9.2% PDB &amp; 5.1% PDB</td>
<td>Akhmedov et al., 1996</td>
</tr>
<tr>
<td>Namsalsinskaya suite, Khanin basin and Amunninskaya suite, Uguysky basin, Aldan Shield, Southern Siberia</td>
<td>1.95 ± 0.11 - 2.5 Ga</td>
<td>7.1% PDB &amp; 5.9% PDB</td>
<td>Akhmedov et al., 1996; Salop, 1982</td>
</tr>
<tr>
<td>Nash Fork Fm., Wyoming</td>
<td>2.01 - 2.43 Ga</td>
<td>4 - 8% PDB</td>
<td>Bekker &amp; Karhu, 1996</td>
</tr>
<tr>
<td>Karelia, Russia</td>
<td>2.1 - 2.33 Ga</td>
<td>6.3 - 9.1% PDB, 5.5 - 18% PDB</td>
<td>Galimov et al., 1968, 1975; Yudovich et al., 1990; Karhu, 1993; Akhmedov et al., 1993; Tikhomirowa &amp; Makarikhin, 1993; Melezhik &amp; Fallick, 1996; Akhmedov et al., 1996</td>
</tr>
</tbody>
</table>

Table 7.2: Studies of Paleoproterozoic $\delta^{13}$C - enriched carbonates. References to ages with an asterisk superscript are in Stratigraphy of the USSR, 1989.
7.3. CARBON ISOTOPIC STUDY OF CARBONATES FROM THE SNOWY PASS SUPERGROUP: DATA AND THEIR INTERPRETATION

7.3.1 Vagner Formation

**Data.** The carbon isotope composition of carbonates in the Vagner Formation was studied for the following reasons: a) to provide geochemical data for the interpretation of the depositional paleoenvironment (marine, lacustrine, etc.); b) to learn how geochemical signatures may reflect cold climate environments, c) to compare obtained carbon and oxygen isotope data with the available data from correlative carbonates of the Espanola Formation in the Huronian Supergroup of Ontario (Veizer et al., 1992a) and carbonates in the Karelian Supergroup of the Kola Peninsula and Karelia, Russia (Akhmedov et al., 1996) to assess their importance as proxies to the sea water secular variations in the Paleoproterozoic time; and d) to examine correlation between carbonates of Cooper Hill (a klippe on the Cretaceous and Tertiary rocks to the east of the Medicine Bow Mountains) and carbonates in the Vagner Formation of the Medicine Bow Mountains that were traditionally considered correlative (Karlstrom et al., 1981) but are structurally separated by fault blocks containing younger rocks of Phanerozoic age (Dan Hause!, 1994).

Fourteen samples covering most of the outcrop area were studied. All of them show depleted carbon isotope values with an average of $\delta^{13}C = -2.1\%$ PDB and depleted oxygen isotope values (Fig. 7.3.1 and Appendix 2). These data support correlation of the carbonate unit in Copper Hill with the Vagner Formation of the Medicine Bow Mountains.

**Interpretation.** The low $\delta^{18}O$ values (average for the Vagner Formation: $\delta^{18}O = -18.7\%$, PDB) compared to other Paleoproterozoic carbonates (e.g. Veizer et al. 1992a, b) might be due to fresh water influx from melting glacier ice (Bekker & Karhu, 1996). Carbon isotope data support the deeper-water marine environment of deposition inferred from the analysis of sedimentary structures and comparison with better exposed and studied Neoproterozoic cap dolomites (Kennedy, 1996). Low carbon isotope values might be explained by the upwelling of $^{12}C$-enriched deeper-waters during eustatic sea level rise that lasted until isostatic rebound occurred.

7.3.2 LOOKOUT SCHIST

The Lookout Schist has an intermediate stratigraphic position between the Vagner Formation and the Nash Fork Formation (Fig. 2.1). In light of the observed carbon isotope excursion during Nash Fork time (discussed in 7.3.3), it is very important to determine where in the stratigraphic section the excursion started. The Lookout Schist is the only unit between the Vagner and the Nash Fork Formation that locally contains thin layers of brown impure dolomite. Only one sample was analyzed since others appeared to be too impure, containing less than 20% carbonate. It showed an intermediate value of $\delta^{13}C$ to the $^{13}C$ - rich Nash Fork Formation and normal/depleted Vagner Formation ($\delta^{13}C = 2.7\%$; Fig. 7.3.1. and Appendix 2). More data are needed to verify that the rise in carbon isotope values continued without
departures from the low values of the Vagner Formation through intermediate values of the Lookout Schist to the high values of the Nash Fork Formation.

7.3.3 NASH FORK FORMATION

Four samples were analyzed from the Nash Fork Formation. Three showed high positive carbon isotope ratios (average: $\delta^{13}C = 5\%$ PDB, highest: $\delta^{13}C = 8.23\%$ PDB, Fig. 7.3.1 and Appendix 2). The sample with a normal value came from the upper part of this formation and a possible explanation for this distribution of carbon isotope ratios in the stratigraphic section is that the excursion ended sometime during the deposition of the Nash Fork Formation. Similar trend of carbon isotope values from high positive to normal/depleted values has been observed in the Lower Albanel Formation of the Mistassini basin, Quebec (Schidlowski et al., 1983; Mirot & Veizer, 1994; and Bekker et al., 1997) and the Upper Jatuli/Ludikivi groups, Fennoscandian Shield (Yudovich et al., 1991). All these sequences including the Nash Fork Formation have black graphitic shales with pyrite at the change in the trend of carbon isotope values.

7.4. CARBON ISOTOPIC STUDY OF THE PALEOPROTEROZOIC CARBONATES FROM THE GREAT LAKES AREA

The following study grew as an extension to the project in the Medicine Bow Mountains and was stimulated by suggested correlations between the Snowy Pass Supergroup, Marquette Range Supergroup, and Huronian Supergroup (Young, 1983; Roscoe and Card, 1993; Houston et al., 1992). Even though there is general agreement about correlation of the lower parts of these supergroups, correlation of their upper parts still remains unresolved. Since there are carbonate units/beds in each of these supergroups on the above-mentioned stratigraphic level, this study was undertaken in hopes to resolve or at least provide new data relevant to the old argument. Thus samples of carbonates were collected from carbonate units traditionally considered correlative: the Chocolay Group in Michigan (Kona Dolomite and Randville Dolomite), Wisconsin (Bad River Dolomite and Saunders Formation), Minnesota (Trout Lake and Denham formations), and the Gordon Lake Formation of the Cobalt Group of the Huronian Supergroup. The following is a presentation of preliminary data assembled at the time the thesis was written and in Chapter 10 these data will be used to constrain correlations between the Snowy Pass Supergroup, the Marquette Range Supergroup, and the Huronian Supergroup.

7.4.1. Kona Dolomite, Marquette Trough, Michigan

The Kona Dolomite of the eastern part of the Marquette range lies above the Mesnard Quartzite and is overlain by the Wewe Slate; it is part of the Chocolay Group of the Marquette Range Supergroup (Morey and Van Schmus, 1988). The Kona Dolomite is composed of white to dark brown cherty
Figure 7.3.1. Scatter diagram of $\delta^{13}$C (‰ PDB) vs. $\delta^{18}$O (‰ PDB) for the studied Paleoproterozoic carbonates from the Medicine Bow Mountains, Wyoming.
dolomite interstratified with layers of slate, graywacke, and quartzite. Taylor (1972) subdivided the Kona Dolomite into eleven informal members and the collected set of carbonate samples from Mount Mesnard was tied in to his informal members (Fig. 7.4.1.1). Carbon isotope measurements were done by Feng (1986) on the Kona Dolomite before the present study but he did not realize the significance of carbonates enriched in $^{13}$C. Samples analyzed in this study came from three areas: 1) Mount Mesnard (NW1/4, Sec. 34, T. 48 N., R. 25 W.), 2) the Lindberg pit (SW1/4, Sec. 8, T. 47 N., R. 25 W.), and 3) a State Highway 28 roadcut outside of Marquette, MI (NE1/4, Sec. 1, T. 47 N., R. 25 W.). All samples except two showed enrichment in $^{13}$C above +4%o PDB (highest: $\delta^{13}$C = 8.29%o PDB, Fig. 7.4.1.1 and Appendix 2). During the summer of 1996, a set of samples was collected covering most of the stratigraphic section of the Kona Dolomite in the Mount Mesnard area. Preliminary data from these samples showed that most of the section except for the very base of the Big Cusp algal dolomite member has carbon isotope values above +4%o PDB. Furthermore, these two samples from the very base of the Big Cusp algal dolomite that have "normal" carbon isotope values (+1.94 and +2.38%o PDB), have also depleted oxygen isotope values (-15.53 and -16.22%o PDB, respectively), suggesting that these samples experienced postdepositional alteration (Fig. 7.4.1.2).

7.4.2 BAD RIVER DOLOMITE, UPPER PENINSULA, MICHIGAN

The Bad River Formation was assigned to the Chocolay Group of the Marquette Range Supergroup and was traditionally considered correlative with the Kona Dolomite and Randville Dolomite in Michigan and the Saunders Formation in Wisconsin (Morey and Van Schmus, 1988). The formation in the Wakefield area consists of grey to buff dolomite and cherty dolomite with stromatolites. The degree of metamorphism increases to the east and near Grandview Quarry the Bad River Dolomite is composed of siliceous and tremolitic dolomite. Two samples of the Bad River Dolomite from an area to the east of Wakefield, Michigan, were donated by R. W. Ojakangas. Carbon isotope analyses showed normal values of carbon isotope ratios at around 0 %o, PDB (Appendix 2). During the summer of 1996, a set of samples was collected from several localities along the strike of this unit in Wisconsin and Upper Peninsula, Michigan, and these samples are under study but will not be completed for this thesis.
<table>
<thead>
<tr>
<th>Lithologic Unit</th>
<th>Height (ft)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wewe Slate</td>
<td></td>
</tr>
<tr>
<td>Upper Dolomite Member</td>
<td>490'</td>
</tr>
<tr>
<td>Ragged Hills Member</td>
<td>260'</td>
</tr>
<tr>
<td>Upper Quartzite Member</td>
<td>60'</td>
</tr>
<tr>
<td>Colour-banded dolomite Member</td>
<td>370'</td>
</tr>
<tr>
<td>Valley Member</td>
<td>565'</td>
</tr>
<tr>
<td>Big cusp algal dolomite</td>
<td>130'</td>
</tr>
<tr>
<td>Middle Quartzite Member</td>
<td>140'</td>
</tr>
<tr>
<td>Grey-green argillite Member</td>
<td>300'</td>
</tr>
<tr>
<td>Thin-bedded cherty dolomite Member</td>
<td>50'</td>
</tr>
<tr>
<td>Lower quartzite Member</td>
<td>145'</td>
</tr>
<tr>
<td>Grey argillite Member</td>
<td>180'</td>
</tr>
<tr>
<td>Mesnard quartzite</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7.4.1.1. Variations in isotopic composition of carbon in carbonates of the Kona Dolomite, Mount Mesnard, MI. The lithologic column and subdivision into members is after Taylor (1972).
Fig. 7.4.1.2. Carbon and oxygen isotope values of carbonates from the Gordon Lake Formation and Kona Dolomite. Note: samples with depleted carbon isotope values have also depleted oxygen isotope values.
7.4.3 TROUT LAKE AND DENHAM FORMATIONS, EAST-CENTRAL MINNESOTA

The Trout Lake Formation was first defined by Marsden (1972) on the Cuyuna Range based on subsurface data and described as “fine-grained lithographic, locally granular, massive, gray to buff, somewhat cherty dolomite”. Since this formation is not exposed at the surface, only drill core material was used in this study. Ten samples were collected from different levels of the drill core in NE1/4, NE1/4, sec. 32, T. 138 N., R. 26 W. (This drill core is stored at the University of Minnesota, Duluth. The number after the dash in the sample number is depth in feet below the surface). All analyzed samples showed normal carbon isotope values around 0% PDB (Fig. 7.4.3).

The Denham Formation was defined by Morey (1978) near Denham in the northwestern Pine County as composed of a heterogeneous sequence of quartz-rich arenites with thin beds of dolomite, schist, volcaniclastic rocks, and pillow basalts. The Denham Formation was metamorphosed to the staurolite zone of the amphibolite facies (~530°C, 4.5 kb; Holm, 1986). Samples of dolomite were donated by R. W. Ojakangas, the University of Minnesota, Duluth, and additional samples were later collected by the author in the same outcrop in an abandoned river valley in the NE1/4, SE1/4, sec. 25, T. 45 N., R. 21 W., approximately 1.6 km southeast of the village of Denham. This area belongs to the McGrath - Little Falls terrane of the Penokean orogen, east-central Minnesota (Morey, 1996). Carbon isotope study showed that carbonates of this formation have normal carbon isotope values around 0% PDB (Fig. 7.4.3).

The Mille Lacs Group that includes the Denham and Trout Lake formations was deposited in a foreland basin which is now dissected by at least four major thrusts into four separate structural terranes making it impossible to correlate rocks between separate structural terranes (Morey, 1996). The Glen Township Formation of the Glen Township - Moose Lake structural terrane overlies quartz arenite of the Denham Formation and has yielded a Sm - Nd isochron age of 2,197 ± 39 Ma (reference to Beck, 1988 in Morey, 1996). If the Denham Formation of the Glen Township - Moose Lake terrane is correlative with the Denham Formation of the McGrath - Little Falls terrane as was suggested originally by Morey (1978) and might be implied from the discussion in Morey (1996), the Denham Formation should be older than 2.2 Ga.

7.4.4 RANDVILLE DOLOMITE, MICHIGAN AND SAUNDERS FORMATION, WISCONSIN

The Randville Dolomite and the Saunders Formation located in Michigan and Wisconsin (Fig. 7.4.4) respectively were assigned to the Chocolay Group by James (1958). Age constraints for the Randville Dolomite are wide open. It is older than 1910 ± 10 Ma (a U-Pb method age of zircon from rhyolite of the overlying Hemlock Formation, Banks and Van Schmus, 1972) and younger than Archean basement. The Saunders Dolomite can only be constrained in time to the Paleoproterozoic without applying traditional correlations with the Kona and Randville Dolomites. During the summer of 1996 samples were collected from several locations of the Randville Dolomite and Saunders Formation.
Figure 7.4.3. Comparison of carbon and oxygen isotope values of carbonates of the Chocolay Group, Lake Superior area. Note the significant differences between the Kona Dolomite and other formations.
Fig. 7.4.4. Geographical position of studied carbonates of the Chocolay Group in the Lake Superior area (after Morey, 1996).
but only a few samples have been analyzed at this time.

Analyzed samples of the Randville Dolomite were collected in the Kiernan Quadrangle (central part and SE 1/4, Sec. 4, T.43N., R. 31W.), Iron Mountain 7.5' Quadrangle (NE1/4, SE1/4, Sec. 29, T.40N., R. 30W.) and the southern margin of the Sagola basin in central Dickinson County (S1/2, Sec. 5, T. 43N., R. 28W. and border of Sec. 3 and 4, T. 43N., R. 28W.). The Randville Dolomite is composed of pure buff to pink massive to thin-bedded, fine-grained dolomite with stromatolite structures, quartzose dolomite, quartzite, slate, and schist.

The Saunders Formation was defined by Allen (1910, p. 36) and consists of cherty dolomite, massive white and pink finely crystalline dolomite with stromatolite structures, quartzose dolomite, and impure calcareous slates. Samples were collected in two areas to the south of the Brule River in Wisconsin; on the border of Sections 19 and 30, T. 41 N., R. 16 E., and W1/2, T. 41 N., R. 15 E. (see James et al., 1968 for locations of outcrops). Samples from the latter location appeared to be highly sheared and rich in silica and therefore have not been analyzed.

Both units have normal to slightly enriched carbon isotope values. These values are not sufficiently high to consider the Randville Dolomite and Saunders Formations to be really enriched in $^{13}$C and correlative to the Kona Dolomite.

### 7.4.5. Gordon Lake Formation of the Huronian Supergroup, Ontario

The age of the upper part of the Huronian Supergroup is poorly constrained by the U-Pb age of the Nipissing Diabase cutting it (2219 ± 3.5 Ma; Krogh et al., 1987), the rhyolitic Copper Cliff Formation in the lower part of the supergroup (2450 + 25/-10 Ma; Krogh et al., 1984), and the granitic Murray Pluton cutting only the lower part of the supergroup (2388 + 20/- 13 Ma; Krogh et al., 1984).

