Petrography and discontinuities, growth rates and stable isotopes of speleothems as indicators of paleoclimates from Oregon Caves National Monument, southwestern Oregon, USA

by

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ABSTRACT

Paleoclimatic data were obtained from speleothems of Oregon Caves National Monument, a dissolutional cave system located in southwest Oregon. The speleothems are composed mainly (>90%) of vertical columnar calcite crystals, and contain numerous discontinuities arising from short-lived (<100 years) events. Minor fabrics, such as transitional- and randomly-oriented elongate calcites are seeded on these discontinuities and accompanying detrital layers. Large (~750 μm) crystal terminations indicate growth under increased water film thickness resulting from greater flow and/or ponding. The age of the speleothems is provided by 14 U-Th TIMS dates in conjunction with global paleoclimatic proxies, and indicates growth rates between 1.54×10^{-3} to 3.15×10^{-2} mm/yr during early- to mid-interglacial periods of the last 500 000 years of the Quaternary. Stable isotopic (O and C) signatures obtained from the cave calcites show direct relationships to global paleoclimates. $\delta^{18}\text{O}$ values vary from -6.38 to -16.86‰, while $\delta^{13}\text{C}$ values range from +5.45 to -11.19‰ (V-PDB). Whereas the oxygen isotopes in the cave calcites reflect glacial to interglacial atmospheric transport processes, the carbon isotopes are thought to be controlled by varying water-rock ratios. Prominent positive carbon excursions, unmatched to oxygen variations, also occur within the records. These excursions are possibly modulated by the episodic lowering of treeline below the altitude of the cave site. Outcrop-scale discontinuities, representing periods of prolonged pauses in sedimentation, correspond to hiatuses ranging from 14 to 102 kyrs and are presumed to be caused by groundwater freezing during periods of extended periglacial conditions related to glaciations. These hiatuses increase in duration over the course of the

Quaternary and are coupled to an increase in growth rates. This suggests an opening of the cave and shallowing of the overburden, which shifts the dissolutional system from closed to open. A simple “start-stop” growth model is presented, based on minimum and maximum $\delta^{18}\text{O}$ values of marine records before or during terminations and shortly after the onset of climatic deterioration. Although this model shows a general correspondence between growth periods of speleothems and interglacials, correlation of paleoclimate proxies with calcite precipitation initiation and cessation shows mixed results, possibly owing to uncertainties related to global records which might not be reflective of local conditions.

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TABLE OF CONTENTS

ABSTRACT	iii
ACKOWLEGEMENTS	v
TABLE OF CONTENTS	viii
LIST OF TABLES	x
LIST OF FIGURES	xi
 1.0 GENERAL INTRODUCTION	 1
1.1 General setting and sample location	1
1.2 Personal contribution	2
1.3 Scientific contribution	3
1.4 Results not reported in this dissertation	4
 2.0 CHRONOLOGY OF DISCONTINUITIES AND PETROLOGY OF SPELEOTHEMS AS PALEOCLIMATIC INDICATORS OF THE KLAMATH MOUNTAINS, SOUTHWEST OREGON, USA	 10
2.1 Abstract	10
2.2 Introduction	11
<i>2.2.1 Site and sample description</i>	12
2.3 Methodology	14
2.4 Mineralogy and petrology of the OCNM cave calcites	15
<i>2.4.1 Crystal fabrics</i>	16
2.4.1.1 Columnar crystals	16
2.4.1.2 Transitional basal crystals (blocky or elongate)	17
2.4.1.3 Randomly oriented, elongate “scaffolding” crystals	18
2.4.1.4 Pillar calcites	18
2.4.1.5 Zoned equant crystals	19
<i>2.4.2 Discontinuities and detrital layers</i>	19
2.4.2.1 Outcrop-scale discontinuities	19
2.4.2.2 Detrital intervals and drapings	20
2.4.2.3 Crystal termination layers	21
2.4.2.4 Vertical linear inclusions	21
<i>2.4.3 Speleothem geochronology</i>	22
2.5 Discussion	25
<i>2.5.1 Primary nature of calcite crystals</i>	25
<i>2.5.2 Environmental factors affecting speleothem deposition</i>	26
2.5.2.1 Initial growth phase: effects of surface configuration and water depth	27
2.5.2.2 Columnar calcites growth mechanisms: stable growth conditions	29
<i>2.5.3 Duration of events: periglacial controls on precipitation</i>	30
2.6 Conclusions	32
 3.0 ESTABLISHING A SPELEOTHEM CHRONOLOGY FOR SOUTHWESTERN OREGON: CLIMATIC CONTROLS AND GROWTH MODELLING	 47
3.1 Abstract	47
3.2 Introduction	48
3.3 Cave calcite deposition	50
<i>3.3.1 Parameters involved in speleothem growth</i>	54
3.4 Study area	59
3.5 Sample description	60
3.6 Methodology	61
3.7 Results and discussion	62
<i>3.7.1 OCNM cave calcites as paleoenvironmental indicators</i>	62
<i>3.7.2 Speleothem geochronology and isotopic signatures</i>	66

3.8 Growth modelling	71
3.8.1 <i>Evidence for linear growth rates</i>	73
3.8.2 <i>Extending the chronology of the OCNM speleothems</i>	75
3.8.3 <i>Climatic implications of outcrop-scale discontinuities</i>	76
3.9 The start-stop model of cave calcite precipitation	79
3.10 Conclusions	81
 4.0 A 500 KA TERRESTRIAL STABLE ISOTOPE RECORD OF INTERGLACIALS FROM SOUTHWESTERN OREGON: PALEOCLIMATIC AND PALEOENVIRONMENTAL IMPLICATIONS	 99
4.1 Abstract	99
4.2 Introduction	100
4.3 Physical setting	101
4.4 Methodology	103
4.5 Results	106
4.5.1 <i>WFP stalagmite</i>	108
4.5.2 <i>ETC flowstone</i>	109
4.5.3 <i>NG flowstone</i>	110
4.6 Discussion	113
4.6.1 <i>OCNM isotopes as paleoclimatic indicators</i>	113
4.6.2 <i>Fractionation controls on OCNM cave calcite oxygen isotopes</i>	117
4.6.2.1 Ocean effects	118
4.6.2.2 Meteoric water effects	120
4.6.2.3 Cave temperature effect	121
4.6.3 <i>Overall $\partial\delta^{18}O_{calcite}/\partial T$ in OCNM speleothem</i>	122
4.6.4 <i>Fractionation controls on OCNM cave calcite carbon isotopes</i>	123
4.6.4.1 Isotopic composition of soil CO ₂	124
4.6.4.2 Water-rock interaction	125
4.6.4.3 Photosynthetic pathway effect	126
4.6.4.4 Rainfall effect	127
4.6.4.5 Drip rate effect	127
4.6.5 <i>Periglacial control on speleothem precipitation</i>	127
4.7 Conclusions	131
 5.0 GENERAL CONCLUSIONS	 155
 6.0 REFERENCES	 159
 APPENDICES	 181
Appendix 1 – OCNM cave survey	182
Appendix 2 – Microscopic petrology of OCNM samples	190
Appendix 3 – X-ray diffraction results	196
Appendix 4 – Microprobe results expressed as weight %	198
Appendix 5 – Oxide (weight %) and elemental data (ppm) obtained by XRF analyses	199
Appendix 6 – Trace- and rare earth elemental data obtained by ICP-MS	200
Appendix 7 – OCNM stable isotopes and growth model ages	201
Appendix 8 – Rainwater isotope data for OCNM	213

LIST OF TABLES

Table 2.1 Data for OCNM samples dated using the U-Series method	35
Table 3.1 Growth rate changes in response to increases in growth parameters	84
Table 3.2 U-series dates for OCNM speleothems	85
Table 4.1 Isotopic rain- and dripwater data and calculated $\delta^{18}\text{O}_{\text{cave calcite}}$ values	133
Table 4.2 U-series dates for OCNM speleothem samples	134
Table 4.3 Summary of fractionation effects on the composition of cave calcite	135
Table 4.4 Estimated sea surface temperature (SST) at 18 ka for various NE Pacific Ocean sites	136