During the Penokean Orogeny, the Sault Ste. Marie - Elliot Lake area experienced low-pressure, dynamothermal metamorphism of subgreenschist- to lower greenschist grade (Card, 1978). The Gordon Lake Formation is comprised of a thin unit of varicolored siltstone and sandstone with rare beds and nodules of dolomite (Hofmann et al., 1980; Young 1991a; Jackson, 1994). During the last two decades, several localities have been described in which thin carbonate beds (Plummer Township; Hofmann et al., 1980), siliceous-dolostone-bearing beds and dolostone nodules (Meredith and Johnson townships; Jackson, 1994), and impure carbonate beds (Welcome Lake of the Cobalt Area; Chandler, 1986) occur at the base of the Gordon Lake Formation. Bennett et al. (1989) discovered a dolostone unit in a fault-bounded block in Fenwick Township, Ontario, close to Sault Ste. Marie and correlated it, based on lithostratigraphic arguments, with the Gordon Lake Formation. Thirteen samples of the Gordon Lake Formation were analyzed from Fenwick, central Meredith, Plummer, and Johnson townships. All of them have high carbon isotope ratios (highest: $\delta^{13}$C = 8.18‰, see Fig. 7.4.1.2). Since the oxygen isotope ratio is more susceptible to changes during postdepositional alteration than the carbon isotope ratio, it is worth noting that the sample with the highest $\delta^{13}$C value also has the highest $\delta^{18}$O ratio, thus indicating a low degree of post-depositional alteration.
7.5. APPLICATION OF CHEMOSTRATIGRAPHY FOR CORRELATION OF PALEOPROTEROZOIC CARBONATES

This study and similar studies elsewhere (e.g. Veizer et al., 1992a, b; Karhu, 1993; Melezhik and Fallick, 1996; Akhmedov et al., 1996; Karhu and Holland, 1996) suggest that at least three distinctive time periods can be defined based on carbon isotope data in the Paleoproterozoic: (1) \(^{18}\)O- and \(^{13}\)C-depleted carbonates associated with glaciation: Vagner Formation (Wyoming), Bruce Member of the Espanola Formation of the Huronian Supergroup (Ontario), Kumsinskaya suite (Onega basin, Karelia, Russia), and Akhrnalakhtinskaya suite of the Sarioli informal group (Pechenga basin, Kola Peninsula, Russia); (2) \(^{13}\)C - enriched carbonates (≥2.22 - 2.06 Ga), and (3) post-excursion \(^{87}\)Sr/\(^{86}\)Sr-depleted carbonates (~2.0 Ga). This study is concerned with the first two time periods. Carbonates associated with the Paleoproterozoic glaciation have not been well-constrained geochronologically. The following is a discussion of carbon isotope signatures of these time periods and their possible application for correlation.

7.5.1. Cold climate carbonates of the Paleoproterozoic

Carbonates associated with the middle diamictite unit occur in the Snowy Pass Supergroup, Wyoming (Vagner Formation) and in the Huronian Supergroup, Ontario (Espanola Formation). The stable isotope composition of the Bruce Member of the Espanola Formation was analyzed by Viezer et al. (1992a) and they interpreted depleted \(^{18}\)O and \(^{13}\)C and enriched \(^{87}\)Sr/\(^{86}\)Sr signatures as a possible indicator of meltwater admixture in a lacustrine environment during a recession of the Bruce glacier. Bernstein and Young (1990) argued for shallow marine deposition for the Espanola Formation at Moose Point, about 70 km to the southeast of the area Veizer et al. (1992a) studied. To solve this contradiction, carbonates of the Espanola Formation in the Moose Point area were sampled in the course of this investigation during the summer of 1996 to compare stable isotope signatures in these two key areas. Carbonates from the Espanola Member of the Espanola Formation were also collected near Denison Mines Ltd. No. 2 shaft (Bouck Township, northwest shore of Quirke Lake, 46°29'30"N, 82°35'50"W) close to the area Veizer et al. (1992a) sampled in their study. They have similar carbon and oxygen isotope values (Appendix 2) to the samples of the Bruce Member studied by Veizer et al. (1992a).

Similarity in carbon and oxygen isotope ratios of the Vagner Formation and the Espanola Formation led Bekker & Karhu (1996) to accept an interpretation similar to the one that Veizer and others (1992a) suggested for the Bruce Member.

Comparison with the Neoproterozoic cap dolomites studied by Kennedy (1996) suggest that the Vagner and Espanola formations may represent a short-term (< 10^5 yrs) non-steady state of the ocean mixing during the upwelling of \(^{13}\)C-enriched deep-waters as a result of glacioeustatic sea level rise. Depleted oxygen isotope values still require significant terrestrial water admixture such as would occur during melting of a continental glacier. Melting of glacier ice brought cold waters that after mixing with
marine waters sank to the bottom of the ocean and started oceanic turnover. Deep waters rich in \(^{12}\text{CO}_2\) from degradation of organic matter (oxidation, sulfate reduction, and methanogenesis) were imposed on the shallow zone and degassed precipitating carbonate with depleted carbon isotope values. Depleted oxygen isotope values can be explained by either admixture of meteoric waters or as a signature of the post-glacial ocean. Sedimentological observations also agree with the deep environment of deposition for the Vagner Formation (see Chapter 4).

Akhmedov et al. (1996) presented carbon and oxygen isotope data from Karelian carbonates deposited among the Sariolian glacial sediments. Figure 7.5.1 represents a comparison of stable isotope data for the Bruce Member of the Espanola Formation, Huronian Supergroup, ON; the Vagner Formation, Snowy Pass Supergroup, WY; and Sariolian carbonates of the Karelian Supergroup, Karelia and the Kola Peninsula. Carbonates associated with the Sariolian glacial sediments are rare and even when they occur, their stable isotope composition often indicates that they either have been significantly altered or they are not primary sedimentary rocks (Karhu, pers. com., 1996). There are some difficulties in correlation between the Fennoscandian and North American sequences since there are three glacial horizons in the Huronian and the Snowy Pass Supergroups but only one glacial horizon on the Fennoscandian Shield. Geochronological studies do not resolve the question about synchronicity of these sequences but it is generally assumed that they represent the same ice-house event (Ojakangas, 1985). It is generally accepted as, for example, in the case of the Paleoproterozoic diamictites in Michigan, that if only one glacial horizon is preserved it is probably the youngest glacial horizon (Young, 1983). It is therefore of some interest that even though direct correlation between the Fennoscandian and North American glacial units is at present indefinite, the carbonates associated with these units show similar depleted carbon and oxygen isotope values.

The importance of these data for the isotopic composition of the hydrosphere in Paleoproterozoic time remains to be resolved since none of these four sequences has been proven to be marine in origin but on the other hand all four of them appear to have similar isotopic compositions. Nevertheless, even if they are terrestrial, they can still have the isotopic composition of the hydrosphere at that time due to a high rate of exchange of \(\text{CO}_2\) between the atmosphere and the hydrosphere (Chapter 7).
Figure 7.5.1. Scatter diagram for Paleoproterozoic carbonates associated with diamictites. Data for the Bruce Member of the Espanola Formation, the Huronian Supergroup, ON from Veizer et al. (1992), the Kumsinskaya and Akhmalakhtinskaya suites from Akhmedov et al. (1996), and the Vagner Formation from Bekker & Karhu (1996).
7.5.2. Summary of stable isotope signatures of 2.22 - 2.06 Ga carbonates

It seems useful at this point to review age constraints on deposition of $^{813}$C-enriched carbonates (see Table 7.2). The oldest $^{813}$C-enriched carbonates on the Fennoscandian Shield are older than 2210 Ma (defined by 2121 - 2215 Ma U-Pb age of zircon, titanite, and baddeleyite from albite diabase sills within the quartzites of the Kivalo Formation overlying $^{13}$C-enriched dolomite beds of the Sompujärvi Formation and 2206 ± 9 Ma U - Pb age of zircons, two concordant titanite fractions and nearly concordant baddeleyite fraction from the Jäkäläniemä albite diabase sills cutting both the Greenstone Formation II and Siltstone Formation which include $^{13}$C-enriched carbonate beds, ref. in Karhu (1993)) and younger than the underlying Sariolian 2324 ± 28 Ma andesite - basalt suite of the Akhmalakhinskaya suite of the Pechenga basin (Rb-Sr method, Balashov et al., 1990). These andesite-basalts were exposed and weathered to produce regolith, and after this time interval of non-deposition the Jatulian succession was deposited. The first isotopically normal carbonates after the excursion are older than 2062 ± 2 Ma (carbonates of the uppermost Petonen Formation at Kuopio, Finland; Karhu, 1993). A 2062±2 Ma age was obtained by the U-Pb method on zircons from a felsic ash-flow metatuff in the Koivusaari Formation in the Siilinjärvi area, north of Kuopio, which is considered correlative with the Vaivanen Formation of the Kuopio area (Karhu, 1993). The Vaivanen Formation directly overlies the Petonen Formation in the Kuopio area (Karhu, 1993, Fig. 18). Data from other shields (see Table 7.2) generally have poorer time constraints but fit well into the $\geq2.22 - 2.06$ Ga interval. The only known exception at this point are carbonates of the Duitschland Formation of the Chuniespoort Group, Transvaal Sequence, South Africa (Bekker, Karhu, & Beukes, unpubl. data) which have heavy carbon isotope values (up to +8‰ PDB) and occur above diamicite and 2.43 Ga old BIF (single-zircon dating from a tuff bed in the BIFs in the Griqualand West basin, Trendall et al., 1990) and below the 2.35 Ga old Bushy Bend Lava Member at the base of the Timeball Hill Formation (preliminary zircon date, F. Walraven, 1994, pers. com. cited in Eriksson et al., 1995).

In this respect it is worth noting that the analyzed formations from North America that are enriched in $^{813}$C_carb have poor age constraints. They all are younger than the Paleoproterozoic glacial event and older than the Penokean or Cheyenne Belt orogenic events. The only other age constraint for the Kona Dolomite comes from the rhyolite in the Hemlock Formation of the overlying Menominee Group that was dated at 1,910 ± 10 Ma by the U-Pb method on zircon from volcanic layer (Banks and Van Schmus, 1972). The Gordon Lake Formation was deformed and later intruded by the Nipissing Diabase at 2219 ± 3.5 Ma (Krogh et al., 1987). On the other hand, sedimentological and general geological data (presence of soft sediment deformation structures in the Gordon Lake Formation on the contact with the Nipissing Diabase and fluidization structures in the diabase) indicate that the Gordon Lake Formation was wet and unconsolidated at the time of the Nipissing Diabase intrusion (G. Young, pers. comm., 1996). Both the Kona Dolomite and the Gordon Lake Formation contain red beds, pseudomorphs after sulfates, copper stratiform mineralization, and were interpreted to have been deposited in sabkha environments (Taylor, 1972; Chandler, 1989). Stratiform copper deposits and red beds also
occur in the underlying Lorrain and Gowganda formations (Chandler, 1980, 1986). All this evidence indicates that the transition to the oxygen-rich atmosphere started before the Gordon Lake Formation and Kona Dolomite were deposited (Bekker & Karhu, 1997b), because red beds, sulfates, and stratiform copper deposits require presence of oxygen in the atmosphere to be formed.

Karhu (1993) and Karhu and Holland (1996), using all available carbon isotope analyses of the Paleoproterozoic carbonates with well-constrained ages, compiled a curve of secular carbon isotope changes (Fig. 7.5.2). This curve has a simple shape with one apex. A new database from the Kola Peninsula compiled by Melezhik & Fallick (1996) indicates that carbonates of some lithostratigraphic subdivisions that were considered to be Upper Jatulian in age have "normal" carbon isotope values different from that of the classical Upper Jatulian carbonates. Karhu & Melezhik (1992) interpreted this dissimilarity in carbon isotope values as an indication of a younger age. Another interpretation that was suggested by Melezhik & Fallick (1995) is the possibility of three separate excursions with carbonates deposited during the two latest excursions being absent in the Kola Peninsula. Review of published carbon isotope analyses from Africa (Master et al., 1993), new carbon isotope data for carbonates of the Transvaal Sequence (Master et al., 1993; Buck et al., submitted; Bekker, Karhu, & Beukes, unpublished data), and data for the Watterson and Tavani formations, Hurwitz Group, NWT (Bekker, Karhu, & Aspler, unpublished data) suggest that between 2.43 and 2.06 Ga several carbon isotope excursions occurred. The Duitschland Formation, Transvaal basin, South Africa (see Martini, 1979 for regional geology) was deposited during the interglacial interval between 2.43 - 2.35 Ga, and shows heavy carbon isotope values. Carbonates are rare in the overlying succession as are carbon isotope analyses, but data from Master et al. (1993) suggest that another carbon isotope excursion occurred during the deposition of the Lucknow Formation, Olifantsloek Sequence, and was preceded by the depleted carbon isotope values of the Houtenbek Formation, Pretoria Group. New data from the Watterson and Tavani formations, Hurwitz Group, Northwest Territories also suggest that after glaciation and deposition of an aluminous quartzite unit (Kinga Formation) but before 2.11 Ga (U-Pb baddeleyite age of gabbro sills, Heaman & LeCheminant, 1993) there was a time interval when carbon isotope values of the ocean were around 0‰ PDB. Normal carbon isotope values of carbonates from the 2.2 - 2.1 Ga Birumian Supergroup (Master et al., 1993) seems to support the last suggestion. Since geochronological data are lacking to support this interpretation based on large-scale lithostratigraphic correlations of units from separate basins, the interpretation of Karhu & Holland (1996) which assumed one peak in secular variation of carbon isotope values will be used in this work. More data from well-dated sequences are required to choose between these two interpretations.

This approach allows the assigning of the Nash Fork Formation, Kona Dolomite, and the Gordon Lake Formation to the time interval during which δ^13C-enriched carbonates were deposited (≥ 2.22 - 2.06 Ga) and correlating them with each other and with other δ^13C-enriched carbonates (Bekker et al., 1996; see Table 7.2 for the data). Heavy Paleoproterozoic carbonates were described from North America, Baltica, Siberia, Africa, and Australia. New data (Bekker & Karhu, unpub.) indicate that the
Fig. 7.5.2. Karhu & Holland (1996) curve of secular variations in isotopic composition of carbon in sedimentary carbonates during Paleoproterozoic time. Note: vertical bars represent 1 standard deviation of carbon isotope values; horizontal bars indicate uncertainty in age of each stratigraphic unit.
Paleoproterozoic Fechado do Funil Formation, Brazil also records this excursion. It is assumed that there was a global perturbation in the composition of the ocean. Geochronological resolution does not allow at the present time the compilation of a detailed curve of the secular variations in carbon isotope values. The highest carbon isotope values of the Kona Dolomite and the Gordon Lake Formation that were deposited before 2.219 Ga reach up to +8% PDB; the highest values of carbonates from the Labrador Trough (2.17-2.14 Ga, Melezhik et al., 1997), Magondi Supergroup, Zimbabwe (2.05-2.16 Ga, Master et al., 1990; Master, 1991), and the middle/upper part of the Jatuli Group (2.11-2.06 Ga, Yudovich et al., 1991; Melezhik & Fallick, 1996) have carbon isotope values up to +15% PDB and higher. Carbonates deposited before the end of the excursion around 2.06 Ga - the Nash Fork Formation (this study), Lower Albanel Formation (Schidlowski et al., 1983; Miyota & Veizer, 1994; Bekker & Karhu, prelim. data), and Upper Jatuli (Yudovich et al., 1991; Melezhik & Fallick, 1996) - have carbon isotope values up to +8% PDB.

The age of the Gordon Lake Formation is now better defined, as it apparently was deposited during the carbon isotope excursion after ~2.3 Ga and close to 2.22 Ga (Nipissing Diabase intrusion). This unit is therefore significantly older than the Nash Fork Formation which based on correlation of carbon isotope. The present study supports the correlation of Bennett et al. (1989, 1993, 1994) of a fault bounded dolostone unit in Fenwick Township (about 27 km north of Sault Ste. Marie) with classical sections of the Gordon Lake Formation in Plummer, Johnson, and central Meredith townships about 50 km to the southeast (data from Bekker et al., 1996 and Bekker & Karhu, preliminary data) and the Kona Dolomite of the Marquette Trough in Michigan. All samples of Kona Dolomite show enrichment in $^{13}$C similar to the samples of the Gordon Lake Formation and this similarity of carbon isotope data supports a similar age of deposition. Other carbonate sequences in the Lake Superior area that were traditionally considered to be correlative with the Kona Dolomite appear to have "normal" marine carbon isotope signatures (Trout Lake Formation and Bad River Dolomite, Bekker et al., 1996) or are "normal"/slightly enriched in $^{13}$C (Randville Dolomite, Saunders and Denham formations, Bekker & Karhu, 1997b). These units with "normal" carbon isotope values must be either younger or older than the carbon isotope excursion. The first interpretation would require a major change in stratigraphy of the Chocolay Group, involving a significant period of nondeposition since the excursion lasted until 2.06 Ga and a fortuitous similarity in their position within lithostratigraphic sections and lithology of these units with the Kona Dolomite. I suggest that they are older than the carbon isotope excursion and the Kona Dolomite for the following reasons: there is no evidence for red beds and copper stratiform mineralization in these units or in underlying quartzites, nor for a sabkha environment with sulphate pseudomorphs in these dolomites although there are not many good exposures. Therefore, both climatic change and transition to the oxygenated atmosphere might have occurred after their deposition but before/during deposition of the Gordon Lake Formation and Kona Dolomite. The Kona Dolomite was probably deposited shortly after the onset of the excursion, and the age difference between this unit and other units may be relatively small. This interpretation is based on evidence from the Fennoscandian Shield that the carbon isotope excursion lasted between ≥2.22 and ~2.06 Ga without returns to normal carbon isotope values (Karhu,
New carbon isotope data from the Tavani and Watterson formations of the Hurwitz Group, NWT cast some doubt on this interpretation. These units were deposited after glaciation and based on lithostratigraphic correlations (Young, 1988) are close in age to the Gordon Lake Formation and older than 2111 ± 1 Ma cutting gabbro sills (Heaman & LeCheminant, 1993). Both units with the possible exception of the lower part of the Watterson Formation appear to have “normal” carbon isotope values (Bekker, Karhu, & Aspler, unpub. data). Even though it is likely that these units were deposited during time of the carbon isotope excursion as was defined by Karhu & Holland (1996), poor geochronologic constraints preclude suggesting that period with “normal” carbon isotope values punctuated time of the carbon isotope excursion. In the context of these new data the possibility that “normal” carbon isotope values of carbonate units from the Lake Superior Area indicate deposition during the same time interval of “normal” carbon isotope values punctuating time of the carbon isotope excursion remains open.

Karhu & Holland (1996) observed a shallow minimum in carbon isotope records at 2.0 Ga. This minimum was recorded in the Belcher and Nastapoka Groups (δ13C = -1.3 ± 0.9‰, 1.99 ± 0.04 Ga), and the Eraheedy Group of Western Australia (δ13C = -0.7 ± 1.2‰, 1.98 ± 0.03 Ga). None of the carbonates analyzed in the present study from North America showed those depleted characteristics.

Chapter 8.
COMPARATIVE STUDY OF PALEOPROTEROZOIC CARBONATES WITH AGES BETWEEN 2.22 - 2.06 GA: EVIDENCE FOR EVAPORITES, SABKHA MINERALIZATION, AND HIGH ORGANIC MATTER CONTENT

It was noted, based on studies of the Fennoscandian Shield, that there is a change from dominance of limestones to sulphate-enriched dolomites at around 2.2 Ga, and back to limestones at about 2.1 Ga ago (Melezhik et al., 1993). Akhmedov (1990) and Akhmedov et al. (1996) suggested that a worldwide evaporitic epoch followed the glacial epoch at about 2.3 Ga ago. Even though these suggestions were based mostly on lithostratigraphic correlation and led to mistakes in correlation, there is some merit in their approach. The present study allows the extension of these observations into North America. Several features became obvious about the Paleoproterozoic carbonates when chemostratigraphy was applied to define the time interval with heavy carbon isotope values (see Table 8.1): (1) chemically they are dolomites, (2) organic matter occurs stratigraphically above or within them, and (3) sulphate minerals, red beds, and the sediment-hosted stratiform copper deposits became widespread during the deposition of these carbonates.

Sulphate nodules are typical of coastal tidal flats (coastal sabkas) in hot dry climates such as in the present Persian Gulf. Sulfate nodules precipitate from interstitial groundwater that reaches oversaturation with respect to sulfate as a result of evaporation (Kinsman, 1969). Chandler (1988) did a detailed petrographic study of chert nodules at the base of the Gordon Lake Formation at Welcome Lake and Lady Evelyn River of the Cobalt area; Stag Lake, Flack Lake, Cobre Lake of the Elliot Lake area;
and Narrow Bay of the Espanola-Whitefish Falls area. His data proved that these nodules were formed by replacement of early diagenetic anhydrite. Taylor (1972) described pseudomorphs after gypsum and anhydrite, copper mineralization, and red beds in the Kona Dolomite of the Marquette Trough and suggested that this unit was formed in a sabkha lagoonal reducing environment with red beds deposited in an oxidized fluvial-aolian (?) environment. Similar evidence for an evaporite environment of deposition was reported from: a) carbonate units that were deposited at the end and after the carbon isotope excursion (Peribonca Formation in the Otish basin, Albanel Formation in the Mistassini basin, Nash Fork Formation on the Wyoming craton; see Table 8.1), b) units which are possibly close in age to the $^{13}$C-enriched carbonates: Tavani Formation, Hurwitz Group, Northwest Territories [post-glacial unit cut by 2.11 Ga gabbro sills (Miller & Reading, 1993); for age constraints see Heaman & LeCheminant (1993), and Aspler & Chiarenzelli (1997)]; ≥2.22 Ga Timeball Hill Formation of the Pretoria Group, Transvaal Basin, South Africa (Martini, 1990); 2.05 Ga lower part of the Liaote Group, eastern Liaoning Province, China (Peng & Paimer, 1995; Jiang et al., 1997); c) slightly younger units in North America (1.9 Ga-old Seton, Gibraltar, and McLeod Bay formations of the Kahochella Group, and the top of the Pethi Group, Great Slave Lake, Northwest Territories (Hoffman, 1968; 1978; 1989), ~ 2.0 Ga Kasegalik and McLeary formations of the Belcher Group (Bell & Jackson, 1974; Ricketts & Donaldson, 1981; Chandler & Parrish, 1989); ~ 2.07- Ga Wollaston Lake Foldbelt (Chandler, 1978, Delaney, 1995); and the ~1.8 Ga Vepsy Group of Russian Karelia (Akhmedov, 1990; Akhmedov et al., 1996). These climatic indicators suggest a significant climatic change after the glaciation to a warm and arid climate within the Superior and Wyoming cratons, and along with worldwide data from carbonates of similar age, could be interpreted as an indication of a global warming event. This suggestion is further enforced by the presence of paleosols above glacials (e.g. Young, 1973, Nesbitt & Young, 1982, Marmo, 1992), and red beds (Chandler, 1980). Barite crystals, lenses, and layers have been described from the Gordon Lake Formation in the Welcome Lake area (Chandler, 1986), Fenwick Township (Bennett et al., 1989, 1993), and the Lower Umba suite of the Imandra-Varzuga zone (Melezhik & Fetisova, 1989, Grinenko et al., 1989).

Barite crystals and probable pseudomorphs after gypsum were reported from the 3.5-3.4 Ga greenstone sequence of the lower part of the Warrawoona Group at North Pole in the Pilbara Block, Western Australia (Dunlop et al., 1979), from the correlative Upper Onverwacht and ~3.2 Ga Fig Tree Groups, Swaziland Sequence in Barberton Mountain Land, South Africa (Perry et al., 1971). These Archean occurrences are associated with stromatolites and probably represent local environments enriched in oxygen released during photosynthesis by algae.

Grotzinger & Kasting (1993) suggested that precipitation of gypsum/anhydrite prior to halite did not occur before 1.9 Ga during evaporation. They explained it by higher $P_{\text{CO}_2}$ in the Archean and Paleoproterozoic atmosphere and, therefore, higher bicarbonate concentration in the ocean leaving no calcium for sulphate to precipitate ($[\text{HCO}_3^-] \gg [\text{Ca}^{2+}]$), based on the following reaction: $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$). Low concentrations of sulfates in marine water are to be expected in an anoxic atmosphere since sulfates have been formed by photochemical oxidation of volcanic $\text{SO}_2$ and $\text{H}_2\text{S}$. 59
However, the change from an anoxic to an oxygenated atmosphere was suggested at around 2.2-2.0 Ga (Karhu & Holland, 1996) or even at 2.4 Ga (Kirkham & Roscoe, 1993). An increase in oceanic sulfate concentration was suggested by Cameron (1982), based on the decrease in the sulfur isotope ratios of sulfides around 2.2 Ga [presently the age of the Malmani Dolomite in which Cameron (1982) observed isotopic transition was constrained to 2.55 Ga (Barton et al., 1994)]. Ironically, an even more significant isotopic shift was noticed by Cameron (1982) in the Timeball Hill Formation, right above the Duitschland Formation in which oldest heavy carbonates were found indicating oxygen level rise (Bekker, Karhu, & Beukes, unpublished data); however, Cameron (1982) did not attach much importance to it. Pseudomorphs after gypsum in the Kona Dolomite preceded halite precipitation (pseudomorphs after halite were observed just a few meters above pseudomorphs after gypsum by author and Dr. R. W. Ojakangas (pers. com.) saw halite less than a meter above gypsum pseudomorphs in the roadcut) and occur above red-coloured siltstones/mudstones indicating a post-oxyatmoversion age of this unit. The presence of pseudomorphs after sulfates in $^{13}$C-enriched carbonates with ages around $2.22-2.06$ Ga argues that with the increase in oxygen level, sulfates became available in the world ocean and precipitated in sabkha environments.

Sediment-hosted stratiform copper deposits (SHSCD) often occur in evaporite environments (Gustafson and Williams, 1981). SHSCD were formed in widespread desert environments by "diagenetic infiltration of oxic brines, derived from evaporites, that extracted ore metals from redbed aquifers and deposited them in anoxic sediments" (Kirkham, 1989, p. 3). These deposits occur only in rocks of Paleoproterozoic or younger age because they require an oxygenated environment for brines to form. The earliest deposits (see Table 8.1) occur in either $^{13}$C-enriched carbonates with an age around $2.22-2.06$ Ga or just below them. Small SHSCD and red beds formed during early diagenesis in the upper part of the Lorrain Formation and Gordon Lake Formation of the Huronian Supergroup in Desbarats, Cobre Lake, and Stag Lake, ON (Pearson, 1979; Chandler, 1989) and in the upper part of the Gowganda Formation at Rib Lake north of Temagami Lake, Cobalt mining area (Wood, 1979). Therefore, before $2.219$ Ga, the age of the Nipissing dikes cutting the Gordon Lake Formation, the atmosphere had enough oxygen for these brines to form. SHSCD often form in desert environments during diagenesis before cementation and compaction (Kirkham, 1989). Cu solubility increases at low temperatures with an increase in the concentration of chloride ion, making anoxic algal sabkhas particularly good environments to host SHSCD.

Dolomite formation is currently limited at Earth's surface to supratidal evaporite (i.e. sabkha) and nonevaporite environments and some ephemeral lakes. During the Phanerozoic, dolomite was formed by replacement processes on supratidal flats during sedimentation or diagenesis (Tucker, 1982). Tucker (1982) suggested that in the Precambrian, dolomite was the main carbonate precipitate related to a higher Mg/Ca ratio, higher partial pressure of CO$_2$, higher temperature, and lower SO$_4^{2-}$. He also suggested that fluctuation in sea water chemistry can produce time intervals with preferential calcite or dolomite precipitation. Sulfate serves as an inhibitor of dolomite precipitation; therefore, dolomite formation occurs in areas with reduced concentration of dissolved sulfate such as low-sulfate alkaline
lakes, mixing zones of fresh and marine waters, and zones of microbial sulfate reduction (Baker & Kastner, 1981). Precipitation of carbonate led to an increase in the Mg/Ca ratio by exhaustion of Ca\textsuperscript{2+}, making dolomitization common in the Precambrian ocean, especially on tidal flats. Analysis of \textsuperscript{13}C-enriched carbonates with ages between 2.22 and 2.06 Ga (Figure 8.1) shows that all of them are composed of dolomite, but older and younger carbonates are limestones (e.g. Vagner Formation, Bruce Member of the Espanola Formation). This observation, along with similar observations from the Fennoscandian Shield (e.g. Melezhik et al., 1993), suggests that whether these dolomites are primary or early diagenetic they indicate a significant global change in the composition of sea water, possibly related to climatic or tectonic changes during their precipitation. Further evidence for a high Mg/Ca ratio in open marine water and a warm arid climate during deposition of heavy carbonates is presented by occurrences of magnesite and boron-enrichment within these successions in Karelia, Russia (Aksenov et al., 1976; Akhmedov et al., 1993; Melezhik et al., 1996) and the Otish basin, Quebec (Genest, 1985).

Widespread preservation of organic matter-rich layers requires a stagnant ocean with reducing bottom-waters and high productivity. In several basins they are younger than the carbon isotope excursion (Lower Albanel Formation of the Mistassini basin; shungites in the Karelian Ludikovii sequence, Russia; Nash Fork Formation, Snowy Pass Supergroup, WY) even though the carbon isotope excursion should coincide with the high relative rate of organic matter burial. In other basins carbonaceous shales occur within carbonates with \textsuperscript{13}C-enrichment (e.g. Francevillian Series, Gabon). Since organic-rich layers can be expected in the deeper parts of a basin, it is suggested that shungites and organic-rich layers of the Lower Albanel Formation and the Nash Fork Formation were deposited during a flooding event that preceded or coincided with the end of this excursion. There are also organic-rich shales at the base of sequences with minimum ages determined by geochronological studies of overlying volcanics to be around or younger than 2.0 Ga (Ramah and Mugford groups of Labrador; Katildidian Group of the south-west Greenland). Stratigraphic position of these shales in respect to the carbon isotope excursion remains to be investigated.

The model suggested by Bekker & Karhu (1997a) attempted to resolve the significance of these features. It was suggested that glaciation (ice-house event) was followed by warming (greenhouse event). This warming was already noticed in studies of paleosols and quartzites with red beds above glacialis (Nesbitt & Young, 1982). These quartzites (Lorrain Formation, Mesnard and Medicine Bow Quartzites) were deposited in tidal or fluvial-colian (?) environments, have red beds, and some of them have copper mineralization, and aluminium-rich layers in the lower part indicating deep weathering. Petrographic observations (e.g. Chandler, 1989) indicate that feldspars were altered in situ. Segregation into aluminium-rich and quartz-rich sandstones was facilitated by fluvial and colian (?) activity. These sandstones were overlapped by pelites and carbonates such as the Gordon Lake Formation and Kona Dolomite. They represent a shallow marine to deeper marine (below fairweather base) spectrum of depositional environments and were laid down during a transgression / highstand at the beginning of the greenhouse event. It is interesting to note that at least in North America, indirect evidence for an oxygen increase (red beds and copper stratiform mineralization) occurs stratigraphically below evidence for the
carbon isotope excursion which apparently led to oxygen release. It can be partially explained by the transgressive overlap of carbonates and the low preservation potential of carbonates deposited during the end of the lowstand and beginning of transgression (due to non-deposition as a result of “poisoning” by high siliciclastic input during lowstand and beginning of transgression; their location in the distal part of the basin; and possible erosion during transgression). Therefore preserved enriched-carbonates cannot be taken as a constraint for the age of the beginning of the carbon isotope excursion. Indeed, new data from the Duitschland Formation, South Africa, of the interglacial age indicate that the carbon isotope excursion (or one of several carbon isotope excursions) started before the Kona Dolomite and the Gordon Lake Formation were deposited. If the Bad River and Randville Dolomites, Trout Lake, Saunders, and Denham Formations are older than the Kona Dolomite as will be discussed in Chapter 11, it would be important to see if any indications of an oxygenated atmosphere are preserved in underlying quartzites (Sunday Quartzite and Sturgeon Quartzite). Presently I am not aware of any description of red beds and stratiform copper deposits from these quartzites.

A sea level rise would lead to significant areas with shallow marine pericratonic environments of deposition. These vast areas combined with a warm and arid climate and surrounding deserts would produce extensive sabkha environments. Short-term sea level drops would introduce quartz sandstones into carbonate sabkha environments (e.g. Middle Quartzite Member of the Kona Dolomite) and short-term sea level rises would move the depositional environment into deeper waters. Depending upon the amplitude of the relative sea level rise, deposition of organic-rich shales might become possible. A sabkha environment explains copper stratiform deposits, primary or early diagenetic dolomite, and sulphate pseudomorphs typical for Paleoproterozoic 13C-enriched carbonates. Sulphate was introduced into ocean water by oxidation of H2S and SO2.

A major greenhouse event would lead to an earth without ice caps. The absence of cold water at the poles would break ocean circulation cells and therefore stagnant ocean bottoms would occur. Organic matter burial would exhaust available oxygen in bottom waters and the reducing deeper ocean would enhance organic matter burial. The high rate of organic matter burial would release oxygen into the atmosphere which otherwise would be used to oxidize organic matter, and would produce an excursion in carbon isotope ratios of carbonates. Released oxygen would have been used to oxidize Fe2+ into Fe3+ and to increase sulfate content in ocean water. Iron-formation were deposited mostly after this excursion which might be related to the breakup of the ocean circulation at the end of the carbon isotope excursion. Sulfide iron-formation in the Nash Fork Formation is associated with the black shale unit and was deposited in the deeper part of the basin below oxygenated waters.

Why this excursion ended is a matter of speculation at present. Tectonic development such as final breakup of the supercontinent Kenorland ending the protracted rifting event that started around 2.45 Ga and opening new seaways leading to enhanced circulation and oceanic overturn can be suggested. This oceanic overturn would bring up to the shallow zone of basins deep waters enriched in 12C and would release CO2 that was dissolved in the deep waters. These factors would lead to the end of the carbon isotope excursion in carbonates and to lighter carbon isotope values of organic matter in overlying
units, respectively. These lighter carbon isotope values of organic matter were already measured in the Francevillian basin (Weber et al., 1983), on the Fennoscandian Shield (Karhu, 1993; Melezhik et al., 1997), and in the Frunzenskaya suite on the Ukrainian Shield (Lazarenko et al., 1979).