LIST OF FIGURES

Figure 1.1 Location map of Oregon Caves National Monument	7
Figure 1.2 Sketches of the cave showing sampling sites	8
Figure 1.3 Daily rainfall values for 1995 and long-term (1928-1993) monthly rainfall values and temperature for Grants Pass (Oregon)	9
Figure 2.1 Location map of Oregon Caves National Monument	36
Figure 2.2 Geology of the Applegate Formation	37
Figure 2.3 View of Neptune's Grotto flowstone	38
Figure 2.4 Crystal fabrics of OCNM calcites	40
Figure 2.5 Discontinuities and detrital layers	42
Figure 2.6 U-series sample distribution for OCNM flowstones	43
Figure 2.7 Model for the development of columnar calcite through competitive growth	44
Figure 2.8 Model for the establishment of crystal termination layers in flowstones	45
Figure 2.9 Syntaxial overgrowth crystallite coalescence	46
Figure 3.1 CO ₂ partial pressure control on carbonate dissolution	86
Figure 3.2 Effects of different parameters on cave calcite growth rate	87
Figure 3.3 Location map of Oregon Caves National Monument	88
Figure 3.4 Cross-section of Neptune's Grotto flowstone	89
Figure 3.5 Hendy Tests results for two speleothem samples	90
Figure 3.6 WFP-2L $\delta^{18}\text{O}$ values compared to the GIPS2 and Vostok ice-core records	91
Figure 3.7 NG $\delta^{18}\text{O}$ values for the Termination II/5e period	92
Figure 3.8 Tentative correlation of NG $\delta^{18}\text{O}$ values relative to the GRIP ice core for MOIS 7	93
Figure 3.9 NG $\delta^{18}\text{O}$ values relative to SPECMAP for MOIS 11 through 9	94
Figure 3.10 NG $\delta^{18}\text{O}$ values relative to Devils Hole and SPECMAP for MOIS 12 through 11	95
Figure 3.11 NG $\delta^{18}\text{O}$ values relative to SPECMAP MOIS 13	96
Figure 3.12 Composite OCNM $\delta^{18}\text{O}$ record	98
Figure 4.1 Location map of the study area	137
Figure 4.2 Cross-section of Neptune's Grotto flowstone	138
Figure 4.3 Raw $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for OCNM samples	140
Figure 4.4 Composite stacked age versus depth relationships for the OCNM speleothems	142
Figure 4.5 WFP-2L $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope values compared to GIPS2 and Vostok	143
Figure 4.6 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic values for the ETC flowstone section	144
Figure 4.7 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values for the Termination II/5e period	146
Figure 4.8 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to GRIP and SPECMAP for MOIS 7	147
Figure 4.9 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to SPECMAP for parts of MOIS 11 through 9	148
Figure 4.10 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to Devils Hole and SPECMAP for MOIS 12/11	149
Figure 4.11 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to SPECMAP for MOIS 13	150
Figure 4.12 Hendy Tests results for two speleothem samples	151
Figure 4.13 Calculated $\delta^{18}\text{O}_{\text{calcite}}$ values for translated Destruction Island rainwater data	152
Figure 4.14 Summary of controls on oxygen isotopes	153
Figure 4.15 OCNM $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records	154

1.0 GENERAL INTRODUCTION

This dissertation relates to paleoclimatic information contained within calcite speleothems from Oregon Caves National Monument (OCNM) in southwestern Oregon. It has been written as a series of articles destined for scientific journals or books: Chapter 2 presents petrologic data from the speleothems and the implications of these observations for paleoclimatic reconstructions. Chapter 3 proposes a paleoclimate-based modelling scheme designed to assign age to tracts of speleothems located either between well-dated samples or lying beyond the range of conventional dating methods. Chapter 4 presents and discusses carbon and oxygen stable isotopic data and its relation to global and regional paleoclimates.

1.1 General setting and sample location

The cave system is located on westward-facing slopes in the Klamath Mountains (Figure 1.1). The cave (a phreatic maze) is described below in Section 2.2. Figure 1.2 shows the location of the samples described later in the text. This map shows only the main passages (a more complete representation is included in Appendix 1). All samples were taken along the main passages and chambers, as these areas contain thick, well-developed flowstones and several decorations. Figure 1.1b shows a generalised cross-section of the cave and indicates that the samples have been taken at various altitudes and depths (ETC ~50 m; NG ~55 m; WFP ~90 m) with respect to the land surface above the cave. It is assumed that most water in the subsurface travels only a short lateral distance owing to

the steepness of the hydraulic gradient (some of slopes exceed 100%) and the presence of vadose shafts developed along joints in the cave.

The cave site is located within the west coast rain forest. In general, thin soils cover the area. Figure 1.3 shows the daily rainfall pattern for Grants Pass, Oregon, located approximately 34 km NNE of the cave site, during 1995 (National Weather Service, Portland, Oregon website). The figure illustrates the variability of rain not only with the seasons (most rainfall occurs during the winter), but also through single rainfall events: recharge events occur infrequently and vary in magnitude.

1.2 Personal contribution

As all of the articles written for this dissertation are co-authored by my supervisor (Joyce Lundberg), this section provides information regarding my contribution to the individual research topics, as well as the contributions of each paper to the scientific community.

I have performed all the fieldwork (on two separate occasions) for this dissertation, as well as taken all samples, except for the flowstones and rainwater samples, which were provided to me by John Roth and Steve Knutson of OCNM (flowstone sampling required heavier electrical and gas-operated tools that were unavailable during my stays). The rainwater samples were taken during 1998, after winning a research prize from Geochron Labs that funded stable isotope analyses. I designed a simple rainwater-sampling instrument that was installed at OCNM and operated for approximately six weeks.

I performed all the petrologic work, including the X-ray diffraction analyses, all the way down to the cutting and polishing of the thin sections, as well as all of the stable isotopic research regarding the cave calcites, including precise sampling at millimeter intervals using a 0.6 mm drill bit, CO₂ extractions using H₃PO₄ digestion, and operation of the mass spectrometer at the University of Ottawa. I performed all calculations involved in this thesis. Joyce Lundberg analysed the samples for determining the uranium series dates.

All of the writing is original work stemming from my keyboard. All observations, analyses and discussions are my own, facts for which I claim senior authorship of all papers herein, and were discussed at great length with my supervisor, who is second author on all the papers presented below.

1.3 Scientific contribution

To the best of my knowledge, no petrologic, stable isotopic, or luminescence data from OCNM has ever been published. Chapter 2 presents information relating to long- and short-term events recorded in the petrologic record of the cave. It presents a model explaining the genesis of large crystals terminations as a function of slightly increased water film depth flowing over the flowstones. It also demonstrates that growth of the flowstones occurred during interglacial and widespread growth cessation occurred during glacial intervals, in response to periglacial conditions brought about by a decrease in the

altitudinal snow limit line. This article has been accepted for publication in *Carbonates and Evaporites* (Turgeon and Lundberg, in press a).

Chapter 3 discusses the use of paleoclimatic proxies in establishing growth rates of speleothems for which no precise chronological control is available. It discusses the effects of temperature on growth parameters involved in speleothem formation and then uses established paleoclimatic proxies in order to determine growth rates. Growth rates appear to be linear between U-Th dated samples on glacial to interglacial time-scales, and local processes are at least partly responsible for the stable isotopes observed within the speleothems at OCNM. It has been accepted for a book entitled “Studies of cave sediments”, edited by Ira Sasowsky and John Mylroie (Kluwer Academic/Plenum Publishers, due out in the summer of 2001) (Turgeon and Lundberg, in press b).

Chapter 4 presents the stable isotopic data and its relation to global paleoclimate. It shows that OCNM isotopes contain global paleoclimatic signals. It presents a model for the transfer of the oxygen isotopic signatures along the ocean-atmosphere-cave system and highlights glacial-interglacial atmospheric processes as the main control on oxygen isotope variability.

1.4 Results not reported in this dissertation

In addition to the laboratory work described in the methodology sections of the following chapters, two other techniques have been used with varying degrees of success:

catholuminescence (CL) and laser-induced luminescence. The catholuminescence was performed at Carleton University, but several attempts failed to show anything except a very few (<10) isolated particles that glowed a bright orange. These were assumed to be of detrital origin, possibly resting on discontinuities (described below). Given these results, no further work was done with CL.

The laser-induced luminescence of the samples was performed at the University of Waterloo using a high-resolution confocal scanning laser microscope (Ribes *et al.*, 2000). Polished thin sections or speleothem slabs were mounted on a scanning stage. A laser ($\lambda = 488 \text{ nm}$) was used to excite the samples. 100 mm^2 areas were scanned with the laser at a resolution of 2048×2048 pixels, producing images of the luminescence of the cave calcites. These were saved as greyscale images, with intensities ranging from 0 (black) to 255 (white). The stage was then moved along the growth axis of the flowstones by 9.5 mm, in order to insure an overlap of 0.5 mm between each scan area. The images were then “stitched” manually using computer drawing software. Given the size of the resulting stitched images, the files were exported and reduced by a factor of two, providing final resolutions of approximately $10 \text{ }\mu\text{m}$ per pixel, down from the original resolution of $4.88 \text{ }\mu\text{m}/\text{pixel}$.

The images were then imported into MultiSpec™, a free image analysis program (available at <http://dynamo.ecn.purdue.edu/~biehl/MultiSpec/Index.html>). Greyscale intensities values were then extracted from the images in transects parallel to the growth axes of the samples following paths containing the least porosity (producing values

trending towards black) or other surface defects such as microfractures or polishing marks. In order to minimise the effects of defects and pore space, the resulting transects take the average of 5 pixels perpendicular to the growth axes. Greyscale intensity corrections were made when two overlapping areas contained visible contrast differences in the vicinity of the transect. These corrections affected less than half of the overlapping areas and while the corrections changed the intensity of the luminescence values: the shapes of the luminescence curves remained essentially identical. Spectral (Fourier) analyses were then performed on the resulting luminescence curves in order to identify cycles within the luminescence signatures.