Another interesting feature of rocks deposited at the transition to “normal” carbon isotope values and shortly after it, is that some of them are enriched in phosphorus (apatite). These are the Aravalli Group, India, (Sreenivas et al., 1996); Michigan, USA (carbonate-apatite in the iron formation at the base of the Michigamme Slate, Baraga Group (Mancuso et al., 1975, dated by the Pb-Pb method at 1930 Ma as cited in Morey & Southwick, 1995) and redeposited phosphorite pebbles at the base of the Ajibik Quartzite, Menominee Group (Cannon & Klasner, 1976), both of the Marquette Supergroup; Fennoscandian Shield (Tulomozero suite, southern Karelia, Russia - Aksenov et al., 1976; Akhmedov et al., 1993; Kolasjoki Formation, Pechenga basin and Il’mozero Formation, Imandra/Varzuga basin, Kola Peninsula, Russia - Melezhik & Predovskii, 1982; redeposited phosphate conglomerates in the Pil’guyarvi suite, Pechenga basin, Kola Peninsula, Russia - Bekasova, 1979 referenced in Melezhik & Predovskii, 1982; Lower Kalevian (~2.0 Ga, Karhu, 1998 pers. com.) Pääkkö BIF, Finland), Ukrainian Shield (Yur’ev, 1968), 2.025 Ga Pachi Formation of the Richmond Gulf Group (Chandler & Parrish, 1989). The temporal relationship of these phosphate deposits to the carbon isotope excursion is unclear; some of them occur in 13C-enriched carbonates (e.g. Tulomozero suite) but most of them were deposited after the carbon isotope excursion ended. Phosphorus is an important nutrient that can enhance organic productivity and is usually released from organic matter and delivered by upwelling to shallow zone.

Nevertheless, evidence for red beds (Chandler, 1980), copper stratiform deposits (Kirkham, 1989), and sulphate pseudomorphs (see above) continue to occur in slightly younger successions of North America. Apparently at least North America and the Fennoscandian Shield remained in a warm arid climate for some time in the Paleoproterozoic.

Generally, the amplitude of sea level change is higher during an ice-age than during a greenhouse age. It might be a possible test for the above model to log carbonate sequences of this age and estimate the amplitude of sea level changes in shallowing-upward sequences.
<table>
<thead>
<tr>
<th>Location, Formation</th>
<th>Dolomite/Calcite</th>
<th>Sediment-hosted stratiform copper deposits</th>
<th>Organic matter</th>
<th>Sulfate minerals/red beds</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lofoten - Vesteralen, Norway</td>
<td>Dolomite in amp. facies, calcite in amp. and gran. facies</td>
<td>Sulphide-bearing schist</td>
<td>Present, not in the same layer</td>
<td>Unknown</td>
<td>Baker &amp; Fallick, 1989b</td>
</tr>
<tr>
<td>Loch Maree Group, Scotland</td>
<td>Dolomite</td>
<td>Unknown</td>
<td>Present, not in the same layer</td>
<td>Sulfates</td>
<td>Baker &amp; Fallick, 1989a</td>
</tr>
<tr>
<td>Einasleigh Metamorphics, Georgetown Inlier, N Queensland</td>
<td>Dolomite &gt; Calcite</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Anhydrite</td>
<td>McNaughton &amp; Wilson, 1983</td>
</tr>
<tr>
<td>Lomagundi Group, Zimbabwe</td>
<td>Dolomite</td>
<td>Magondi Copper Belt</td>
<td>Graphitic argillites in the underlying Piriwiri Formation, carbonaceous members of the overlying Striped Slate Formation</td>
<td>Gypsum, anhydrite in the underlying Deweros Group</td>
<td>Schidlowski et al., 1976; Master, 1991</td>
</tr>
<tr>
<td>Francevillian Series, Gabon</td>
<td>Dolomite</td>
<td>Sulfide mineralization (including Cu)</td>
<td>Carbonate layers surrounded by black shale rich in organics (up to 10 - 15%)</td>
<td>Anhydrite, gypsum, barite</td>
<td>Gauthier - Lafaye and Weber, 1989</td>
</tr>
<tr>
<td>Tulozero suite, Upper Jatulian Group, Karelia, Russia</td>
<td>Dolomite</td>
<td>Cu-rich argillites</td>
<td>Overlain by organic-rich black shales</td>
<td>Anhydrite, gypsum, barite, red beds</td>
<td>Akhmedov, 1990, 1993; Yudovich et al., 1990; Tikhomirova &amp; Makarikhin, 1993; Melezhik &amp; Fallick, 1996</td>
</tr>
<tr>
<td>Pechenga, Imandra-Varzuga Complex, Kola Peninsula, Russia</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td>Barite</td>
<td>Karhu &amp; Melezhik, 1992; Prilutsky et al., 1992; Pokrovsky &amp; Melezhik, 1995</td>
</tr>
<tr>
<td>Albanel Formation, Mistassini basin, and Peribonca Formation, Otish basin, Quebec</td>
<td>Dolomite</td>
<td>Stratabound Cu-Zn-Pb deposits</td>
<td>Black graphitic shales overlie δ13C-rich carbonates</td>
<td>Mudcracks; tepees; gypsum; anhydrite; magnesite; B-enrichment; red beds</td>
<td>Rescoee, 1967; Schidlowski et al., 1983; Genest, 1985; Mirota &amp; Veizer, 1994</td>
</tr>
<tr>
<td>Nash Fork Formation</td>
<td>Dolomite</td>
<td></td>
<td>Black graphitic shales occur in the middle part of the section above δ13C-rich carbonates</td>
<td>Pseudomorphs after gypsum in the upper part of the section</td>
<td>Present study</td>
</tr>
<tr>
<td>Location</td>
<td>Sediment Type</td>
<td>Characteristic Features</td>
<td>References</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-----------------------</td>
<td>-------------------------------------------------------------------------------------------------------------</td>
<td>------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rodionovskaya and Sachkinskaya suites, Ukraine</td>
<td>Dolomite</td>
<td>Graphitic slates interlayered with and underlie dolomites</td>
<td>Salop, 1982; Zagnitko &amp; Lugovaya, 1985; Prilutsky et al., 1992</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lower part of Odantsevkaya suite, Ukraine</td>
<td>Dolomite</td>
<td>Organic matter-rich/graphitic slates above heavy dolomites</td>
<td>Salop, 1982; Zagnitko &amp; Lugovaya, 1985; Prilutsky et al., 1992</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yakovlevskaya &amp; Rogovskaya suites, Voronezh Massif</td>
<td>Dolomite</td>
<td>Organic-rich slates above dolomites</td>
<td>Salop, 1982; Zagnitko &amp; Lugovaya, 1985; Prilutsky et al., 1992</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kona Dolomite, Marquette Trough, Michigan</td>
<td>Dolomite</td>
<td>Copper stratiform deposits</td>
<td>Taylor, 1972; Larue, 1981; Hemzacek et al., 1982; Perry et al., 1984</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butunskaya suite (Chineiskaya series), Udokan basin, South Siberia</td>
<td>Dolomite</td>
<td>Copper sulfides</td>
<td>Salop, 1982; Akhmedov et al., 1996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jahamarkotra Formation, Aravalli Supergroup, India</td>
<td>Dolomite</td>
<td>Copper sulfides</td>
<td>Sreenivas et al., 1996</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dunphy, Portage, Alder, and Uve formations, Labrador Trough</td>
<td>Dolomite</td>
<td>Cu-stratiform deposits in Dunphy Fm., Romanet Lake</td>
<td>Cheve et al., 1985; Kirkham, 1989; Melezhik et al., 1997</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.1: Characteristic features of Paleoproterozoic $^{13}$C-enriched carbonates. Note that they are dolomites, that graphitic shales occur in the same successions, and that sulphate minerals and sediment-hosted stratiform copper deposits are confined to them. Amp. facies is amphibolite facies of metamorphism; gran. facies is granulite facies of metamorphism.
Chapter 9.
Carbon and oxygen cycles during the Paleoproterozoic and possible models for their evolution

Carbon dioxide comes from the mantle during igneous activity (mostly MORB) or during metamorphism of sedimentary rocks (carbonates, calc-silicates), and is used up by organic matter during photosynthesis, by carbonate precipitation, and by weathering (Schidlowski & Aharon, 1992, Figure 9.1). It is very difficult to estimate the CO₂ level of the atmosphere from sedimentary records or simple balance calculations. The variables in the carbon dioxide cycle are barely known for the Paleoproterozoic, and would depend on many other factors. For example, the rate of weathering taken alone would depend on the areas of continents/supercontinent, the latitudinal position of these continents/supercontinent, the freeboard of land, the surface temperature, and many other factors.

Carbon dioxide was the dominant greenhouse gas on the Archean-Paleoproterozoic Earth (Grotzinger & Kasting, 1993). Kasting (1987) estimated that CO₂ partial pressure during the Paleoproterozoic (Huronian) glaciation was between 0.03 (sixty times present atmospheric level) and 0.3 atm (six hundred times present atmospheric level) to keep the mean surface temperature between 5° and 20°C. A higher CO₂ partial pressure is expected for pre- and postglacial Earth during the Paleoproterozoic to keep Earth above freezing temperatures, since solar luminosity was lower. The luminosity at the beginning of the Proterozoic was 18% lower than now (Kasting, 1987). Evidence for a higher level of CO₂ in the Paleoproterozoic also comes from a larger difference in δ between carbon isotope values of organic matter and carbonates of the same age (Des Marais et al., 1992); δ = 40% was reported from the Jatulian formations of Fennoscandia (Karhu, 1993). The higher CO₂ level allowed more isotopic discrimination during photosynthesis (Des Marais et al., 1992).

It was suggested that weathering of the emergent supercontinent Kenorland that was assembled in the Late Archean (Williams et al., 1991) led to a decrease in the level of CO₂ (Young, 1991b). There is evidence for three glacial episodes, separated by periods of intense weathering, that indicate significant fluctuation of surface temperature/climate and probably CO₂ level as well (Nesbitt & Young, 1982; Young, 1991b). Young (1991) explained them by a negative feedback between widespread development of glaciation and the rate of weathering leading to accumulation of CO₂ in the atmosphere. If the suggested model for the deposition of carbonates of the Vagner and Espanola formations by upwelling of deep waters rich in CO₂ during glacioeustatic sea level rise is accepted, their precipitation would also lead to a short-term release of carbon dioxide into the atmosphere based on the equation of carbonate precipitation (Berger, 1982, Opdyke & Walker, 1992):

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \]
Fig. 9.1. Box model of the global carbon cycle (after Schidlowski & Aharon, 1992) showing bipartition into an organic and inorganic reservoirs. Note that the amount of carbon stored in the crust exceeds that residing on the surface by three orders of magnitude. Carbon fluxes into the biosphere are beset with the kinetic isotope effects (KIE).
A final warming was related by Young (1991) to the breakup of the supercontinent leading to higher relative sea level due to thermal subsidence and, therefore, less area exposed to weathering and a smaller rate of CO₂ consumption.

Unusually heavy carbon isotope values that were reported from carbonates deposited between ≥2.22-2.06 Ga were explained by: (1) local processes - deposition in a hypersaline environment (Schidlowski et al., 1976; McNaughton and Wilson, 1983; Pokrovsky & Melezhik, 1995); (2) a high rate of organic matter burial (Baker & Fallick, 1989a, b; Karhu, 1993); (3) methane production (Yudovich et al., 1990); (4) rise and drop in oxygen level and, respectively, an increase and decrease in bacterial sulfate reduction (Tikhomirova & Makarikhin, 1993; Tikhomirova, 1991); and (5) a tectonically-quiet period allowed sequestering by organic matter of light carbon isotopes during photosynthesis between orogenic events which released CO₂ into the atmosphere via metamorphism (Galimov et al., 1975) or volcanism (Ivlev, 1986).

An increase in organic matter productivity, in the absence of an accompanying increase in the rate of organic matter recycling, was suggested as a cause for a high rate of organic matter burial (Baker & Fallick, 1989a, b). Stromatolite fertility as a result of expanded favourable environments after formation of stable passive margins was argued as a way to fix ¹³C in organic matter, leading to deposition of ¹³C-enriched carbonates (Melezhik & Fallick, 1996). Assessments using different numbers for δ¹³C have led to different numbers of R (fraction of the total carbon flux buried as organic matter) but all of them have shown it to almost double relative to the present value (Karhu, 1993). Based on similar studies in the Phanerozoic, a number of models could be suggested, but the amount of data available as yet is not enough to select any one model as best. The general consensus is divided between the rise in organic production (Melezhik & Fallick, 1996) and environmental changes (e.g. changes in sedimentation rate as a result of rifting and/or orogeny, Des Marais, 1994) leading to higher rates of organic matter burial in sedimentary rocks (Karhu, 1993). It is safe to conclude at this point that high δ¹³Ccar values indicate a high rate of organic matter burial (Karhu, 1993). Whatever the cause of this perturbation, since it reflects the geochemistry of the open ocean, it could be used as a tool to correlate carbonate sequences from different continents and basins (Karhu & Melezhik, 1992). Even terrestrial carbonates will show this perturbation since interaction of water, in which they were deposited, with the atmosphere would trend to equilibrate their isotopic composition with that of the ocean. The absence of terrestrial life during the Paleoproterozoic time would have made this equilibration process even more efficient. In fact, the carbon isotope study of terrestrial sediments of the Paleoproterozoic (~ 2.06 Ga) Deweras Group, Zimbabwe, indicated an δ¹³C excursion above +11% (Master, Verhagen, and Duane, 1990).

There is some paradox between the inferred relative decrease in CO₂ level as a result of a high rate of organic matter burial (usually organic matter is recycled back to the atmosphere as CO₂) and evidence for a warm climate. This paradox might arise from the absence of data about other parameters which participate in the carbon dioxide cycle, such as degassing of CO₂ from the mantle (increase of degassing as a result of the breakup of Kenorland would lead to a higher CO₂ level), rate of weathering (a
sea level rise would lead to less area exposed and therefore less CO$_2$ would be used to weather rocks), the amount of CO$_2$ released during metamorphism, and the amount of carbonates buried during that time.

Other greenhouse gases that became prominent in the Paleoproterozoic are oxygen and ozone. The content of oxygen in the atmosphere changed around 2.3 Ga from less than $10^{-13}$ PAL (present atmospheric level) to 0.03 PAL (Kasting, 1987). Ozone absorbs strongly in the infrared and ultraviolet wavelengths, and weakly in the visible wavelengths (Kasting, 1987). Oxygen participates in warming by helping pressure to broaden the absorption lines of CO$_2$ and H$_2$O (Kasting, 1987). The appearance of an oxygenated atmosphere can increase the surface temperature by 5°C (Kasting, 1987). Karhu (1993) estimated that the fraction of total carbon buried as organic matter ($R = C_{org}/(C_{org} + C_{carb})$) during the carbon isotope excursion between 2.22-2.06 Ga was around 0.38-0.55, with the latter figure exceeding the burial rate of inorganic carbon and the present value for organic burial rate of carbon around 0.2. This would lead to liberation of about 11x10$^{12}$ mol/yr to 15x10$^{12}$ mol/yr of oxygen and during 100 Ma (a conservative estimate of the duration of this excursion) it would produce 5x10$^{20}$ to 9x10$^{20}$ mol O$_2$ which is about 12 to 22 times the present amount of oxygen in the atmosphere (Karhu, 1993). Recently Ohmoto (1996) challenged the well-accepted model of oxygen level rise in the atmosphere around 2.2-2.0 Ga (Holland, 1994) based on Fe$^{3+}$/Ti, Fe$^{2+}$/Ti, and $\Sigma$Fe/Ti changes in paleosol profiles with ages between 3.0-1.8 Ga. Using Ti as a basically immobile element, his argument is centered on the absence of paleosol profiles with ferric iron depletion.
CHAPTER 10. GLOBAL CHANGES DURING DEPOSITION OF THE SNOWY PASS SUPERGROUP

Climatic changes in the Paleoproterozoic left very scarce records. Nevertheless, Nesbitt & Young (1982) argued, based on petrographic study and major element analyses of lutites, for significant climatic changes during deposition of the Huronian sequence, Ontario, from an early period of intense, probably tropical weathering (McKim and Elsie formations) to continental glaciation (Ramsay Lake, Bruce, and Gowganda formations), and a return to a warm arid climate (Lorrain, Gordon Lake, and Bar River formations). Evidence for intense tropical weathering before the deposition of the Huronian succession came from thick (>10 m) regoliths on Archean rocks and also major element analyses of the McKim and Elsie formations (Nesbitt & Young, 1982). It was also inferred, based on the presence of thin regolith with a low degree of chemical but substantial mechanical weathering and carbonatization on Archean rocks, Paleoproterozoic (2.45 Ga) layered gabbros, and 2.42 Ga volcano-sedimentary units, that an arid or semi-arid low latitude paleoclimate existed on the Fennoscandian Shield (Pechenga greenstone belt) around 2.4 Ga, just before the Sariolian glaciation (Sturt et al., 1994). The age of the Sariolian glaciation was confined to 2.423 (Sm - Nd) - 2.33 Ga (Rb - Sr) and might be even further constrained to 2.396 - 2.33 Ga (Sturt et al., 1994; Melezhik & Sturt, 1994). A lower age limit for the Petsamo Supergroup which includes Sariolian diamictites was constrained by an Sm - Nd age of 2453 ± 42 Ma for the layered gabbro-norite of Mt. Generalskaya (Bakushkin et al., 1990 cited in Sturt et al., 1994); and 2423 ± 7 Ma U - Pb zircon age of weathered felsic volcanics of the Seidorechka Formation (Mitrofanov et al., 1991, as cited in Sturt et al., 1994). Furthermore, the Seidorechka Formation underlies the Polisarka Formation in the Imandra-Varzuga Zone, Kola Peninsula and in the uppermost part of the Polisarka Formation dropstones were recorded (Melezhik, 1992, as cited in Sturt et al., 1994). The Seidorechka Formation was intruded by the Imandra Lopolith dated by U - Pb zircon method at 2396 ± 7 Ma (Mitrofanov et al., 1991, as cited in Melezhik & Sturt, 1994). An upper age limit is imposed by 2.330 ± 36 Ga Rb - Sr age for the Akhmalakhti volcanics (Balashov et al., 1990) which overlie fluvialite deposits and their regolith substrate.

Nesbitt and Young (1982) presented evidence for several repeated glacial episodes such as low CIA values of the Pecors, Serpent, and Gowganda formations, diamictites of the Ramsay Lake, Bruce, and Gowganda formations separated by periods with intense weathering/warm climate indicated by the aluminous nature of the Pecors Formation and the presence of dolomite in the Espanola Formation (Nesbitt & Young, 1982; Young, 1991ba). Fedo et al. (1997) argued based on the predominance of plagioclase over potassium feldspar, REE, major and trace element analyses of sandstones and mudstones of the Serpent Formation, that this unit was deposited in a cold climate preceding the Gowganda glaciation. Post-Gowganda climatic amelioration was inferred from the presence of diaspore, kaolinite, pyrophyllite, andalusite and kyanite in the Lorrain Formation (Young, 1973); gypsum and anhydrite in the Gordon Lake Formation (Wood, 1973; Chandler, 1988); and kaolinite and pyrophyllite in quartzite of the Bar River Formation (Wood, 1973).
Since the work of Blackwelder (1926), a glacial origin for the Headquarters Formation and correlation with the Gowganda Formation of the Huronian Supergroup has been well-excepted (Young, 1970, 1973; Houston et al., 1981; Ojakangas, 1985, 1988). Houston et al. (1981) suggested a glacial origin for the underlying Vagner and Campbell Lake formations. Kurtz (1980) challenged this interpretation based on comparison of facies changes in the Headquarters Formation and on the Antarctic slope and rise. Even though he inferred a frigid climate based on the presence of “pebbly argillites”, he disagreed with continental-scale glaciation. Some of his interpretations about heterogeneity of facies can be questioned, since this area was involved in thrusting and, therefore, movement on faults might have caused this heterogeneity of facies. Furthermore, heterogeneity by itself hardly can be considered as negative evidence in the argument about continental-scale origin of diamictites since it is typical for glaciomarine deposits formed by downslope resedimentation and “rain-out” from ice-rafts (Eyles, 1993, p. 28). Diamictites of similar age have been described from Michigan (Pettijohn, 1944, Puffett, 1969, Gair, 1981), Northwestern Territories (Young & McLennan, 1981), Northern Quebec, Canada (Long, 1981), S. Africa (Visser, 1971, 1972, 1981), Australia (Trendall, 1976, Trendall, 1981), Fennoscandian Shield (Negrutsa & Negrutsa, 1981c; Marmo & Ojakangas, 1984), and Siberia (Salop, 1982), suggesting a global icehouse event (Young, 1970, 1973; Ojakangas, 1988).

Global significance of this event is further supported by paleomagnetic evidence indicating that the Paleoproterozoic glaciation in South Africa (Evans et al., 1997), on the Canadian Shield (Huronian Supergroup; Williams & Schmidt, 1997) and on the Fennoscandian Shield (Mertanen et al., 1989) occurred in low latitudes. Therefore, I prefer the continental- and even global-scale glaciation model for the preserved diamictites rather than the local influence of mountains. Data of this study support a frigid climate during deposition of the Headquarters and Vagner formations; ambiguous CIA-values from the Campbell Lake Formation cannot be interpreted with confidence at this stage.

Flurkey (1983) described kyanite, kaolinite, pyrophyllite, and sericite as in situ alteration products of feldspars during diagenetic/metamorphic processes. A similar enrichment in aluminosilicates of the Lorrain and Gordon Lake formations was interpreted as having occurred during the diagenetic stage, and a warm and dry (not necessarily arid) climate during their deposition was inferred (Chandler, 1986). However, Ojakangas (1997) has noted a paleosol within the Lorrain Formation; a manuscript is currently in preparation. A regolith on the top of the Sarioli Group (Akhmalahti volcanics) is constrained by the Rb-Sr method on the underlying volcanics to be younger than 2.33 (Sturt et al., 1994).

Bekker & Karhu (1997a) carried out a comparative sedimentological study of 13C-enriched carbonates of Paleoproterozoic age, including the Nash Fork Formation. They suggested that a greenhouse event occurred during deposition of these carbonates based on the following evidence for a warm arid climate: 1) dolomite composition of carbonates; 2) magnesite deposits in the Jatulian carbonates of Karelia, Russia (Melezhik, et al., 1996) and in the Peribonca Formation of the Otish basin (Genest, 1985; Tyson Birkett, 1997, pers. com.); 3) pseudomorphs after sulfates (anhydrite and gypsum; see Chapter 8) and halite, and presence of tepee-structures and dessication cracks; 4) the presence of stratiform copper deposits requires a sabkha environment for their deposition; 5) high boron
concentrations in carbonates (Peribonca Formation, Otish basin - Tyson Birkett, 1997, pers. com.) and Jatulian carbonates of Karelia, Russia (Akhmedov, 1990)); 6) the carbon and sulfur isotope excursions; and 7) the presence of organic-rich black shales. The first five listed lines of evidence require a warm arid climate of formation, and the last two lines of evidence require a stratified anoxic ocean, as often coexists with a greenhouse event.

Crichton & Condie (1993) found that the French Slate, Snowy Pass Supergroup, WY (Fig. 2.1) is depleted in Ca, Na, and Sr and has higher CIW (chemical index of weathering) values than Phanerozoic shale. Therefore they suggested intense chemical weathering and a humid (hot?) climate during the deposition of the French Slate.

All these data indicate that a significant climatic change from a cold (icehouse) climate to a warm arid (greenhouse) climate occurred between \(-2.3-2.2\) Ga. Presented data suggest that this climatic change was global. It seems that the supercontinent position in low latitudes led to this climatic change. More detailed and quantitative treatment of climatic changes during that time is not available as yet, since many factors influencing Paleoproterozoic climate are either unknown or poorly known.

It was suggested, based on data from the Fennoscandian Shield (Akhmedov, 1990), that this warm and arid climate was followed again by a glacial event during Kalevian time (2.0 - 1.9 Ga) which in turn was followed by a warm and arid climate during Vepsian time (1.8 -1.9 Ga). Diamictites were described on the Fennoscandian Shield at several other stratigraphic levels: Ladoga Group (Kalevi group) and Lammas Suite (Ludikov group) (e.g. Negrutu & Negrutu, 1981 a, b; Salop, 1982) but information about these occurrences is too scarce to judge their significance. There are very limited data at this point to support a global or even a local glacial event during the 2.0-1.9 Ga time interval, for diamictites need not have a glacial origin.

The following scenario seems to be compatible with the presented data. Widespread paleosols were formed during pre-glacial time. As the CO\(_2\) level decreased, Paleoproterozoic continental glaciation ensued. During this glaciation several advances and retreats of ice relate to climatic oscillations from warm to frigid. These fluctuations in climate were probably related to: changes in CO\(_2\) content of the atmosphere caused by decreases in the weathering rate as continents were ice-covered and by low temperatures at the surface, melting of ice, oceanic overturn due to input of cold waters, and release of CO\(_2\) from deeper part of basins (e.g., during deposition of the Vagner limestone). What caused final cessation of the glaciation is a matter of speculation at this stage, but it was followed by a change to a warm and, possibly, humid climate that led to post-glacial paleosols and quartz arenites. Location of the supercontinent at a low latitude led to the greenhouse event. Stagnant ocean with an anoxic bottom layer was formed and the carbon reservoir was divided between organic matter buried in the deeper parts of the ocean and heavy carbonates deposited in the shallow parts of the ocean and intracratonic basins. A high burial rate of organic matter led to the release of a significant amount of oxygen into the atmosphere. Red beds and new types of mineral deposits started to form such as are typical of an oxygenated environment (e.g., copper stratiform deposits). The excursion ended with the final breakup of Kenorland, ending the protracted rifting event that started around 2.45 Ga. Opening of new seaways,
transgression, change/ensuing of circulation, upwellings, oceanic turnover, and mixing, brought $^{12}\text{CO}_2$-enriched deep waters to the shallow areas. Deep waters were enriched in $^{12}\text{CO}_2$ due to oxygenation of organic matter, and, later as oxygen was exhausted, due to methanogenesis and sulfate reduction. This mixing led to the end of the excursion and depleted $\delta^{13}\text{C}_{\text{org}}$ of organic matter. This depletion of organic matter was influenced by two factors: 1) low $\delta^{13}\text{C}$ of $\text{CO}_2$ in the atmosphere and hydrosphere; 2) a high $\text{CO}_2$ level led to more successful fractionation by organic matter. Transgression most likely led to a more humid climate. A high concentration of $\text{CO}_2$ caused higher acidity of the ocean and could have influenced the stromatolite decline observed on the Fennoscandian Shield and in North America (Melezhik et al., 1997; Bekker et al., 1997c; Bekker & Karhu, 1998).

CHAPTER 11. CORRELATION OF THE SNOWY PASS SUPERGROUP WITH THE MARQUETTE AND HURONIAN SUPERGROUPS

Correlation of Precambrian sequences is mostly based on lithostratigraphic correlation, radiometric age dating, and limited biostratigraphic data. Changes in the oxygen content of the atmosphere and evidence for a global glacial event have also been used for correlation of the Paleoproterozoic sequences. A model for oxygen level rise around 2.2-1.8 Ga (Holland, 1994) was recently challenged (Towe, 1994; Ohmoto, 1996). Even though some amount of oxygen might have existed in the early atmosphere, most evidence indicates that the significant rise in oxygen level occurred around 2.2-2.0 Ga, in agreement with carbon isotope data. Therefore, after passing on this note of caution, I am accepting earlier correlations which are based on the oxygen level rise (e.g. Houston et al., 1992). Evidence, pro and con, for a glacial origin of several Paleoproterozoic diamictite units and global glaciation have been discussed for quite a long time (e.g. Kurtz, 1980). In my opinion, all data indicate a global glacial event rather than sporadic mountain glaciations and/or landslides. Therefore, correlations based on these climatic changes were accepted in this work as well. Radiometric dating of these sequences is poor since magmatism mostly occurs during rifting and collisional stages and is uncommon on passive margins or in intracratonic basins. Penokean and correlative orogenies that deformed these sequences were well-dated around 1.89-1.74 Ga (Hoffman, 1989). Iron-formation that were assumed earlier to represent a single depositional event, especially in the Lake Superior area, are now considered as multiple events (Ojakangas, 1994; Morey & Southwick, 1996) and cannot be used in correlation of Lake Superior sequences.

In the last few decades, a new method of indirect dating and correlation of sedimentary rocks developed - chemostratigraphy. This method applies temporal variations in chemical composition of sedimentary rocks to date and correlate rock sequences. Carbon and strontium variations in chemical composition of ocean water and, therefore, carbonates which were precipitated chemically or biologically from this water, are the most useful (Kuvin et al., 1993). In this study, carbon isotope values of analysed Paleoproterozoic carbonates were used to suggest possible correlations.
Houston et al. (1992) correlated the Magnolia Formation of Wyoming and the Matinenda Formation of Ontario, based on the presence of pyritic and radioactive quartz-pebble conglomerates. The assumption that underlies this correlation is that pyrite and uraninite are unstable in an oxygenated atmosphere. Even though this assumption has been challenged in the past, a recent study by Maynard et al. (1991) indicated that although some uraninite grains survive transport in the Indus River, this is not a comparable environment to the Archean-Paleoproterozoic uraninite deposits since a very low degree of weathering (high sedimentation rates in the foreland basin) prevented oxidation, whereas Precambrian uraninite deposits were formed in an environment with a low rate of sedimentation and a high degree of weathering as evidenced by high CIA values. Recently, Barnicoat et al. (1997) suggested a hydrothermal origin for the gold and uraninite mineralization in the Witwatersrand basin based on observations using the scanning electron microscope; they concluded that uraninite and gold postdate a regional high-temperature alteration event. Detrital zircons from the Magnolia Formation, WY produced a 2,451±9 Ma U-Pb age (Premo & Van Schmus, 1989), closely comparable with the 2,450+25/-10 Ma U-Pb age of the Copper Cliff Formation (Krogh et al., 1984) which underlies the Matinenda Formation.

Houston et al. (1992) and Roscoe & Card (1993) correlated glacial diamictites in Wyoming and Ontario (Campbell Lake, Vagner, and Headquarters formations of Wyoming and Ramsay Lake, Bruce, and Gowganda formations of Ontario). Carbon and oxygen isotope data for the carbonate unit of the Vagner Formation presented in this work, available published data, and our preliminary data for the Bruce Member of the Espanola Formation fall into the same field, supporting this correlation. Hofmann et al. (1980) reported crustose and columnar stromatolites from the Espanola Formation and interpreted them as biologically induced localized precipitates similar in mode of formation to lacustrine stromatolites of the Paleoproterozoic Murky Formation of the East Arm of Great Slave Lake. Similar stromatolites were also found in the Vagner Formation in the present study. Our sedimentological observations and CIA values calculated for matrices of diamictites support a glacial environment of deposition for the Vagner and Headquarters formations. CIA values for the Campbell Lake Formation are limited in number and ambiguous, and, therefore, no inferences are made about its origin. The Rock Knoll Formation, WY and the Serpent Formation, ON are both arkosic pre-glacial sandstone units which have a similar predominance of plagioclase over potassium feldspar, making them different from other arkosic units in the Snowy Pass and Huronian Supergroups, respectively. Fedo et al. (1997) interpreted the presence of feldspar in the Serpent Formation to indicate low weathering rates preceding the Gowganda glaciation. Correlations of the youngest diamictite unit in the Huronian and Snowy Pass Supergroups with diamictite units in other areas (Michigan, Fennoscandian Shield) where only one glacial horizon developed have been carried out in the past (Young, 1970, 1973; Ojakangas, 1988).

Glaciation should be followed by a sea level rise (transgression) during deglaciation and some time later regression as a result of isostatic rebound and sea level drop. The upper part of the Gowganda Formation in the Cobalt (Rainbird & Donaldson, 1988) and Whitefish Falls areas (Junnila & Young, 1995) was interpreted to have been deposited in a deltaic environment, whereas the Lorrain Formation was deposited in an alluvial environment. The lower part of the Gordon Lake Formation was interpreted
to have been deposited in a tidal flat environment, and the upper part of the Gordon Lake on a fairly deep marine shelf (Chandler, 1986). The upper part of the Headquarters Formation contains laminated schists and phyllites and was interpreted to have been formed by prodeltaic mudflows and turbidites, and the lower part of the Heart Formation was presumably deposited in a prodelta environment whereas the upper part of this unit was interpreted to represent a delta-front environment (Karlstrom et al., 1983). A similar sea level rise followed by a sea level drop in the Snowy Pass Supergroup and the Huronian Supergroup can be explained by postglacial adjustments.

Paleoproterozoic diamictites are followed by paleosols enriched in aluminosilicates and they are in turn overlain by pure quartzites on the Fennoscandian Shield, Michigan, Ontario, and Wyoming (Young, 1973; Ojakangas, 1996). These aluminosilicate-rich units (e.g., Lorrain Formation, ON) are considered correlative with the Medicine Peak Quartzite (Young, 1970, 1973; Houston et al., 1992) and possibly the upper part of the Heart Formation (this study). The upper part of the Medicine Peak Formation is composed of orthoquartzites and is possibly correlative with the upper part of the Lorrain Formation.

Roscoe & Card (1993) correlated the Lookout Schist, WY with the Gordon Lake Formation, ON whereas Houston et al. (1992) preferred correlation of the Lookout Schist with the Lorrain Formation, ON (Fig. 11.1). Carbonate samples were analysed from the Gordon Lake Formation and the Lookout Schist to resolve this contradiction. Only one sample of the Lookout Schist was sufficiently pure to be analysed and it has intermediate values between highly enriched carbonates deposited during the carbon isotope excursion and “normal” carbonates (Bekker & Karhu, 1996). Carbonates of the Gordon Lake Formation appeared to be $^{13}\text{C}$-enriched (Bekker et al., 1997). These data suggest, although they are not conclusive since only one sample of the Lookout Schist was studied, that the Lookout Schist is older than the Gordon Lake Formation and support the correlation of Houston et al. (1992).