This work was done with the intention of writing a chapter on the paleoclimatic significance of luminescence in OCNM speleothems. The results, however, did not produce coherent patterns or return comparable periodicities, from one sample to the next, which could be assigned to known paleoclimatic frequency modulators (porosity and discontinuities seem to overwhelm any organic luminescence signal). As a result, it was decided that they were not conducive to such designs and this project has been shelved.

Figure 1.1 Location map of Oregon Caves National Monument showing maximum extent of glaciers and continental ice sheets during the Pleistocene.

Figure 1.2 Sketches of the cave showing sampling sites: A) map of the main passages and chambers; B) cross-section through the cave. Modified from Orr *et al.*, 1992.

Figure 1.3 Daily rainfall values for 1995 (A) and long-term (1928-1993) monthly rainfall values and temperature (B) record for Grants Pass (Oregon) (data from the National Weather Service, Portland (Oregon) website at: <http://www.wrh.noaa.gov/Portland/climate/daily/prec3445.lf>).

2.0 CHRONOLOGY OF DISCONTINUITIES AND PETROLOGY OF SPELEOTHEMS AS PALEOCLIMATIC INDICATORS OF THE KLAMATH MOUNTAINS, SOUTHWEST OREGON, USA

2.1 Abstract

Speleothems from Oregon Caves National Monument, a dissolutional cave system located in the Klamath Mountains of southwest Oregon, are composed mainly (>90%) of columnar calcite crystals. Columnar calcites form through syndepositional lateral coalescence of crystallites and precipitate under stable hydrodynamic conditions in humid, temperate climates. Numerous discontinuities from short-lived events (<100 years) punctuate the crystal stratigraphy. Minor fabrics, such as transitional- and randomly-oriented elongate calcites are seeded on these discontinuities and detrital layers. Columnar calcites eventually overrun sub-horizontally oriented crystals as a result of competitive growth. Large (~750 μm) crystal terminations indicate growth under increased water film resulting from greater flow and/or ponding. Fourteen U-series dates provide mean growth rates of 5.6 to 27.9 mm/kyr during interglacial periods (marine isotope stages 11 through 9, substage 5e, and late stage 2 through stage 1), and indicate short growth intervals during early- to mid-interglacial periods. Several outcrop-scale discontinuities represent periods of prolonged growth stoppage. Growth cessation occurred during the colder phases of stages 8-9 and 6-7, which translate into hiatuses of 77.5 and 99 kyrs respectively. Given the sensitivity of alpine regions to climate change and the lack of evidence for continental or alpine glaciation, the pauses in sedimentation

are presumed to be caused by groundwater freezing during periods of extended periglacial conditions, triggered by the lowering of periglacial thresholds by as much as 1800 m during glacial periods.

2.2 Introduction

Analogous to many marine carbonate and siliciclastic systems, caves may contain extensive, even uninterrupted, Quaternary stratigraphic sequences commonly sheltered from surface erosional processes. Cave calcites (speleothems) potentially contain abundant paleoenvironmental information useful for reconstructing terrestrial surface conditions (Lauritzen and Lundberg, 1999). Cave calcites are formed by the dissolution of a carbonate substrate, transport and precipitation of Ca^{2+} and CO_3^{2-} ions by water in vadose or phreatic settings. These processes can be interrupted by several factors such as aridity, cave flooding (with the potential for the dissolution of speleothems), re-routing of drip-water pathways, and by ground freezing during winter or during longer-term climatic trends such as glaciations. These events will stop the precipitation of speleothems. Alternatively, bands may record shorter depositional breaks or drapes by allogenic sediment, both organic and mineral, flushed into the cave from the surface via percolating meteoric water.

While many studies of spelean deposits have focused on growth mechanisms (Kendall and Broughton, 1978), petrology (Folk and Assereto, 1976; Frisia *et al.*, 1993; Frisia, 1996a; Genty and Quinif, 1996), and geochemistry (Lohmann, 1988; González *et al.*,

1992), few papers (Gradzinsky *et al.*, 1996; Hercman *et al.*, 1996) have dealt with discontinuities and allogenic contaminants within calcareous cave deposits. In this paper, we present results of a detailed petrologic study (fabrics and discontinuities) of two flowstones (22 and 73 cm thick) and a 5 cm stalagmite from Oregon Caves National Monument (OCNM), a dissolutional cave system located in southwestern Oregon. Discussion will focus on links between crystal fabric, detrital intervals and the chronology of discontinuities as they relate to paleoenvironmental factors.

2.2.1 *Site and sample description*

Oregon Caves National Monument (OCNM) is located approximately 65 km inland from the Pacific Ocean on steep, northwest facing slopes of the Klamath Mountains in southwestern Oregon (Figure 2.1). The site was selected owing to its location south of the maximum limit of Pleistocene ice sheets (Figure 2.1). It was hoped that this location would minimise freezing of the ground and increase the chance of a continuous spelean depositional record as well as avoiding the effects of evaporation owing to a more southern location. The Monument is located at an altitude of approximately 1400 m ASL, covers 1.9 km², and is nested amidst old-growth Douglas- and white firs, providing abundant organic matter to the soils overlying the caves. Rocks of the Monument belong to the Triassic Applegate Formation of the Rattlesnake Creek subterrane (Orr *et al.*, 1992). While this formation is mainly composed of volcanic arc basalts (Orr *et al.*, 1992), most of the Applegate rocks within the boundaries of the Monument are friable

argillites with a marble lens (Figure 2.2), as well as metabasalts, serpentine, andesite, chert, and talc.

Oregon Caves National Monument consists of a main dissolutional phreatic cave with vadose drawdown shafts developed in a marble lens bounded by pyrite-rich argillites. Cave development was controlled by a NE-SW joint system and high-angle (60° to 85°) N-S trending normal faults within the marble lens. Most of these joints and faults formed in response to tectonic activity during the Miocene (Wells and Heller, 1988) and allowed penetration of water deep into the subsurface and regulated the alignment of passages in the cave. The cave contains several subhorizontal levels, representing former water table positions controlled by river down-cutting. The most laterally extensive level, located approximately 28 m above the main entrance contains thick, well-developed flowstones. Few speleothems suitable for paleoenvironmental reconstruction are located in the older, higher levels consisting mainly of vadose shafts.

Two flowstones, one approximately 73 cm thick from *Neptune's Grotto* (NG) (Figure 2.3) and another 22 cm-thick flowstone from the *Exit Tunnel Cave* (ETC), as well as a 5 cm stalagmite from the *White Formation Passage* (WFP-2L), were analysed for this study. The NG and WFP-2L samples were taken from areas deep within the cave in order to minimise evaporative effects and temperature variations stemming from air flow near natural entrances. The *Exit Tunnel Cave* flowstone sequence was collected in a cave discovered in the 1930's during the excavation of a tunnel permitting access to the cave at a higher elevation. No natural entrances are known for the Exit Tunnel Cave.

2.3 Methodology

Twenty-five thin sections were cut parallel to growth direction, to provide documentation of the entire flowstone sections and the stalagmite. In order to establish growth mechanisms and depositional history of the speleothems, outcrop-scale features such as discontinuities, as well as microscopic features such as banding, fabrics and micro-discontinuities, drapings and inclusions were observed. Powdered XRD samples of the speleothems, analysed with a Philips PW1730 at Carleton University, were used in conjunction with microscopic features to confirm mineralogy. Selected thin sections were polished and carbon-coated for study with a JEOL JSM 6400 scanning electron microscope (SEM) and Cambridge Microscan 5 electron microprobe at Carleton University. This analysis was undertaken in order to determine the microscopic structure of the calcites and to characterise the composition of micro-discontinuities and drapings. Trace element concentrations were determined using the electron microprobe. In addition, whole-rock analyses of the NG flowstone were done (by XRF on a Philips XRF apparatus and by ICP-MS on a Perkin-Elmer ELAN 6100) at the Geological Survey of Canada to provide major-, trace-, and rare earth element compositions.

Chronological control is provided by 14 high-precision thermal-ionisation mass spectrometry (TIMS) U-series dates performed at the University of Bergen (Norway) on a Finnigan-MAT 262 solid source mass spectrometer. Because of low uranium content, sample sizes ranged from 1 to 2 g, and represent vertical segments of between 2 and 7 mm of the speleothems. Samples were cleaned ultrasonically and ignited to remove

organics, and a ^{229}Th - ^{223}U - ^{236}U spike was added. U and Th were separated in anion exchange columns, loaded onto single filaments with silica gel (U fraction) or graphite (Th fraction), and the isotopic ratios were measured in peak-switching, ion-counting mode.