Houston et al. (1992) correlated the Nash Fork Formation with the Randville Dolomite and the Gordon Lake Formation whereas Roscoe & Card (1993) correlated this unit with the Kona Dolomite. Our study showed (Bekker & Karhu, 1996 and unpub. data) that the lower part of the Nash Fork Formation has heavy carbon isotope values up to $+8\%\text{ PDB}$ and the upper part of this formation has carbon isotope values between $+1 - +2\%\text{ PDB}$. Our data for the Gordon Lake Formation and the Kona Dolomite showed steady $^{13}\text{C}$-enriched values (Bekker & Karhu, 1997b, Bekker et al., 1997) with the exception of two samples of the Kona Dolomite which do not have $^{13}\text{C}$-enriched values. However, their primary nature has not been confirmed; based on depleted oxygen isotope values of these two samples in respect to other samples of the same unit it is likely that their carbon isotope values have been affected by post-depositional alteration processes. Therefore, it is assumed, based on Karhu & Holland’s (1996) curve of carbon isotope variations during the Paleoproterozoic, that the Gordon Lake Formation and Kona Dolomite were deposited at about the same time (at the beginning of the carbon isotope excursion), before Nipissing Diabase intrusion at 2.219 Ga, and that the Nash Fork Formation is significantly younger since the time of its deposition encompasses the end of the carbon isotope excursion which was dated on the Fennoscandian Shield at around 2.06 Ga.
Fig. 11.1 (previous page). Comparative stratigraphy of metasedimentary rocks of the Sierra Madre; Medicine Bow Mountains, WY; north shore of Lake Huron, ON, Canada; and Dickinson County, MI (after Houston et al., 1992 with changes and corrections). Changes and corrections do not affect piercing points in their correlation (highlighted in bold), for suggested changes to their correlation scheme in this study see text. **Corrections and changes:** Hemlock Formation dated at 1910 ± 10 Ma (Banks & Van Schmus, 1972) is not exposed in Dickinson County and, furthermore, recently was correlated with the Badwater Greenstone (Sims, 1992 as cited in Ojakangas, 1994). Carbonateapatite bed in the iron-formation member at the base of the Michigamme Formation in the East Baraga basin was dated by Pb-Pb method at 1929 ± 17 Ma (as cited in Morey & Southwick, 1995). References to ages: 1 - Corfu & Andrews, 1986; 2 - Premo & Van Schmus, 1989.

Better correlation can be established for the Nash Fork Formation with the Lower Albanel Formation (Mistassini basin, Quebec) and the Upper Jatulian-Ludikovian succession (Karelian Supergroup, Fennoscandian Shield). The Lower Albanel Formation, based on Schidlowski et al. (1983), Mirota and Veizer (1994), and our preliminary data (Bekker et al., 1997c), and the Upper Jatulian-Ludikovian succession based on Yudovich et al. (1990) data, both show a transition from high to normal carbon isotope values. Organic-rich black shales occur in all these successions as well as in the Francevillian basin (Gauthier-Lafaye & Weber, 1989) at the transition from heavy to normal carbon isotope values. This correlation supports the contention by Houston et al. (1992) that a significant amount of time elapsed between deposition of the upper and the lower parts of the Libby Creek Group, which were later juxtaposed by movement along the Lewis Lakes thrust fault.

Correlation between the Kona Dolomite and the Gordon Lake Formation was suggested earlier based on lithostratigraphic arguments (Young, 1966, 1983; Bennett et al., 1994): similar stratigraphic position, depositional environment, paleoclimate, and mineral deposits (copper stratiform deposits). Young (1983) correlated the Kona Dolomite and the Gordon Lake Formation based on their fine-grained composition with cherty layers, position in stratigraphic sequence (above tillites and orthoquartzites), presence of evidence for benthic microbial life in both formations, folding, and an unconformable contact of the Chocolay and Cobalt groups with the overlying successions. This correlation was reinforced by the discovery in a fault-bounded basin of carbonates in a fine-grained clastic unit that was correlated with the Gordon Formation (Bennett et al., 1989, 1993, 1994). Evaporite casts were observed in the Kona Dolomite and the Gordon Lake Formation (Taylor, 1972; Larue, 1981; Perry et al., 1984; Hemzacek et al., 1982; Wood, 1973; Chandler, 1986, 1988, 1989). New carbon isotope data and sulfur isotope data from the remains of sulfates in their pseudomorphs from these two units (Cameron, 1983, Perry et al., 1984) are very similar, indicating that they were deposited from sea water with similar composition. Therefore, these data support correlation of the Gordon Lake Formation and the Kona Dolomite.

Based on lithostratigraphic correlation, the Kona, Bad River, and Randville dolomites, and the Saunders, Denham, and Trout Lake formations were long considered correlative (Morey and Southwick,
1996). Our study showed that the Kona Dolomite is $^{13}$C-enriched whereas all the other units have "normal" carbon isotope values. Combined with other climatic and atmospheric composition indicators, it was interpreted in Chapter 7.5.2 as an indication that all these units with the exception of the Kona Dolomite were deposited before the carbon isotope excursion, and that the Kona Dolomite was deposited during the early stage of this excursion (Bekker & Karhu, 1997b).
1. Field and petrographic observations as well as major element analyses support a glacial environment of deposition for the Vagner and Headquarters formations, and possibly the Campbell Lake Formation. These observations and analyses, along with carbon isotope data, support earlier correlations of these three glacial units with the Ramsay Lake, Bruce, and Gowganda formations of the Huronian Supergroup of Ontario, respectively.

2. Even though paleosols were not observed in outcrop, a definite trend to higher CIA values in the middle and upper parts of the Heart Formation allows the inference of climatic amelioration during deposition of this unit. Overlying quartz arenites of the Medicine Bow Quartzite might have formed due to high weathering rates induced by a warm climate. The Medicine Bow Quartzite is likely correlative with the Lorrain Formation of the Huronian Supergroup, Ontario.

3. Carbon isotope study of the limestone overlying diamicites of the Vagner Formation shows that it has depleted carbon and oxygen isotope values. Samples from most of the areal exposure of the Vagner Formation and the carbonate unit from Cooper Hill have similar carbon and oxygen isotope values, supporting correlation of these units. Furthermore, the likely correlative Bruce “Limestone” Member of the Espanola Formation, Huronian Supergroup, ON (Veizer et al., 1992) shows similar depletion of carbon and oxygen isotope values. Depleted carbon and oxygen isotope values can be explained by either an admixture of meteoric waters or as a signature of the postglacial ocean during the oceanic overturn. Sedimentological observations suggest a deep environment of deposition for the Vagner Formation, possibly supporting the second interpretation.

4. Carbon isotope analyses of the Nash Fork Formation indicate that this unit has heavy carbon isotope values in the lower part and normal values in the upper part. The end of the carbon isotope excursion was constrained in time on the Fennoscandian Shield to 2.06 Ga, and the Nash Fork Formation was likely deposited around this time as well. It was not possible in the present study to constrain where within the Libby Creek Group the carbon isotope excursion started.

5. Carbon and oxygen isotope values of the Kona Dolomite (Chocolay Group, Marquette Supergroup, MI); the Gordon Lake Formation (Cobalt Group, Huronian Supergroup, ON); and an unnamed dolomite unit in a fault-bounded block in Fenwick Township, ON are similar, supporting their correlation. These units were probably deposited during the early stage of the carbon isotope excursion. These units seem to be correlative with the lower Jatuli Group of the Fennoscandian Shield and are older than the Nash Fork Formation that was deposited at the end of the carbon isotope excursion.

6. Lake Superior carbonate units of the Chocolay Group (Denham and Trout Lake Formations, Bad River Dolomite, Saunders Formation, and Randville Dolomite) were traditionally considered correlative with the Kona Dolomite, but it is herein suggested, based on their carbon isotope values, that they have different age, were deposited before the carbon isotope excursion started, and are likely slightly older than the Kona Dolomite.
7. This study shows that combined chemostratigraphic and paleoclimatic analysis has great potential for the understanding and correlation of Paleoproterozoic successions. A sequence of markers can be reconstructed for the Paleoproterozoic: (1) regolith on Archean and Paleoproterozoic rocks (~2.4 Ga); (2) Paleoproterozoic glaciation (2.4 - 2.3 Ga); (3) regolith on glacial and package of rocks including glaciars, quartz arenites, red beds, and stratiform copper deposits (~2.3 Ga); (4) 13C-enriched carbonates with evidence for a warm arid climate, and stratiform copper deposits (~2.22 - 2.06 Ga); (5) black organic-rich shales (~2.06 Ga). A sequence in which one of these markers is absent or poorly developed can still be interpreted and should be reexamined keeping in mind the suggested sequence of markers.

This should be considered only as a tentative model based on presently available data.
APPENDIX 1. PETROGRAPHIC DESCRIPTION OF THIN SECTIONS

Note: The following abbreviations are used in this appendix: Q = quartz; K-Fsp = potassium feldspar; R. F. = rock fragment; Bi = biotite, Plg = plagioclase, Chl = chlorite, Ser. = sericite, Mgt = magnetite, Musc = muscovite, Amp = amphibole, Cal = calcite, Mi = microcline, Zr = zircon.

BE-95-6 Rock Knoll Fm. Graywacke with mudstone clasts.
Common Q and Q with polycrystalline undulatory extinction (metamorphic Q); Plg altered to Chl., Ser.; orthoclase; Musc.; perthite; Bi.; plutonic R.F. (Plg + Q); quartzite R.F.; chert fragments; schist fragments
Plg >> K-Fsp

BE-95-8 Vagner Fm. Diamictite.
Common Q and recrystallized Q, Plg, Mi, Bi, plutonic R. F., schist fragments, hypabyssal felsic R.F., porphyritic felsic volcanic R. F., quartzite R. F., altered grains of K-Fsp and Plg, sericite
Plg >> K-Fsp

BE-95-9 Cascade Quartzite. Arkose Sandstone.
Q, K-Fsp, chloritized Bi, Plg, Musc

BE-95-9a Siliciclastic layer in the Vagner Fm. Marble.
Undulatory and common Q, Plg, Bi, Cal, Mi, Musc, actinolite, clinozoisite

BE-95-13 Rock Knoll Fm. Arkose Sandstone.
Undulatory and polycrystalline Q, orthoclase, Mi, Plg, Bi

BE-95-15 Cascade Quartzite. Quartz sandstone.
Q, Musc, chlorite

BE-95-20 Headquarters Fm. Diamictite Member.
Q, Plg, Bi, felsic vol. R.F., felsic plutonic R.F., Mgt, chlorite

BE-95-21 Headquarters Fm., Arkose Member/Arkosic graywacke.
Common, undulatory, and recrystallized Q, Plg, Musc, Bi

BE-95-29 Vagner Fm., Diamictite Member/graywacke.
Recrystallized and common/undulatory Q, Musc, Plg, Bi, schist R. F., felsic volcanic R. F., Fsp altered to sericite

BE-95-30 Headquarters Fm., Schist Member.
Musc, undulatory Q, pyrite, chlorite, plagioclase

BE-95-31 Headquarters Fm., Diamictite Member/Arkosic graywacke.
Altered Plg, Musc, common/undulatory and recrystallized Q, Mi, perthite
Plg >> K-Fsp

BE-95-33A Headquarters Fm., Schist Member.
Plg, perthite, undulatory Q, Musc, felsic plutonic R. F., mudstone/schist R. F.
Plg >> K-Fsp

BE-95-34. Headquarters Fm., Diamictite Member. Well-laminated (silty-sandy layers).
Bi, undulatory and polycrystalline Q, Plg, Musc, orthoclase, Zr, plutonic and volcanic R.F.

BE-95-36 Campbell Lake Fm. Diamictite Member/Graywacke.
Plg, undulatory Q, Bi, Musc, recrystallized Q, felsic and porphyritic volcanic R.F., quartzite R. F., felsic plutonic R. F., Mi
Plg >> K-Fsp
BE-95-38. **Campbell Lake Fm.** Graywacke.
Musc, Plg, common Q, plutonic R.F., perthite

BE-95-39. **Campbell Lake Fm.** Graywacke.
Musc., undulatory Q., perthite, Mi, Bi, Amp, rutile?, plutonic R. F.

BE-95-40. **Lindsey Quartzite.** Arkosic Sandstone.
Recrystallized Q, Bi, Musc, perthite, Plag, plutonic R. F.

BE-95-41. **Campbell Lake Fm.** Schist/graywacke.
Undulatory fractured Q, Musc

BE-95-43. **Campbell Lake Fm.** Q sandstone.
Undulatory Q, Musc, K-Fsp., apatite, altered Plg

BE-C-95-2 **Vagner Fm.** Silicified limestone.
Cal, undulatory Q, perthite, Mi, Plg, Chl

BE-C-95-3. **Vagner Fm.** Grey-blue limestone.
Carbonate, undulatory Q, garnet

BE-C-95-3. **Vagner Fm.** Grey-blue limestone.

BE-C-95-5. **Nash Fork Fm.** Grey dolomite.
Dolomite, undulatory Q. Finely laminated.

BE-C-95-7. **Vagner Fm.** Pink limestone.
Dolomite, undulatory Q, Plg., perthite

BE-C-95-8. **Vagner Fm.** Grey limestone.
Musc, limestone, undulatory Q, epidote

BE-C-95-9. **Vagner Fm.** Pink limestone.
Musc, common Q., limestone, Plg., Mi, epidote (clinozoisite)

BE-C-95-16. **Lookout Schist.**
Undulatory and recrystallized Q., dolomite, Musc

BE-C-95-17. **Nash Fork Fm.** Dolomite.
Undulatory and recrystallized Q, dolomite, Plg, felsic plutonic R.F., perthite

BE-C-95-18. **Nash Fork Fm.** Dolomite.
Musc, dolomite, common Q
APPENDIX 2. CARBON AND OXYGEN ISOTOPE RATIOS OF THE STUDIED PALEOPROTEROZOIC CARBONATES

Note: Exact locations for Wyoming samples are given in Appendix 3. The $\delta^{13}$C and $\delta^{18}$O of CO$_2$ extracted from carbonates were determined on a Finnigan MAT 251 gas source mass spectrometer using the international NBS-20 standard (Solenhofen limestone). They are expressed as a per mil deviation from the PDB standard (belemnite of the Cretaceous Peedee Formation in South Carolina). The $\delta^{18}$O values were recalculated into the units of the SMOW standard (standard mean ocean water). The yield tells the carbonate content of the sample. It is given in micromoles of CO$_2$/mg of sample. For pure calcite it would be 10 $\mu$mol/mg, and for pure dolomite it would be about 10.8 $\mu$mol/mg. All samples were analysed using a semi-quantitative X-ray diffraction method to determine the proportion of dolomite in the total carbonate (last column). In the most impure samples (e.g. BE-C-95-2) silicate peaks interfere and in those cases Cal indicates that calcite peaks are present. All samples were analyzed by Dr. J. A. Karhu of the Geological Survey of Finland.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Outcrop number, Location, Collector</th>
<th>Mineral</th>
<th>$\delta^{13}$C, PDB</th>
<th>$\delta^{18}$O, PDB</th>
<th>$\delta^{18}$O, SMOW</th>
<th>Yield, umol/mg</th>
<th>Dolomite wt % in total carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vagner Fm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-1</td>
<td>N2, Cooper Hill, Bekker Calcite</td>
<td>-2.34</td>
<td>-19.75</td>
<td>5.93</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-2</td>
<td>N2, Cooper Hill, Bekker Calcite</td>
<td>-2.43</td>
<td>-19.36</td>
<td>1.03</td>
<td>Cal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-3</td>
<td>N3, Cooper Hill, Bekker Calcite</td>
<td>-2.00</td>
<td>-20.51</td>
<td>7.48</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-4</td>
<td>N4, Cooper Hill, Bekker Calcite</td>
<td>-2.46</td>
<td>-18.24</td>
<td>6.58</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-5</td>
<td>N9, Rock Creek, Bekker Calcite</td>
<td>-1.86</td>
<td>-18.78</td>
<td>6.3</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-6</td>
<td>N10, Rock Creek, Bekker Calcite</td>
<td>-1.5</td>
<td>-19.93</td>
<td>2.67</td>
<td>Cal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-7</td>
<td>N18, Dipper Lake, Bekker Calcite</td>
<td>-2.59</td>
<td>-16.44</td>
<td>3.4</td>
<td>Cal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-10a</td>
<td>N21, Dipper Lake, Bekker Calcite</td>
<td>-2.28</td>
<td>-17.44</td>
<td>5.26</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-10b</td>
<td>N21, Dipper Lake, Bekker Calcite</td>
<td>-2.17</td>
<td>-19.58</td>
<td>5.26</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-11</td>
<td>N24, NE of Dipper Lake, Bekker Cal</td>
<td>-1.91</td>
<td>-19.41</td>
<td>5.63</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-12</td>
<td>N24, NE of Dipper Lake, Bekker Cal</td>
<td>-1.73</td>
<td>-18.88</td>
<td>5.96</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-15</td>
<td>N35, Trail Creek, Bekker Calcite</td>
<td>-1.66</td>
<td>-18.95</td>
<td>2.95</td>
<td>Cal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-21</td>
<td>N35, Trail Creek, Bekker Calcite</td>
<td>-2.19</td>
<td>-17.65</td>
<td>2.21</td>
<td>Cal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-24</td>
<td>N44, Reservoir/Vagner Lakes, Bekk</td>
<td>-2.22</td>
<td>-16.71</td>
<td>6.3</td>
<td>2.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nash Fork Fm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-5</td>
<td>N5, Road 101, Bekker Dolomite</td>
<td>0.21</td>
<td>-7.37</td>
<td>10.34</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-17</td>
<td>N29, Big Telephone Lake, Bekker</td>
<td>4.78</td>
<td>-17.18</td>
<td>9.53</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-18</td>
<td>N30, Big Telephone Lake, Bekker</td>
<td>6.8</td>
<td>-15.93</td>
<td>10.17</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-19</td>
<td>N31, Libby Creek, Bekker Dolomite</td>
<td>8.23</td>
<td>-10.07</td>
<td>10.15</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lookout Schist</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-16</td>
<td>N28, Big Telephone Lake, Bekker</td>
<td>Total</td>
<td>2.54</td>
<td>9.15</td>
<td>96.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-C-95-16</td>
<td>N28, Big Telephone Lake, Bekker</td>
<td>Dolomite</td>
<td>2.7</td>
<td>-19.05</td>
<td>8.57</td>
<td>96.2</td>
<td></td>
</tr>
<tr>
<td>Kona Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>93 - MI - 61 - B</td>
<td>HW 480, R. W. Ojakangas Dolomite</td>
<td>6.06</td>
<td>-13.81</td>
<td>16.67</td>
<td>8.2</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>93 - MI - 61 - D</td>
<td>HW 480, R. W. Ojakangas Dolomite</td>
<td>6.09</td>
<td>-13.79</td>
<td>16.69</td>
<td>7.17</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>93 - MI - 61 - F</td>
<td>HW 480, R. W. Ojakangas Dolomite</td>
<td>5.88</td>
<td>-13.23</td>
<td>17.27</td>
<td>7.95</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>93 - MI - 61 - G</td>
<td>HW 480, R. W. Ojakangas Dolomite</td>
<td>5.19</td>
<td>-12.48</td>
<td>18.04</td>
<td>9.06</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>MI-KN-1</td>
<td>HW 480, Lindberg Pit, A. Galarowicz Dolomite</td>
<td>4.94</td>
<td>-13.65</td>
<td>16.84</td>
<td>3.76</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MI - KN - 2</td>
<td>HW 480, Lindberg Pit, A. Galarowicz Dolomite</td>
<td>6.01</td>
<td>-14.1</td>
<td>16.37</td>
<td>8.0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MI-95-C-2</td>
<td>HW 28, Marquette, MI, Bekker Dolomite</td>
<td>6.88</td>
<td>-12.41</td>
<td>18.12</td>
<td>9.91</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>MI - 95 - C - 4</td>
<td>HW 28, Marquette, MI, Bekker Dolomite</td>
<td>6.66</td>
<td>-15.29</td>
<td>15.14</td>
<td>9.84</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>17072/USGS</td>
<td>Marquette District, USGS, LaBerge</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO-1-2(2)</td>
<td>Mount Mesnard, NW1/4, Sec. 34, T.48 N., R. 25 W., Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 3</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 14</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 5</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 6</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 7</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 8</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 9</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 10</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 11</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 16</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 17</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 17a</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 20</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 21</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KO - 1 - 23</td>
<td>NEI/4, SWI/4, Sec. 8, T.47N, R.25W., Hole 21, Depth 1222', Cliff Mining Services Company, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 - BR - 1</td>
<td>2 mi E of Wakefield, Mi, R. W. Ojakangas</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1 - BR - 2</td>
<td>2 mi E of Wakefield, Mi, R. W. Ojakangas</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-2</td>
<td>Grand View Quarry, Marengo Lake Quadrangle, sec. 15, T.44N, R.5W</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-3</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-4</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-5</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-6</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-10</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD-96-12</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trout Lake Fm.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 1 - 391</td>
<td>Drillcore 18224 collected by Ralph W. Marsden, University of Minnesota, Duluth. NEI/4, NEI/4, Sec. 32, T.138, R. 26, Cuyuna Range, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 2 - 395</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 3 - 408</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 4 - 420</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 5 - 435</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 6 - 451</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 7 - 463</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 8 - 481</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 9 - 510</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN - 10 - 514</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denham Fm.</td>
<td>Birch Creek</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-96-D-2</td>
<td>SEI/4, sec. 25, T. 45 N., R. 21 W., Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-95-D-4</td>
<td>as above, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-96-D-5</td>
<td>as above, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE-96-D-7</td>
<td>as above, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ryb - 1/1</td>
<td>as above, R. W. Ojakangas</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ryb - 5b</td>
<td>as above, R. W. Ojakangas</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saunders Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA-2</td>
<td>Brule River, on the border of sec. 19 and sec. 30, T.41 N., R.16 W., WI, Bekker</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA-3</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA-4</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA-5</td>
<td>as above</td>
<td>Dolomite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Description</td>
<td>Dolomite</td>
<td>Calcium</td>
<td>Magnesium</td>
<td>Iron</td>
<td>Percentage</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>----------</td>
<td>---------</td>
<td>-----------</td>
<td>------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>SA-6</td>
<td>as above</td>
<td>Dolomite</td>
<td>0.58</td>
<td>-13.56</td>
<td>16.93</td>
<td>8.19</td>
<td>99</td>
</tr>
<tr>
<td>SA-9</td>
<td>as above</td>
<td>Dolomite</td>
<td>1.91</td>
<td>-11.73</td>
<td>18.82</td>
<td>8.09</td>
<td>99</td>
</tr>
<tr>
<td>SA-10</td>
<td>as above</td>
<td>Dolomite</td>
<td>2.44</td>
<td>-11.13</td>
<td>19.43</td>
<td>9.19</td>
<td>99</td>
</tr>
<tr>
<td>SA-12</td>
<td>as above</td>
<td>Dolomite</td>
<td>-1.16</td>
<td>-15.04</td>
<td>15.41</td>
<td>7.21</td>
<td>100</td>
</tr>
<tr>
<td>SA-13</td>
<td>as above</td>
<td>Dolomite</td>
<td>0.42</td>
<td>-16.36</td>
<td>14.04</td>
<td>10.08</td>
<td>100</td>
</tr>
<tr>
<td>SA-14</td>
<td>as above</td>
<td>Dolomite</td>
<td>1.50</td>
<td>-13.24</td>
<td>17.26</td>
<td>6.93</td>
<td>100</td>
</tr>
<tr>
<td>Randville Dolomite</td>
<td></td>
<td>Dolomite</td>
<td>2.11</td>
<td>-9.26</td>
<td>21.37</td>
<td>10.2</td>
<td>100</td>
</tr>
<tr>
<td>24973-USGS Crystal Falls District, MI, USGS, LaBerge</td>
<td></td>
<td>Dolomite</td>
<td>1.09</td>
<td>-15.47</td>
<td>14.96</td>
<td>8.19</td>
<td>100</td>
</tr>
<tr>
<td>RA-1-1</td>
<td>Kiernan Quad., Iron County, SE1/4, sec. A, T.43N., R31W., Bekker</td>
<td>Dolomite</td>
<td>0.47</td>
<td>-14.15</td>
<td>16.33</td>
<td>6.1</td>
<td>100</td>
</tr>
<tr>
<td>RA-1-2</td>
<td>as above</td>
<td>Dolomite</td>
<td>2.63</td>
<td>-10.83</td>
<td>19.74</td>
<td>9.25</td>
<td>100</td>
</tr>
<tr>
<td>RA-2-1</td>
<td>Kiernan Quad., Iron County, central part of sec.A, T.43N., R31W., Bekker</td>
<td>Dolomite</td>
<td>3.13</td>
<td>-8.22</td>
<td>22.44</td>
<td>9.94</td>
<td>100</td>
</tr>
<tr>
<td>RA-2-2</td>
<td>as above</td>
<td>Dolomite</td>
<td>3.14</td>
<td>-8.22</td>
<td>22.44</td>
<td>9.77</td>
<td>100</td>
</tr>
<tr>
<td>RA-2-4</td>
<td>as above</td>
<td>Dolomite</td>
<td>2.93</td>
<td>-9.11</td>
<td>21.52</td>
<td>9.64</td>
<td>100</td>
</tr>
<tr>
<td>RA-3-1</td>
<td>S1/2, sec.5, T.43N., R.28W., Bekker</td>
<td>Dolomite</td>
<td>0.15</td>
<td>-11.07</td>
<td>19.50</td>
<td>10.3</td>
<td>100</td>
</tr>
<tr>
<td>RA-3-2</td>
<td>as above</td>
<td>Dolomite</td>
<td>0.35</td>
<td>-12.00</td>
<td>18.54</td>
<td>10.13</td>
<td>100</td>
</tr>
<tr>
<td>RA-4-1</td>
<td>border of sec. 3 &amp; 4, T.43N., R.28W., Bekker</td>
<td>Dolomite</td>
<td>1.43</td>
<td>-9.99</td>
<td>20.61</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>RA-5-1</td>
<td>NE1/4, SE1/4, sec. 29, T. 40 N., R. 30 W., Bekker</td>
<td>Dolomite</td>
<td>1.46</td>
<td>-7.88</td>
<td>22.79</td>
<td>9.84</td>
<td>100</td>
</tr>
<tr>
<td>RA-5-8</td>
<td>as above</td>
<td>Dolomite</td>
<td>1.2</td>
<td>-10.12</td>
<td>20.48</td>
<td>9.65</td>
<td>100</td>
</tr>
<tr>
<td>RA-6-1</td>
<td>NE1/4, sec. 2, T.39N, R.30W, Bekker</td>
<td>Dolomite</td>
<td>0.84</td>
<td>-9.89</td>
<td>20.71</td>
<td>10.23</td>
<td>100</td>
</tr>
<tr>
<td>RA-7-5</td>
<td>S1/2, sec.35, T.40N, R.30W, Bekker</td>
<td>Dolomite</td>
<td>0.91</td>
<td>-7.99</td>
<td>22.67</td>
<td>8.97</td>
<td>100</td>
</tr>
<tr>
<td>Espanola Member of the Espanola Formation</td>
<td></td>
<td>Dolomite</td>
<td>2.51</td>
<td>-16.54</td>
<td>13.86</td>
<td>3.61</td>
<td>99</td>
</tr>
<tr>
<td>Esp-1-3</td>
<td>NW of Quirke Lake, 46°29'30&quot;N, 82°35'50&quot;W, Bekker</td>
<td>Dolomite</td>
<td>-2.18</td>
<td>-16.7</td>
<td>13.7</td>
<td>6.04</td>
<td>100</td>
</tr>
<tr>
<td>Esp-1-9</td>
<td>as above</td>
<td>Dolomite</td>
<td>-2.06</td>
<td>-16.0</td>
<td>14.42</td>
<td>6.44</td>
<td>98</td>
</tr>
<tr>
<td>Esp-2-1</td>
<td>as above</td>
<td>Dolomite</td>
<td>-2.06</td>
<td>-15.74</td>
<td>14.69</td>
<td>6.43</td>
<td>99</td>
</tr>
<tr>
<td>Esp-3-1</td>
<td>NW Quirke Township, Panel Mine Rd. to the entrance to New Quirke Mine, Bekker</td>
<td>Dolomite</td>
<td>-2.47</td>
<td>-15.57</td>
<td>16.92</td>
<td>7.54</td>
<td>100</td>
</tr>
<tr>
<td>Esp-4-1</td>
<td>N1/2 Bouck Township, Intersection of HW108 and Panel Mine Rd. to New Quirke Mine, Bekker</td>
<td>Dolomite</td>
<td>-2.88</td>
<td>-20.81</td>
<td>9.46</td>
<td>2.56</td>
<td>0</td>
</tr>
<tr>
<td>Serpent Formation</td>
<td></td>
<td>Dolomite</td>
<td>2.55</td>
<td>-17.59</td>
<td>12.77</td>
<td>5.59</td>
<td>99</td>
</tr>
<tr>
<td>SE-1-1</td>
<td>NW Quirke Lake, 46°29'30&quot;N, 82°35'50&quot;W, Bekker</td>
<td>Dolomite</td>
<td>4.24</td>
<td>-13.63</td>
<td>16.86</td>
<td>8.60</td>
<td>100</td>
</tr>
<tr>
<td>SE-2-3</td>
<td>as above</td>
<td>Dolomite</td>
<td>4.08</td>
<td>-13.68</td>
<td>16.80</td>
<td>8.44</td>
<td>100</td>
</tr>
<tr>
<td>GO-2-1</td>
<td>less than 100m south of HW 638, central Meredith Township, Bekker</td>
<td>Dolomite</td>
<td>5.66</td>
<td>-12.70</td>
<td>17.82</td>
<td>7.14</td>
<td>100</td>
</tr>
<tr>
<td>GO-2-3</td>
<td>as above</td>
<td>Dolomite</td>
<td>5.94</td>
<td>-11.94</td>
<td>18.60</td>
<td>6.72</td>
<td>100</td>
</tr>
<tr>
<td>GO-2-5</td>
<td>as above</td>
<td>Dolomite</td>
<td>5.61</td>
<td>-13.21</td>
<td>17.29</td>
<td>5.72</td>
<td>99</td>
</tr>
<tr>
<td>GO-4-1</td>
<td>Plummer Township, Bekker</td>
<td>Dolomite</td>
<td>5.66</td>
<td>-12.70</td>
<td>17.82</td>
<td>7.14</td>
<td>100</td>
</tr>
<tr>
<td>GO-4-2</td>
<td>Plummer Township, Bekker</td>
<td>Dolomite</td>
<td>5.94</td>
<td>-11.94</td>
<td>18.60</td>
<td>6.72</td>
<td>100</td>
</tr>
<tr>
<td>GO-4-3</td>
<td>Plummer Township, Bekker</td>
<td>Dolomite</td>
<td>5.61</td>
<td>-13.21</td>
<td>17.29</td>
<td>5.72</td>
<td>99</td>
</tr>
<tr>
<td>KN-1</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>7.34</td>
<td>-13.36</td>
<td>17.14</td>
<td>5.66</td>
<td>100</td>
</tr>
<tr>
<td>KN-2</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>6.43</td>
<td>-12.79</td>
<td>17.72</td>
<td>8.51</td>
<td>100</td>
</tr>
<tr>
<td>KN-3</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>6.92</td>
<td>-11.77</td>
<td>18.77</td>
<td>8.83</td>
<td>100</td>
</tr>
<tr>
<td>KN-4</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>8.18</td>
<td>-10.34</td>
<td>20.25</td>
<td>10.01</td>
<td>100</td>
</tr>
<tr>
<td>KN-5</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>4.95</td>
<td>-14.82</td>
<td>15.64</td>
<td>9.29</td>
<td>100</td>
</tr>
<tr>
<td>KN-6</td>
<td>Fenwick Township, G. Bennett</td>
<td>Dolomite</td>
<td>6.15</td>
<td>-14.74</td>
<td>15.71</td>
<td>7.68</td>
<td>100</td>
</tr>
</tbody>
</table>

85
<table>
<thead>
<tr>
<th></th>
<th>Location</th>
<th>Formation</th>
<th>True</th>
<th>True</th>
<th>RGS</th>
<th>True</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-1-10</td>
<td>Fenwick Township, Bekker</td>
<td>Dolomite</td>
<td>7.95</td>
<td>-13.3</td>
<td>19.23</td>
<td>9.51</td>
</tr>
<tr>
<td>GO-1-11</td>
<td>Fenwick Township, Bekker</td>
<td>Dolomite</td>
<td>7.48</td>
<td>-13.06</td>
<td>17.51</td>
<td>8.35</td>
</tr>
<tr>
<td>JY-1</td>
<td>Johnson Township, G. Bennett</td>
<td>Dolomite</td>
<td>7.46</td>
<td>-13.06</td>
<td>17.44</td>
<td>6.58</td>
</tr>
</tbody>
</table>
APPENDIX 3. MAJOR AND TRACE ELEMENT ANALYSES OF DIAMICTITES AND OVERLYING UNITS

Note: Analyses were done by Rick Knurr of the University of Minnesota. The concentrations of the following elements were measured in weight percent of oxide: P, Ca, Ti, Fe (total Fe as Fe₂O₃), Mg, Na, K, Al, Si, Mn. The concentrations for the rest of elements were measured in parts per million. CIA was calculated using the following equation (Nesbitt & Young, 1982):

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^\prime + \text{Na}_2\text{O} + \text{K}_2\text{O})}}{100}
\]

where Na₂O, K₂O, Al₂O₃, and CaO' are in mole percentages of oxides. CaO' should be corrected for amount used in apatite and carbonate. Petrographic analyses did not show any significant amount of apatite and carbonate in studied samples. Nevertheless, corrections to the measured concentration of CaO were made assuming that all was P used in apatite.