2.4 Mineralogy and petrology of the OCNM cave calcites

The mineralogy of cave deposits is mainly controlled by the ionic composition of the cave drip-water (Onac, 1997), which in turn generally reflects the water-soluble minerals of the rocks overlying the cave system. As previously described, the OCNM area consists primarily of metasedimentary formations, with some metavolcanics and igneous intrusions, although the caves are contained exclusively within a calcitic marble lens (97.1 weight % CaCO_3 and 1.4 weight % MgCO_3 ; Brooks, 1989). Therefore, calcite should be the main precipitate, given that aragonite predominates only at Mg/Ca ratios greater than about 2.9 (Fischbeck and Müller, 1971; Thrailkill, 1971). Within the cave, the speleothems consist of low-Mg calcite (0.37% MgO by XRF), and microprobe results indicate that the samples contain few impurities.

2.4.1 *Crystal fabrics*

2.4.1.1 Columnar crystals

Over 90% of the spelean calcites in our samples are composed of elongate columnar crystals, 0.2 to 1.0 mm wide and generally 2 to 20 mm long. These are similar to the “palisade” crystals of Folk and Assereto (1976). The *c*-axes are oriented parallel to the crystals’ length and roughly perpendicular to the growth surface (length-fast calcite; Dickson, 1978). These layer-forming length-fast calcite crystals are subparallel and slightly radiating or converging towards one another, with crystal boundaries commonly displaying jagged or serrated edges (Figures 2.4a and 2.4b). The colours of these crystalline layers range from translucent yellow to opaque brown. Detrital particles are virtually absent from the crystal beds although linear air-filled inclusions are present, as well as some intercrystalline accumulation of organic matter. In places, darker laminae (described below) cross-cut the crystals more or less perpendicularly, and do not appear to have interrupted the growth of the speleothems (Figure 2.4a). In some areas, these columnar crystals are underlain by shorter tooth-shaped calcite (see below), or by layers containing abundant impurities. These columnar crystals were probably seeded by these underlying nuclei (Moore, 1962).

While some of these columnar crystals grade into one another (Figure 2.4b), others end at active or previous growth surfaces. We use the term “active” to denote the last growth surface prior to sampling of the subaerial surface. In places, however, discontinuities are

marked by rough outlines of crystal terminations, composed of vertical linear inclusions described below.

2.4.1.2 Transitional basal crystals (blocky or elongate)

At the base of some columnar calcite crystals, laterally discontinuous zones of small equant, euhedral calcite crystals (25-30 μm) represent the initial crystalline stage to precipitate after a discontinuity. The blocky calcites rest upon organo-detrital layers (described below) that have accumulated at or above the discontinuities. These calcites are overgrown by progressively larger blocky crystals, along with some upward-trending (at a high-angle to the surface) elongate crystals with poorly developed terminations (Figure 2.4c). These length-slow calcite crystals (Dickson, 1978) are relatively free of intracrystalline inclusions. Equant basal calcites have also been reported by Gradzinski *et al.* (1996), and elongate length-slow “tooth-shaped” calcites were reported by Folk and Assereto (1976). In one instance, over a 2 mm section of the NG flowstone (interval at 525-526 mm), a transitional zone, less than 70 μm wide, is composed of white (in hand specimen), very friable acicular calcite containing abundant impurities (Figure 2.4d). The size (diameter and length) of the acicular crystals generally increases upwards. These are similar to the coconut-meat calcites of Folk and Assereto (1976) and the botryoidal calcites of Hercman and others (1996). From these crystal assemblages, larger columnar calcites emerge upward. Most of these crystals are elongated parallel to the *c*-axis, with others elongated at 60° to the *c*-axis, possibly owing to development parallel to a rhomb face (Folk and Assereto, 1976).

2.4.1.3 Randomly oriented, elongate “scaffolding” crystals

In a few areas of the NG flowstone, isolated pockets of randomly-oriented elongate calcite crystals are walled-in by columnar crystals (Figure 2.4e). These pockets are typically only a few mm high by a few mm wide. The voids in which these crystals grew may represent defects in the flowstone fabrics or localised areas of non-deposition on the surface of the flowstone. Contained within the pockets are calcite crystals growing at variable angles, with rarer crystals growing downward. Some of these crystal seem to be seeded on the near-vertical crystal walls delimiting the cavity, with some of them terminating at the opposite wall (Figure 2.4e). The numerous intercrystalline voids suggest non-competitive growth. These random crystals are up to 3 mm long and 0.5 mm wide and have poorly developed or hidden terminations (Figure 2.4e). Some of the crystals exhibit internal growth banding and inter-crystallite inclusions that delimit structures (Figure 2.4e) analogous to the crystal termination surfaces described below. Upwards, these pockets are closed by the progressive lateral overgrowth of the columnar crystals on either side of the pocket.

2.4.1.4 Pillar calcites

One interval in sample NG contains structures resembling small pillars up to 1 mm across and 3 mm high (Figure 2.4f). Growth bands on these pillars are downturned towards the edges, suggesting that these pillars are primary features and not the result of mechanical erosion or dissolution. The spaces between the pillars are filled by acicular to columnar

calcite containing numerous linear inclusions. These pillars are rimmed with darker calcite, which could be the result of either trapped colloids near their surfaces or light reflectance by the linear inclusions (Kendall and Broughton, 1978).

2.4.1.5 Zoned equant crystals

A thin wedge (<4 mm) of zoned, equant calcite crystals occurs in one area about 10 cm from the base of the NG flowstone (Figure 2.4g). This zone is characterised by high porosity ($\approx 15\%$). These crystals appear yellow-brown in thin section and are rimmed by a creamy white zone. No boundaries appear between the cores and the exterior rims of these crystals. The rims do not appear to be overgrowths of the crystal cores. This facies represents the only example of possible diagenetic alteration or leaching seen in our samples.

2.4.2 *Discontinuities and detrital layers*

Several types of outcrop-scale to microscopic discontinuities were identified within the flowstones. This section presents relevant observations regarding these discontinuities.

2.4.2.1 Outcrop-scale discontinuities

Four disconformities were found within the NG flowstone (Figure 2.3). The discontinuities are laterally continuous, for several meters, over the entire length of the

outcrop. Although columnar calcite crystals with quadratic terminations protrude from these sub-horizontal surfaces, the discontinuities are generally smooth, and are covered with a thin layer of brownish allogenic mineral detritus and other debris such as broken soda straws and stalactites lying horizontally on these surfaces (Figure 2.3).

2.4.2.2 Detrital intervals and drapings

In this category, we have grouped layers deposited on a flowstone growth surface, including allogenic clastic and organic sediments derived from the ground surface above the cave. These layers are mainly composed of dark grey drapes containing abundant inclusions, as well as brown to orange coloured material (under crossed-nicols) that occurs in layers and inter-crystalline void fillings. This material appears to be an accumulation of organics flushed in from the surface above the cave (Figures 2.5a, b, c and d). In some cases, the organics may have aided in dissolving the calcite growth surfaces (Figure 2.5d) (Frisia, 1996a) during low growth rates or precipitation cessation. Few individual crystals or grains are discernable in the detritus, suggesting that the detritus is composed of colloids or was transported in solution. A total of 120 such detrital intervals have been identified within our samples (68 with organics). The thickness of these detrital layers is usually less than 0.1 mm, although the accumulation in voids can be much greater. These layers usually separate columnar crystals, with columnar crystals commonly retaining the same optical orientation, and crystal boundaries above and below the disconformity (Figure 2.5b).

2.4.2.3 Crystal termination layers

19 intervals exhibit crystal terminations that are more or less along a horizontal plane (Figures 2.5e and 2.5f). The crystal terminations are approximately 750 μm high and are outlined by numerous linear vertical inclusions conferring a grey colour to the layer. These vertical inclusions, as well as some intercrystalline spaces, acted as traps for detritus washed in from above the cave (Figure 2.5g), as shown by the infilling between some crystals. The crystals appear to have continued growing through these intervals as suggested by the pointed terminations (poorly developed acute rhombohedra, $\{40\bar{4}1\}$ of the Miller index, but possibly $\{10\bar{1}1\}$) and the greater quantity of trapped colloids at the tips of the crystals.

2.4.2.4 Vertical linear inclusions

Abundant vertical (air-filled) linear inclusions, that impart a grey colour to the calcite around them, are found within the cave calcites. These inclusions are typically less than 0.5 mm long and only a few tens of micrometers wide (Figure 2.5h). Kendall and Broughton (1978) have attempted, unsuccessfully, to recover insoluble residue from similar linear inclusions by acid etching, suggesting that these inclusions produce the dark colour by dispersing light in the adjacent host calcite crystals. They often occur as groups in roughly horizontal layers parallel to growth banding in the calcite (Figure 2.5h). 14 inclusion horizons have been found within our samples, although none appear

in the ETC flowstone. Although some inclusions are found at crystal boundaries, most are located within columnar crystals.

2.4.3 *Speleothem geochronology*

The chronology of speleothem deposition was established using 14 high-precision uranium disequilibrium series dates (Table 2.1). Ages range from 2.3 ka to 359.3 ka (NG: 359.3-122.9 ka; ETC: 119.3-12.0 ka; WFP: 3.9-2.3 ka). Two U-series dates (NG-D and NG-J) were obtained from coeval intervals of two overlapping samples. The overlapping 2σ errors of these two dates indicate the high degree of reliability of this method. Relative 2σ errors range from 0.32 to 2.62% of the actual age, with the greater errors occurring on older samples. The validity of these dates is further confirmed by the appropriate chronological order of the samples.

The chronology of deposition for the NG flowstone was established using seven U-series dates (Table 2.1). Figure 2.6 illustrates the distribution of the dated material within the NG flowstone. Two growth intervals within the flowstone, constrained by outcrop-scale discontinuities, are anchored by two or more dates (Figure 2.6). The lowermost of these intervals is chronologically validated using the mean date provided by the overlapping samples (NG-D and NG-J), along with a third date (NG-I) from a lower interval. These dates indicate a mean growth rate of 5.6 mm/kyr between these two outcrop-scale discontinuities. Numerous detrital layers (26) and crystal termination layers (12) have been identified between these two outcrop-scale discontinuities. Based on the mean

growth rate, this interval represents approximately 51.35 kyrs of growth, possibly during marine isotope stages 9 and 11 (Emiliani and Shackleton, 1974).

Three dates were obtained from the second growth interval constrained by outcrop-scale discontinuities. This interval overlies the uppermost outcrop-scale discontinuity and extends to the free-air erosional surface at the top of the flowstone. A mean growth rate of 15.7 mm/kyr was calculated based on three dates (NG-F, NG-G and NG-L), indicating growth during interglacial conditions of marine isotope sub-stage 5e) (Table 2.1 and Figure 2.6). The deposition of this interval spanned 13.41 kyrs, and contains 25 detrital intervals and drapings, along with 6 linear inclusion horizons and 3 minor blocky calcite transitional growth intervals near the top of the flowstone. The number of detrital and crystal termination layers within this interval for the NG flowstone suggests that the events generating these features are of very short duration.

A third growth interval, situated between the two intervals described above, yielded a single U-series date owing to the unsuitability of the material for dating, stemming from the incomplete coalescence of the elongate calcite crystals which might allow migration of fluids and detritus within the sample. Given that the growth rates established for the intervals above and below are similar in magnitude to one another as well as to other published growth rates for flowstones (Baker and Smart, 1995), we have used the average of those two rates (~10.6 mm/kyr) as an estimate of the growth rate for this interval. This data indicates that the interval was deposited over 6.20 kyrs during marine isotope stage

Similar growth rates have also been calculated for the ETC flowstone (Figure 2.6). Three dates (ETC-C, ETC-A and ETC-D) range from ~116 to 119 ka (late isotope substage 5e) and indicate a high growth rate (~27.9 mm/kyr) for the lower section of the flowstone. The two dates (ETC-E and ETC-B) in the upper reaches of this flowstone indicate growth during the late Wisconsinan. The growth rate of this interval was ~7.6 mm/kyr. The interval between samples ETC-D and ETC-E broadly corresponds to the colder conditions of stages 4 through 2 (including late stage 5?). Therefore, this thin interval represents either severely reduced growth (~0.3 mm/kyr) or a hiatus in deposition of approximately 100 kyrs. The absence of an outcrop-scale discontinuity, similar to those found within the NG flowstone, in this section of the ETC flowstone is poorly understood but could be linked to the location of the deposit within the cave. The mean growth rate for the section spanning the glacial interval (stage 4-2) represents the slowest growth rate for any of these intervals.

The WFP-2L stalagmite represents calcite deposited during the Holocene, from approximately 3.9 to 2.3 ka (Table 2.1). The growth rate of this sample was about 31.5 mm per 1000 years, representing the highest growth within our samples. This sample is composed entirely of columnar calcite crystals and the main microscopic features present are seven linear inclusion horizons.

2.5 Discussion

2.5.1 *Primary nature of calcite crystals*

Folk and Assereto (1976) suggested that some spelean calcite originates from neomorphism of aragonitic precursors. The following criteria, in order of decreasing reliability, were used in an attempt to recognise the presence of pre-cursor aragonite in the studied flowstones (modified from Folk and Assereto, 1976): (1) preservation of the original aragonite crystals, (2) needle-like inclusions from possible surviving aragonite needle ghosts contained within a randomly-oriented recrystallised polycrystalline euhedral calcite mosaic, (3) presence of a randomly-oriented polycrystalline euhedral calcite crystal mosaic, (4) quadratic or feathery crystal termination possibly indicative of a former aragonitic crystal, (5) presence of extensive dissolution possibly occurring in less stable aragonitic layers, and (6) high primary (non-detrital) Sr-content.

Criteria 3 through 6 should be regarded as indirect evidence, and be used in conjunction with other criteria if possible. Also, considering the growth mechanism described by Kendall and Broughton (1978) discussed below, criterion 4 should be used with caution given that jagged crystal boundaries intersected by the thin section at an acute angle can be confused with crystal terminations. Given that high Sr/Ca ratios occur through incongruent dissolution with increasing water-rock interaction (Brand and Veizer, 1980), criterion 6 arises as aragonite has a distribution coefficient just above unity, indicating a preferred partitioning of Sr into the crystal from solution (Dickson, 1990).

No microscopic evidence of aragonite, or precipitates other than calcite, was found in thin sections of the studied speleothems. Sr-content for two samples were 31 and 35 ppm (by ICP-MS). Only one sample (out of 38), taken from a detrital layer, showed an Sr-content above the lower detection limit of the electron microprobe (1650 ppm). Powder XRD data confirms that no aragonite is present in the samples, indicating that the calcite crystals are primary features, and reflect original environmental conditions in the cave.

2.5.2 *Environmental factors affecting speleothem deposition*

Most cave carbonates from temperate, humid climates are composed of elongate calcite crystals (Kendall and Broughton, 1978; González *et al.*, 1992; Gradzinski *et al.*, 1996), which are thought to indicate stable, unchanging precipitation conditions during speleothem growth. Therefore, variations in crystal fabric within a speleothem should indicate a change in one or several parameters affecting precipitation. These may include changes in: (1) supply of precipitating reactants; (2) drip rate, water film thickness, and turbulence; (3) ambient cave conditions such as cave air P_{CO_2} , temperature, and ventilation; (4) influence of biogenically-mediated precipitation; and (5) post-depositional alteration such as recrystallisation. Parameters 1-3 combine to define growth rates of speleothem by inorganic processes (Baker and Smart, 1995) and are difficult to estimate individually in older, inactive speleothem. However, evidence suggests that some parameters cause physical changes in the calcite, such as the development of large crystal terminations under increased water film thickness, as

discussed below. The role of bacteria in speleothem growth (parameter 4) is thought to be of minor importance, although crystal habit changes have been attributed to the presence of organics in solution (Suess and Fütterer, 1972). Given the high preservation potential of cave deposits, post-depositional alteration of speleothems is seldom encountered and sparsely documented (Frisia, 1996a).

2.5.2.1 Initial growth phase: effects of surface configuration and water depth

Transitional basal calcite crystals are thought to have developed under a relatively turbulent water flow régime (Gradzinski *et al.*, 1996), initially crystallising on discontinuities, representing either drying out (Moore and Nicholas, 1964), dissolution surfaces or discontinuities. Initial crystallisation is facilitated by the presence of crystallites on the growth surface (Kendall, 1993), as well as by increased fluid flow providing a greater number of crystallites due to the increased presence of nuclei in suspension (González *et al.*, 1992). The length-slow calcites are gradually overridden by length-fast palisade crystals as the crystal zone grows out. More favourable, sub-vertical orientation of *c*-axes and non-distorted lattices probably contribute to faster growth of the palisades (Figure 2.7) (Folk and Assereto, 1976; González *et al.*, 1992), as crystals with *c*-axes normal to the substrate extend most rapidly into the available overlying space (Buckley, 1951).

Examples of growth under increased water film thickness could be represented by the crystal termination layers in our samples. Given that large terminations would jut out of

a thin (typically less than 0.2 mm; Baker and Smart, 1995) water film on an active speleothem, large ($\sim 750\ \mu\text{m}$) terminations require additional accommodation space provided by a thicker film of water. As water film thickness increases, crystal terminations develop rapidly under increasingly turbulent flow because of the protruding terminations and trapped detritus, leading to faster CO_2 degassing and increased precipitation rates (Dreybrodt, 1996). Figure 2.8 illustrates a proposed model for the genesis of crystal termination layers. Conditions leading to an increase in water film depth are increased flow and pooling. However, the presence of clays in the terminations suggests additional water influx into the cave system, possibly from increased rainfall or runoff that transported allogenic sediment from the ground surface above the cave.

The minor scaffolding calcite fabric mentioned earlier seems to have grown in restricted micro-pools formed by localised deformations on the surface of the flowstone, as suggested by their limited extent and seeding on the near-vertical walls of the pockets. Conversely, the absence of competitive growth, along with the absence of randomly oriented elongate crystals indicative of pool deposition, suggests that the pillars grew under a relatively thin film of water. Their diameter, less than that of a water drop, preclude these from being formed by dripping water. Also, no evidence of bacterially-mediated growth was observed in the speleothems.