<table>
<thead>
<tr>
<th>Element</th>
<th>BE-95-4</th>
<th>BE-95-26</th>
<th>BE-95-28A</th>
<th>BE-95-28B</th>
<th>BE-95-25</th>
<th>BE-95-26A</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.1167</td>
<td>0.1564</td>
<td>0.1109</td>
<td>0.1579</td>
<td>0.1069</td>
<td>0.0841</td>
</tr>
<tr>
<td>Ca</td>
<td>1.4829</td>
<td>0.8156</td>
<td>1.3142</td>
<td>0.9345</td>
<td>0.9357</td>
<td>0.9128</td>
</tr>
<tr>
<td>Ti</td>
<td>0.6971</td>
<td>0.6971</td>
<td>0.7116</td>
<td>0.8284</td>
<td>0.7544</td>
<td>0.6717</td>
</tr>
<tr>
<td>Fe</td>
<td>5.2838</td>
<td>5.2838</td>
<td>5.4018</td>
<td>5.6013</td>
<td>4.1716</td>
<td>3.6146</td>
</tr>
<tr>
<td>Sr</td>
<td>83.0598</td>
<td>83.0598</td>
<td>66.3797</td>
<td>84.1514</td>
<td>28.3844</td>
<td>49.5953</td>
</tr>
<tr>
<td>Al</td>
<td>495.485</td>
<td>482.75</td>
<td>73.327</td>
<td>59.8446</td>
<td>56.999</td>
<td>253.583</td>
</tr>
<tr>
<td>Mg</td>
<td>1.9421</td>
<td>3.3633</td>
<td>2.1636</td>
<td>3.6498</td>
<td>3.3951</td>
<td>4.1664</td>
</tr>
<tr>
<td>Na</td>
<td>2.9816</td>
<td>4.6115</td>
<td>2.4138</td>
<td>4.2907</td>
<td>0.6679</td>
<td>3.8287</td>
</tr>
<tr>
<td>K</td>
<td>3.6921</td>
<td>2.2049</td>
<td>4.5353</td>
<td>2.3968</td>
<td>4.9021</td>
<td>4.5124</td>
</tr>
<tr>
<td>Si</td>
<td>65.8877</td>
<td>99.960</td>
<td>61.2767</td>
<td>67.0319</td>
<td>59.8465</td>
<td>61.6423</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.6561</td>
<td>0.0955</td>
<td>0.6555</td>
<td>0.6818</td>
<td>0.035</td>
<td>0.3682</td>
</tr>
<tr>
<td>Be</td>
<td>1.9784</td>
<td>1.1325</td>
<td>2.1046</td>
<td>1.0798</td>
<td>1.4292</td>
<td>2.1172</td>
</tr>
<tr>
<td>V</td>
<td>0.1440</td>
<td>0.1149</td>
<td>0.4334</td>
<td>0.2376</td>
<td>0.3228</td>
<td>0.1865</td>
</tr>
<tr>
<td>Cr</td>
<td>10.3979</td>
<td>145.538</td>
<td>83.2859</td>
<td>177.285</td>
<td>169.147</td>
<td>153.06</td>
</tr>
<tr>
<td>Co</td>
<td>0.8484</td>
<td>20.1366</td>
<td>15.6195</td>
<td>25.7027</td>
<td>9.4664</td>
<td>23.3859</td>
</tr>
<tr>
<td>Ni</td>
<td>38.8433</td>
<td>67.2681</td>
<td>33.0755</td>
<td>61.0918</td>
<td>36.2468</td>
<td>61.5847</td>
</tr>
<tr>
<td>Cu</td>
<td>189.296</td>
<td>45.3722</td>
<td>8.4244</td>
<td>48.1339</td>
<td>39.9763</td>
<td>42.2458</td>
</tr>
<tr>
<td>Zn</td>
<td>3.2443</td>
<td>51.5499</td>
<td>19.7312</td>
<td>57.7483</td>
<td>142.966</td>
<td>38.1344</td>
</tr>
<tr>
<td>Ga</td>
<td>18.6195</td>
<td>22.161</td>
<td>19.4996</td>
<td>20.4471</td>
<td>23.2427</td>
<td>22.3892</td>
</tr>
<tr>
<td>Rb</td>
<td>135.563</td>
<td>83.276</td>
<td>21.6371</td>
<td>74.1149</td>
<td>200.319</td>
<td>155.346</td>
</tr>
<tr>
<td>Zr</td>
<td>149.953</td>
<td>132.709</td>
<td>235.313</td>
<td>144.021</td>
<td>210.061</td>
<td>169.809</td>
</tr>
<tr>
<td>Cs</td>
<td>6.0051</td>
<td>2.9923</td>
<td>5.0122</td>
<td>0.9023</td>
<td>0.6911</td>
<td>0.7786</td>
</tr>
<tr>
<td>Hf</td>
<td>3.8737</td>
<td>5.6222</td>
<td>6.4966</td>
<td>3.9021</td>
<td>0.269</td>
<td>4.0803</td>
</tr>
<tr>
<td>U</td>
<td>3.6982</td>
<td>2.557</td>
<td>3.2222</td>
<td>3.3534</td>
<td>3.6441</td>
<td>2.7432</td>
</tr>
<tr>
<td>Th</td>
<td>55.39</td>
<td>59.64</td>
<td>50.37</td>
<td>56.67</td>
<td>7.2</td>
<td>6.9</td>
</tr>
<tr>
<td>Pa</td>
<td>0.66</td>
<td>2.09</td>
<td>0.49</td>
<td>0.8</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>K</td>
<td>0.18</td>
<td>0.18</td>
<td>0.31</td>
<td>0.66</td>
<td>0.44</td>
<td>0.18</td>
</tr>
<tr>
<td>Ca</td>
<td>0.27</td>
<td>0.27</td>
<td>0.32</td>
<td>0.61</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Na</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Note: Analyses were done by Rick Knurr of the University of Minnesota. The concentrations of the following elements were measured in weight percent of oxide: P, Ca, Ti, Fe (total Fe as Fe₂O₃), Mg, Na, K, Al, Si, Mn. The concentrations for the rest of elements were measured in parts per million. CIA was calculated using the following equation (Nesbitt & Young, 1982):

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^\prime + \text{Na}_2\text{O} + \text{K}_2\text{O})}}{100}
\]

where Na₂O, K₂O, Al₂O₃, and CaO' are in mole percentages of oxides. CaO' should be corrected for amount used in apatite and carbonate. Petrographic analyses did not show any significant amount of apatite and carbonate in studied samples. Nevertheless, corrections to the measured concentration of CaO were made assuming that all was P used in apatite.
### Appendix 4. Geographic location and lithology of studied samples

**Samples from Wyoming, collected in the summer of 1995**

**Note:** F. = formation, mbr. = member, δ¹³C = carbon isotope analysis, TS = thin section, CIA = major element analysis.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Formation</th>
<th>Rocktype</th>
<th>Location</th>
<th>Locality</th>
<th>Location</th>
<th>Form.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE-C-95-1</td>
<td>Vagner F.</td>
<td>grey-blue carbonate</td>
<td>Cooper Hill, N-E of Medicine Bow M-tts</td>
<td>NE1/4, Sec. 27, T.18N, R.78W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-2</td>
<td>Vagner F.</td>
<td>brown-red limestone</td>
<td>Cooper Hill, N-E of Medicine Bow M-tts</td>
<td>NE1/4, Sec. 27, T.18N, R.78W</td>
<td>&gt;C, TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-3</td>
<td>Vagner F.</td>
<td>grey-blue limestone</td>
<td>Cooper Hill, N-E of Medicine Bow M-tts</td>
<td>NW1/4, Sec. 27, T.18N, R.78W</td>
<td>&gt;C, polished section, TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-4</td>
<td>Vagner F.</td>
<td>grey-blue limestone</td>
<td>Cooper Hill, N-E of Medicine Bow M-tts</td>
<td>SE1/4, Sec. 27, T.18N, R.78W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-5</td>
<td>Nash Fork F.</td>
<td>grey limestone</td>
<td>Rd 101</td>
<td>NW1/4, Sec. 5, T.16N, R.78W</td>
<td>&gt;C, TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-6</td>
<td>Rock Knoll F.</td>
<td>greywacke with mudstone pebbles</td>
<td>Rock Knoll</td>
<td>E1/2, Sec. 35, T.17N, R.79W</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-7</td>
<td>Cascade F.</td>
<td>arkose sandstone</td>
<td>North side of the Rock Knoll</td>
<td>SW1/4, Sec. 26, T.17N, R.79W</td>
<td>TS, CIA</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-8</td>
<td>Vagner F.</td>
<td>pink limestone</td>
<td>Rock Creek and Hill 1003</td>
<td>SW1/4, Sec. 5, T.17N, R.78W</td>
<td>TS, 8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-9a</td>
<td>Vagner F.</td>
<td>elastic layer in marble</td>
<td>Rock Creek</td>
<td>SE1/4, Sec. 6, T.17N, R.78W</td>
<td>TS, 8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-9</td>
<td>Vagner F.</td>
<td>grey limestone</td>
<td>Dipper Lake</td>
<td>SE1/4, Sec. 6, T.17N, R.78W</td>
<td>Geochemistry, TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-10a</td>
<td>Vagner F.</td>
<td>green limestone</td>
<td>Head of South Brush Creek</td>
<td>SW1/4, NW1/4, Sec. 14, T.16N, R.80W</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-10b</td>
<td>Vagner F.</td>
<td>green limestone</td>
<td>Jeep Trail (to the west of the Dipper Lake)</td>
<td>SE1/4, Sec. 11, T.16N, R.80W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-11</td>
<td>Vagner F.</td>
<td>white-pink limestone</td>
<td>Small lake to the N-E from Dipper Lake</td>
<td>NE1/4, Sec. 11, T.16N, R.80W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-12</td>
<td>Vagner F.</td>
<td>pinkish limestone</td>
<td>Small lake to the N-E from Dipper Lake</td>
<td>NE1/4, Sec. 11, T.16N, R.80W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-15</td>
<td>Cascade F.</td>
<td>quartz sandstone</td>
<td>Jeep Trail</td>
<td>SE1/4, SE1/4, Sec. 2, T.16N, R.80W</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-16</td>
<td>Lookout Schist</td>
<td>dolomite</td>
<td>Big Telephone Lake</td>
<td>SE1/4, Sec. 9, T.16N, R.79W</td>
<td>TS, 8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-17</td>
<td>Nash Fork F.</td>
<td>dolomite</td>
<td>Big Telephone Lake</td>
<td>SE1/4, Sec. 9, T.16N, R.79W</td>
<td>TS, 8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-18</td>
<td>Nash Fork F.</td>
<td>dolomite</td>
<td>Big Telephone Lake</td>
<td>SE1/4, Sec. 9, T.16N, R.79W</td>
<td>TS, 8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-19</td>
<td>Lower part of the Nash Fork F.</td>
<td>dolomite with digital stromatolites</td>
<td>To the North from the Hourglass Lake</td>
<td>SW1/4, NE1/4, Sec. 16, T.16N, R.79W</td>
<td>8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-20</td>
<td>Vagner F.</td>
<td>grey limestone</td>
<td>Trail Creek</td>
<td>NE1/4, Sec. 26, T.17N, R.79W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-21</td>
<td>Vagner F.</td>
<td>grey limestone</td>
<td>Trail Creek</td>
<td>NE1/4, Sec. 26, T.17N, R.79W</td>
<td>&gt;C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-20</td>
<td>Headquarter F., Diamictite mbr., Headquarters F., Ark. mbr.</td>
<td>matrix of diamictite undated sandstone. phylolite</td>
<td>South Twin Lake</td>
<td>NW1/4, Sec. 23, T.16N, R.80W</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-21</td>
<td>Headquarter F., Diamictite mbr., Headquarters F., Ark. mbr.</td>
<td>matrix of diamictite undated sandstone. phylolite</td>
<td>Rock Knoll</td>
<td>SE1/4, Sec. 35, T.17N, R.79W</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>95-WY-87-A</td>
<td>Heart F.</td>
<td>schist</td>
<td>Ad 103 strike symbol on Houston's map</td>
<td>SE1/4, Sec. 27, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-A</td>
<td>Headquarter F., Schist mbr.</td>
<td>schist</td>
<td>North Twin Lake</td>
<td>SE1/4, Sec. 14, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-B</td>
<td>Lower part of the Head F.</td>
<td>arkose sandstone</td>
<td>North Twin Lake</td>
<td>SE1/4, Sec. 14, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-C</td>
<td>Heart F.</td>
<td>quartz sandstone</td>
<td>North Twin Lake</td>
<td>SE1/4, Sec. 14, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-D</td>
<td>Heart F.</td>
<td>argillite</td>
<td>North Twin Lake</td>
<td>SE1/4, Sec. 14, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-G</td>
<td>Heart F.</td>
<td>argillite</td>
<td>North Twin Lake</td>
<td>SE1/4, Sec. 14, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>95-WY-88-K</td>
<td>Medicine Peak F.</td>
<td>quartz-rich sandstone schist</td>
<td>North Twin Lake</td>
<td>NW1/4, Sec. 13, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-26</td>
<td>Headquarter F., Schist mbr.</td>
<td>schist</td>
<td>South of the Dipper Lake</td>
<td>NE1/4, NE1/4, Sec. 4, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-24</td>
<td>Vagner F., Marble mbr.</td>
<td>grey limestone</td>
<td>Pack Trail</td>
<td>SE1/4, NE1/4, Sec. 6, T.16N, R.79W</td>
<td>8°C</td>
<td></td>
</tr>
<tr>
<td>BE-C-95-28a</td>
<td>Vagner F., Pelitic</td>
<td>schist</td>
<td>Reserve Lake</td>
<td>NW1/4, Sec. 5, T.16N, R.80W</td>
<td>CIA</td>
<td></td>
</tr>
<tr>
<td>BE-95-29</td>
<td>mbr.</td>
<td>Vagner F., Diamictite mbr.</td>
<td>matrix of diamictite</td>
<td>N-E of Reservoir Lake</td>
<td>46</td>
<td>R.79W NW1/4, Sec. 5, T.16N, R.79W</td>
</tr>
<tr>
<td>BE-95-30</td>
<td>Shist mbr.</td>
<td>Headquarters F., schist</td>
<td>Crescent Lake</td>
<td>47</td>
<td>SE1/4, Sec. 5, T.16N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-31</td>
<td>Diamic. mbr.</td>
<td>Headquarters F., sandstone</td>
<td>Crescent Lake</td>
<td>48</td>
<td>SE1/4, Sec. 5, T.16N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-33a</td>
<td>Shist mbr.</td>
<td>Headquarters F., schist</td>
<td>Rock Creek Knoll</td>
<td>50</td>
<td>SW1/4, Sec. 35, T.17N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-34</td>
<td>Shist mbr.</td>
<td>Headquarters F., graywacke</td>
<td>South Fork Rock Creek</td>
<td>51</td>
<td>SE1/4, Sec. 34, T.17N, R.79W, CIA</td>
<td></td>
</tr>
<tr>
<td>BE-95-36</td>
<td>Campbell Lake F.</td>
<td>graywacke</td>
<td>Cascade Lake</td>
<td>53</td>
<td>SE1/4, Sec. 35, T.17N, R.80W</td>
<td></td>
</tr>
<tr>
<td>BE-95-38</td>
<td>Campbell Lake F.</td>
<td>graywacke</td>
<td>Brush Creek</td>
<td>55</td>
<td>NE1/4, NE1/4, Sec. 4, T.16N, R.80W</td>
<td></td>
</tr>
<tr>
<td>BE-95-39</td>
<td>Campbell Lake F.</td>
<td>arkose</td>
<td>Cutthroat Lake</td>
<td>56</td>
<td>NE1/4, NE1/4, Sec. 5, T.16N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-40</td>
<td>Lindsay F.</td>
<td>quartz sandstone</td>
<td>Cutthroat Lake</td>
<td>57</td>
<td>NE1/4, NE1/4, Sec. 5, T.16N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-41</td>
<td>Campbell Lake F.</td>
<td>schist</td>
<td>Jeff Lake</td>
<td>58</td>
<td>SE1/4, Sec. 29, T.17N, R.79W</td>
<td></td>
</tr>
<tr>
<td>BE-95-43</td>
<td>Campbell Lake F.</td>
<td>quartz sandstone</td>
<td>Jeff Lake</td>
<td>59</td>
<td>SE1/4, Sec. 29, T.17N, R.79W</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES


Houston, R. S., and Graff, P. J., 1995, Geologic map of Precambrian rocks of the Sierra Madre, Carbon County, Wyoming, and Jackson and Routt counties, Colorado, 1: 50,000: Miscellaneous investigations series, Map I-2452.


Karlstrom, K. E., and Houston, R. S., 1979a, Stratigraphy of the Phantom Lake Metamorphic Suite and Deep Lake Group and a review of the Precambrian tectonic history of the Medicine Bow Mountains: Contributions to Geology, University of Wyoming, v. 17, No. 2, p. 111-133.


96


Knight, S. H., 1968, Precambrian stromatolites, bioherms and reefs in the lower part of the Nash Formation: Contributions to Geology, v. 7, p. 73-116.


Tikhonirova, M. and Makarikhin, V. V., 1993, Possible reasons for the $\delta^{13}$C anomaly of Lower Proterozoic sedimentary carbonates: Terra Nova, v.5, p. 244-248.


Young, G. M., 1988, Proterozoic plate tectonics, glaciation and iron formations; Sedimentary Geology, v. 58, p. 127 - 144.