2.5.2.2 Columnar calcites growth mechanisms: stable growth conditions

Controversy has surrounded the mechanism for generation of elongate columnar crystals in speleothems. Some early petrologic evidence suggested that these “large” crystals were originally precipitated as aragonite and later inverted to calcite (Folk and Assereto, 1976), and the linear inclusions were interpreted as products of recrystallisation (Kendall and Tucker, 1973; Kendall, 1977). Because elongate calcite crystals are formed through precipitation under a thin film of water flowing over the speleothems, one of the main stumbling blocks for the formation of elongate calcite crystals as primary precipitates was that large, rhombohedral terminations of calcite could not develop under thin water films typically found flowing over speleothems.

An alternative growth mechanism for elongate columnar calcite crystals has been suggested by Kendall and Broughton (1978). They postulated that elongate calcite crystals are in fact composed of a series of syntaxial overgrowth crystallites, which coalesce more or less completely during accretion of the speleothem surface (Figure 2.9). Thus, the linear inclusions (Figure 2.5h) represent former inter-crystallite spaces trapped by the accreting growth surface during incomplete coalescence (Figure 2.9) owing to drying or accelerated growth (Kendall and Broughton, 1978). Inclusion-free calcite occurs where lateral coalescence is complete: in this case precipitation occurs on large, planar crystal faces. In contrast, lack of lateral coalescence of the overgrowth crystallites generates acicular calcite. Frisia's (1996b) observations confirmed the validity of this growth mechanism. Kendall and Broughton (1978) also proposed that the crystallites

merge and overgrow each other in standing water, such as during flooding of the cave. However, our stalagmite sample (WFP) contains 7 horizons of partially coalesced linear inclusions, with no evidence of dissolution or detrital deposition, which might be expected during flooding by undersaturated meteoric water. The rapid growth of this sample in just 1.6 kyrs (Table 2.1), suggests that coalescence of crystallites was syndepositional. The jagged nature of the intercrystalline boundaries (Figure 2.4b) lends further support to the suggestion that these crystals are formed by the lateral coalescence of crystallites.

The size of the columnar crystals (up to several cm in length) indicates that they grew under stable hydrodynamic régimes. A constant supply of saturated groundwater, from which the calcite could freely precipitate, could be attributed to a warm and humid climate (Gradzinski *et al.*, 1996), although short-scale variations have been recorded in cave calcites as fine-scale luminescent banding (Baker *et al.*, 1993), with the laminae representing the effects of organic acids derived from overlying soil and incorporated in the calcite matrix. Some bands are thought to form annually (Baker *et al.*, 1993a) in response to variations in the intensity of percolation, thought to reflect seasonality, with greater percolation occurring during spring months, associated with snow-melt runoff.

2.5.3 *Duration of events: periglacial controls on precipitation*

Using the chronology for the middle interval of the NG flowstone, in conjunction with the mean growth rates for the intervals above and below, we have estimated that the

minimum time-lag represented by the two outcrop-scale disconformities to be approximately 77.49 and 99.18 kyrs (lower and upper) respectively. These unconformities broadly correspond to mid-interglacial and glacial conditions of stages 8-9 and 6-7, and point to narrow growth intervals during early to mid-interglacial times (Figure 2.6). Numerous growth-frequency studies have shown that speleothem deposition occurs mainly during interglacial intervals in high-latitude environments (Gascoyne *et al.*, 1983; Gascoyne, 1992; Baker *et al.*, 1993b; Lauritzen, 1995), where calcite precipitation was interrupted by the development of continental ice sheets. No evidence of continental glaciation has been reported in the immediate vicinity of our study area, although cirque-like structures suggesting alpine-style glaciation have been observed at higher elevations elsewhere in the Klamath Mountains (John Roth, USPS, personal communication). We suggest that the discontinuities in the sampled speleothems may be associated with periglacial conditions that caused groundwater to freeze in this region during times of continental glaciation.

Altitudinal glaciation threshold studies in the northwestern United States suggest that climatic gradients during the Last Glacial Maximum (LGM) were similar to those of today, and that average summer temperatures were about 5.5 ± 1.5 °C cooler than today (Porter, 1977; Porter *et al.*, 1983). These LGM glaciation thresholds indicate mountain snowline elevations (currently at about 3200 m ASL in southern Oregon) depressed by approximately 1100 m at 42°N. These conditions place the LGM snowline approximately 700 m above the cave site (Porter, 1977). In addition, Heusser and Heusser (1990) report that sub-alpine vegetation was established, during glacial intervals,

at elevations between 1300 and 1800 m lower than present-day conditions (resulting from an inferred 5-7 °C temperature depression, which is in line with Porter's data). This further suggests that permafrost conditions could have occurred, in the study area, well below the 2100 m snowline during glacial conditions.

Also, Colman and Pierce (1992) concluded that early Wisconsinan alpine glaciers of the western United States were more extensive than their late Wisconsinan counterparts in some areas, thereby contrasting with marine oxygen-isotope records which suggest that world-wide ice volumes were lesser during stage 4 than during stage 2 (Emiliani and Shackleton, 1974; Martinson *et al.*, 1987). This indicates that alpine areas could have responded more rapidly than continental ice sheets to climatic events associated with late stage 5e. This sensitivity to climate change may also have been heightened owing to the location of the cave, which was probably very close to the lower permafrost limit during glacial periods.

2.6 Conclusions

The most prominent features of the speleothem deposits from OCNM are the outcrop-scale discontinuities that seem to represent hiatuses of several tens of thousands of years, mostly during glacial intervals. The chronology of two flowstones was established using 14 U-series dates. They indicate mean growth rates of 5.6 to 27.9 mm/kyr during interglacial periods, from marine isotope stages 11 through 9, substage 5e, and during the later part of stage 2 into stage 1. Glacial intervals are represented either by major calcite

growth-stoppages, or possibly severely reduced calcite precipitation. Complete cessation of growth occurred during the colder phases of stages 8-9 and 6-7, translating into hiatuses of 77.5 and 99 kyrs respectively. This data indicates the influence of climate on calcite precipitation, which was limited to short growth intervals during early- to mid-interglacial conditions. Given the lack of evidence for direct continental or alpine-style glaciation in the study area, and the sensitivity of alpine regions to climatic change, it is assumed that extended periglacial conditions, associated with the lowering of glaciation thresholds by as much as 1800 m during glacial intervals, are responsible for the cessation of calcite precipitation through groundwater freezing.

Speleothem samples from Oregon Caves National Monument are mainly composed of elongate columnar calcite crystals (>90%) and represent fast growth during stable, wet interglacial conditions. These columnar calcite crystals are primary fabrics that grew by lateral coalescence of syntaxial overgrowth crystallites during interglacial times. Vertical linear inclusion horizons within the speleothems represent inter-crystallite voids stemming from the incomplete (syndepositional?) coalescence of syntaxial overgrowths during the growth of columnar calcite crystals. As these represent growth under stable hydrodynamic conditions of warm and humid temperate climates, variations in fabric should indicate changes in environmental conditions in the cave or the influence of surface events occurring above the cave, such as increased rainfall or runoff. Transitional calcites are thought to have developed under turbulent flow and began crystallising on discontinuities. These length-slow calcites are eventually overridden by length-fast palisade crystals as the more favourable orientation of *c*-axes and non-distorted lattices

contributed to the faster growth of the palisades into available overlying space. Minor fabrics include: randomly oriented elongate calcites, which probably grew in isolated pools of stagnant water on the surface of speleothem; pillar-like structures, resembling biogenic structures such as stromatolites; and zoned equant calcites, possibly resulting from diagenetic alteration or leaching.

While the elongate columnar crystals grew under relatively stable conditions, numerous discontinuities and contaminants punctuate these cave deposits. As several of these layers accumulated in relatively short time periods, evidence suggests that the events that generated these features were of very short duration (<100 years). Large (~750 μm) crystal termination layers represent growth under increased accommodation space resulting from an increase in the thickness of the water film flowing over the flowstones due to greater flow and/or pooling.

Most studies concerned with paleoenvironmental reconstructions using cave calcite pay little attention to petrologic features, other than fabric, within speleothems. This study indicates that outcrop-scale observations, as well as petrologic features are useful paleoenvironmental indicators, and should be taken into consideration when attempting such studies.

Table 2.1 – Data for OCNM samples dated using the U-series method.

Sample number	U (ppm)	Distance from base (mm)	$^{230}\text{Th}/^{234}\text{U}$ Age ^a (ka)	$^{230}\text{Th}/^{234}\text{U}^b$	$(^{234}\text{U}/^{238}\text{U})_{\text{initial}}^c$	$^{234}\text{U}/^{238}\text{U}^b$	$^{230}\text{Th}/^{232}\text{Th}^b$
WFP-2-B	0.187	47-49	2.261 ± 0.015	0.02058 ± 0.00014	1.07468 ± 0.00255	1.07420 ± 0.00255	18.32 ± 0.2
WFP-2-A	0.233	1-5	3.882 ± 0.017	0.03508 ± 0.00015	1.07091 ± 0.00198	1.07013 ± 0.00198	134.10 ± 1.2
ETC-B	0.168	127-129	11.980 ± 0.125	0.10450 ± 0.00103	1.12956 ± 0.00163	1.12523 ± 0.00163	7.99 ± 0.1
ETC-E	0.169	109-112	14.294 ± 0.046	0.12342 ± 0.00037	1.11867 ± 0.00220	1.11396 ± 0.00219	7.94 ± 0.0
ETC-D	0.183	74-77	116.692 ^{+0.458} _{-0.456}	0.67317 ± 0.00135	1.15919 ± 0.00128	1.11385 ± 0.00123	69.25 ± 0.5
ETC-A	0.197	36-38	117.496 ^{+0.392} _{-0.390}	0.66967 ± 0.00114	1.13974 ± 0.00149	1.10015 ± 0.00144	91.66 ± 0.7
ETC-C	0.189	1-7	119.254 ^{+0.753} _{-0.746}	0.67487 ± 0.00212	1.13307 ± 0.00315	1.09490 ± 0.00305	224.42 ± 2.3
NG-L	0.102	704-706	122.916 ^{+1.012} _{-1.001}	0.68187 ± 0.00288	1.06698 ± 0.00174	1.04727 ± 0.00170	345.5 ± 2.6
NG-G	0.167	681-684	122.840 ^{+0.536} _{-0.533}	0.68193 ± 0.00150	1.07120 ± 0.00123	1.05026 ± 0.00121	384.10 ± 5.0
NG-F	0.136	574-576	131.219 ^{+0.743} _{-0.737}	0.70513 ± 0.00193	1.05588 ± 0.00126	1.03852 ± 0.00124	123.00 ± 0.8
NG-E	0.085	508-511	234.929 ^{+2.914} _{-2.833}	0.89313 ± 0.00289	1.07200 ± 0.00122	1.03699 ± 0.00118	142.70 ± 1.6
NG-D	0.161	435-437	315.251 ^{+6.931} _{-6.454}	0.95525 ± 0.00251	1.08543 ± 0.00381	1.03495 ± 0.00364	70.07 ± 0.6
NG-J	0.169	435-437	326.587 ^{+8.788} _{-8.053}	0.96462 ± 0.00296	1.11996 ± 0.00425	1.04752 ± 0.00398	115.60 ± 0.6
NG-I	0.086	219-221	359.300 ^{+9.817} _{-9.004}	0.97931 ± 0.00313	1.13926 ± 0.00112	1.05029 ± 0.00104	22.21 ± 0.2

Note: Errors are quoted as 2σ.

^a Calculated using Kaufman and Broecker's (1965) equation and half-lives of ^{230}Th and ^{234}U of 75 383 and 244 500 years respectively.^b Activity ratio.^c Initial $^{234}\text{U}/^{238}\text{U}$ ratio calculated for $^{230}\text{Th}/^{234}\text{U}$ age.

Figure 2.1 Location map of Oregon Caves National Monument showing maximum extent of glaciers and continental ice sheets during the Pleistocene.

Figure 2.2 Geology of the Applegate Formation in the area surrounding Oregon Caves National Monument. The cave is located within the marble lens. From an OCNM internal document.

Figure 2.3 View of Neptune's Grotto flowstone, approximately 73 cm thick, unconformably overlying the Applegate marble. Arrows on the left indicate the outcrop-scale disconformities. The white arrow points to a broken soda straw resting on a disconformity surface. The open triangles to the right indicate the locations of U-Th samples.

Figure 2.4 (following page) Crystal fabrics of OCNM calcites: A) columnar crystals with irregular subhorizontal former growth surface. The subhorizontal fractures (indicated with triangles) were caused during thin section mounting and are not primary structures. White arrows indicate intercrystalline boundaries. Crossed-nicols. B) Jagged columnar crystal boundaries indicated by white arrows. These boundaries are displayed owing to the crystal growth into, or out of, the plane of the thin section. Note also the inclusions that are parallel to the growth direction of the crystals. Crossed-nicols. C) Blocky (equant) to elongate calcites at the base of a transitional layer. Crossed-nicols. D) Elongate transitional calcites (“coconut-meat” of Folk and Assereto (1976) and the botryoidal fabric of Hercman *et al.* (1996). Crossed-nicols. E) Scaffolding crystals. Note former crystal termination with elongate crystals (white arrow). Crossed-nicols. F) Pillar structures. Note downturned bands towards the edge of the pillars. Plane polarised light. G) Zoned equant calcites. White arrows point to rims on crystals. Scale bar is 1 mm for all images. For (A), (B) and (G), the circular structures are ~0.6 mm made by drilling for isotopic analyses (results are to be presented in a separate paper).

Figure 2.5 (following page) Discontinuities and detrital layers: A) View of detrital layer with an organic component. Note fibrous calcite above discontinuity. Plane polarised light. B) Same as (A), under crossed-nicols. C) Organics accumulating in triangular-shaped inter-crystalline voids. Crossed-nicols. D) Organics accumulated on an irregular (dissolutional?) surface. Small, equant calcite crystals formed on the surface of the discontinuity (open triangles). Crossed-nicols. E) Crystal termination layer. Note the overgrowth above the first termination zone (arrow) and the vertical linear inclusions. Plane polarised light. F) Acute rhombohedra ($\{40\bar{4}1\}$) termination layer. Plane polarised light. G) SEM image of a clay particle within the crystal termination layer shown in image 5e (arrow). H) Horizon delimited by vertical linear inclusions. Note how the orientation of the inclusions is parallel to the growth direction of the crystals (black arrows). White arrows indicate crystal boundaries inclined with respect to the plane of the thin section. Plane polarised light. For (A), (B), (D) and (E), the circular structures are ~ 0.6 mm drill holes made for isotopic analyses. All scale bars are 1 mm except for 4g.

Figure 2.6 U-series sample distribution for OCNM flowstones. Error bars are for 2σ errors while the width of the error symbols represents the true sampling interval for the dated sample.

Figure 2.7 Model for the development of columnar calcite through competitive growth from a random array of calcite crystals. A) Randomly-oriented, steep rhombohedral calcite seeded on a substrate or discontinuity. Arrows indicate greatest growth vector of each crystal. B) Crowding out of unfavourably oriented crystals owing to growth into accommodation space above (competitive growth phase). C) Establishment of elongate calcites under a stable growth regime. Modified from González *et al.* (1992).

Figure 2.8 Model for the establishment of crystal termination layers in flowstones: A) growth of elongate calcite crystals under a "normal" thin film of water, B) increase in the water film thickness, and C) progressive formation of acute terminations.

Figure 2.9 Syntaxial overgrowth crystallite coalescence: A) complete coalescence, producing a "flat" growth surface and few linear inclusions, B) incomplete coalescence with a rougher surface and the presence of linear inclusions, and C) incomplete coalescence, resulting in an acicular fabric. After Kendall and Broughton (1978).

3.0 ESTABLISHING A SPELEOTHEM CHRONOLOGY FOR SOUTHWESTERN OREGON: CLIMATIC CONTROLS AND GROWTH MODELLING

3.1 Abstract

Cave calcites from Oregon Caves National Monument (OCNM), a dissolutional cave system located in the Klamath Mountains of southwest Oregon, are shown to have been deposited in isotopic equilibrium with their associated dripwaters and to reflect global paleoclimates. Given the high cost of obtaining numerous U-series dates and that many records lie beyond the range of the U-Th dating method (~ 500 ka), we have explored a technique for modelling the growth of speleothems both between dates and beyond 500 ka using both theoretical and empirical growth data applied to OCNM speleothems. 14 U-series TIMS dates indicate mean growth rates between 1.54×10^{-3} to $3.15 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$ mostly during early interglacials. Speleothem isotopes from dated intervals show direct relationships with temperature, and correlate well with high-frequency Holocene events (~ 200 years) in the GISP2 ice core, as well as to glacial to interglacial terminations. Contrary to theoretical predictions showing that temperature should predominantly control calcite growth, results from our samples indicate that growth rates are linear for given growth periods on time scales of $\sim 10^3$ to 10^4 years. The calculated growth rates, however, are broadly within the 2 to $5\times$ overprediction factors reported for theoretical growth rates. We suggest that in this area, both temperature and water film thickness control growth rates. Outcrop-scale discontinuities, representing prolonged growth

cessation, are presumed to be caused by groundwater freezing during extended periglacial conditions. The associated hiatuses range from approximately 14 to 102 kyrs and get longer over the course of the Quaternary. An accompanying increase in growth rates suggests an opening of the cave system and shallowing of the rock overburden, which shifts the dissolutional system from closed to open. A simple “start-stop” growth model is presented, based on minimum and maximum $\delta^{18}\text{O}$ isotopic values of marine records before or during terminations and shortly after the onset of climatic deterioration. Although this model shows a very good correspondence between growth periods of cave calcites and termination of glaciations, correlation with precipitation initiation and cessation lines show mixed results, possibly owing to uncertainties related to global records which might not be indicative of actual local conditions encountered at OCNM.

3.2 Introduction

Recently, much attention has been focused on cave calcites (speleothems) as archives of climatic and paleoenvironmental changes in terrestrial environments (Dorale *et al.*, 1992; Matthews *et al.*, 1996; Baker *et al.*, 1998; Dorale *et al.*, 1998; Dreybrodt, 1999; Lauritzen and Lundberg, 1999a;). Factors contributing to make speleothems valuable paleoenvironmental indicators include: (i) their high preservation potential, shielded from surficial erosional processes; (ii) their crystalline structure, frequently composed of coarsely crystalline inorganic calcite (CaCO_3) that records geochemical signatures of global and regional events transferred through atmospheric processes; and (iii) the resistance of speleothems to post-depositional recrystallisation and diagenesis.

Speleothems can be dated to a high accuracy and precision using uranium series disequilibrium methods (Edwards *et al.*, 1986; Blackwell and Schwarcz, 1995). Thermal ionisation mass spectrometric (TIMS) U-Th is the preferred dating method because of its high precision (typically $<1\%$ 2σ errors), its potential age range (0-500 ka), its generally small sample size requirements (depending on U-content, but usually <1 g), and its suitability for use in terrestrial carbonates (owing to the solubility of uranium and its subsequent transport and incorporation into secondary carbonates minerals). Most high-resolution paleoclimatic reconstructions from speleothems rely on high-frequency dating along the growth axis of a speleothem. This, however, is time consuming and expensive. For large samples, it is often feasible to do only a few dates on a given speleothem, leaving the intervals between these chronological anchors devoid of absolute chronological control.

An alternative means of modelling growth is hereby sought. Studies have shown that growth rates can be assessed using theoretical considerations of the chemical equilibria and kinetics of calcites in relation to climate (Buhmann and Dreybrodt, 1985a,b; Dreybrodt, 1999). In order to provide chronological controls for intervals between dates, this paper explores how these theoretical aspects might apply to modelling long-term growth for speleothems from a site on the west coast of North America. This is done by using $\delta^{18}\text{O}$ isotopic signatures from dated sections of speleothem, and comparing them to well-established high-resolution paleoclimatic records, since the oxygen isotopes contained within the CaCO_3 crystals of the speleothems have been shown to vary with

climate (Gascoyne, 1992; Bradley, 1999). These concepts can then be applied to paleoclimatic records from older speleothems, lying beyond the range of U-Th dating.

The following section provides an overview of the theoretical aspects of growth modelling, with emphasis on climatic influences. In the second part of this paper, we provide a brief description of the samples and assess their potential to contain climatically-derived stable isotopic signatures. The third part of this paper focuses on modelling the deposition of our samples.

3.3 Cave calcite deposition

The chemical reactions involved in inorganic calcite precipitation are fairly well known with respect to karst environments (Hendy, 1971; Buhmann and Dreybrodt, 1985a,b). As well, the contribution of individual factors involved in the growth of speleothem, such as CO₂ degassing, Ca²⁺ concentration ($[Ca^{2+}]$), and flow conditions over the surface of the speleothem, have been modelled (Dreybrodt, 1996; Dreybrodt, 1999). It has been shown that rates of calcite precipitation in thin sheets of water are mainly dependent on Ca²⁺ concentration and the type of flow (laminar vs. turbulent) over the surface of the speleothem (Dreybrodt, 1996), although most speleothems are only covered with thin films of water (typically <0.01 cm on average; Baker and Smart, 1995). Given the smooth surfaces encountered on most speleothems, flow of thin films of water should be either laminar or quasi-laminar (Boggs, 1987), leaving $[Ca^{2+}]$ as the major growth rate control. This section provides a brief overview of the processes involved in the

dissolution of carbonate bedrock and precipitation of calcite within a spelean environment.

Three stages are involved in speleothem deposition (Holland *et al.*, 1964; Hendy, 1971; Ford and Williams, 1989):

1) *Carbonation of meteoric water* occurs in soils overlying caves. During percolation through soil, meteoric waters, already in equilibrium with atmospheric CO₂, acquire pedogenic CO₂ as the partial pressure of soil CO₂ is much higher ($p\text{CO}_2$ (soil) is up to 5×10^{-2} or about $10^{-1.3}$ at 25°C; Figure 1.1a) than atmospheric CO₂ ($p\text{CO}_2$ (atm) = 3×10^{-4} or $10^{-3.5}$) owing to the oxidation of organic matter and biological respiration (Miotke, 1974; Rightmire, 1978). Carbonic acid, resulting from the mixing of meteoric water and soil CO₂, forms following $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}_2\text{CO}_3$. This weak acid solution is then channeled or percolated through the soil towards the water table and eventually reaches the carbonate bedrock.

The biogenic soil CO₂ ($p\text{CO}_2$ (biogenic)) can be estimated using Drake and Ford's (1981) equation:

$$\log [p\text{CO}_2 \text{ (biogenic)}] = -2 + 0.04T_{\text{air/gw}}$$

where $T_{\text{air/gw}}$ is the annual average air temperature or groundwater temperature (in °C).

The actual $p\text{CO}_2$ (soil) is lower than this biogenic CO₂ because of inhibition processes

caused by elevated CO_2 concentrations (or depleted oxygen concentrations) (Drake, 1980, 1983). It can be estimated using (Drake, 1980):

$$p\text{CO}_2 (\text{soil}) = [(0.21 - p\text{CO}_2 (\text{soil})) / 0.21] \times p\text{CO}_2 (\text{biogenic}).$$

It has also been shown that maximum $p\text{CO}_2 (\text{soil})$ values are reached only during summer growth seasons in temperate mid-latitudes climates (Rightmire, 1978): during winter soil CO_2 equilibrates with atmospheric CO_2 . Figure 3.1a illustrates the long-term influence of temperature on biogenic $p\text{CO}_2$ levels (upper curve) as well as the actual soil CO_2 ($p\text{CO}_2 (\text{soil})$), reaching approximately 5×10^{-2} atmosphere at 25°C .

2) *Dissolution of carbonate bedrock* by the groundwater solution follows $\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$. Given that levels of soil CO_2 in humid environments are generally greater during the summer months, as well as during longer-term warm periods such as interglacials, higher bedrock CaCO_3 dissolution rates occur in response to increasing temperature and vegetation/microorganism levels (Rightmire, 1978; Lohmann, 1988).

Two dissolution system end-members can occur: the first is when the soil is free of carbonates and the meteoric waters reach equilibrium with $p\text{CO}_2 (\text{soil})$. This solution then percolates to bedrock and dissolves carbonates away from the CO_2 source under “closed” (also referred to as “sequential” by Drake, 1983) conditions (Garrels and Christ, 1965; Hendy, 1971). These conditions are illustrated in Figure 3.1b (“closed” curve). The

dashed line represents $[Ca^{2+}]$ in equilibrium with atmospheric conditions (3×10^{-4} atm) (in most cave systems, cave air CO_2 is close to atmospheric CO_2). Below the dashed line (grey area), the solutions are undersaturated with respect to calcite and calcite dissolution occurs until equilibrium is reached. The second end-member is the “open” (“coincident” systems of Drake, 1983) system (Garrels and Christ, 1965; Hendy, 1971), where an “infinite” CO_2 source is in contact with carbonates (“open” curve of Figure 3.1b). This allows for the dissolution of calcite while maintaining high pCO_2 (soil) levels of the groundwater. Carbonate regoliths, shallow soils, or soils in contact with bedrock are example of such settings (Drake, 1983). Conditions between these end-members are probably more common and can occur due to restricted soil air volumes interacting with percolating meteoric water. The $V_{air} = V_{solution}$ curve on Figure 3.1b illustrates the Ca^{2+} concentration with respect to pCO_2 (soil) for mixed system comprised of equal air and solution volumes. In general, the pCO_2 of soils with little or no organic matter, such as those found in cold or dry environments, will lie towards the left of the graph shown in Figure 3.1b. Soils with abundant organics (from warm and wet environments) display higher pCO_2 and require higher concentrations of Ca^{2+} to reach saturation (Figure 3.1b).

3) *Carbonate precipitation* follows. When the carbonate-bearing solution is transported into an air-filled cavity, $CaCO_3$ will precipitate if the solution becomes supersaturated (with respect to $CaCO_3$), either through loss of CO_2 to the cave atmosphere, evaporation, the common-ion effect and/or pressure-temperature changes (Hill and Forti, 1997). Loss of CO_2 by diffusion is the most common mechanism for saturation of $CaCO_3$ -bearing dripwaters for areas of high humidity removed from strong airflow (Dublyansky, 1995;

Hill and Forti, 1997). Deposition from evaporation is limited to situations with high air flow, while the last two mechanisms rarely operate in standard meteoric water carbonate settings.

As shown above, if the initial dissolutional parameters are known (mean annual temperature, type of dissolution system), then the $[Ca^{2+}]$ of the cave dripwaters can be estimated: Drake and Wigley (1975) demonstrated an empirical correlation between regional temperatures and spring water pCO_2 , and thus CO_2 . The next section summarises the controls on precipitation and translates them into growth rates.

3.3.1 *Parameters involved in speleothem growth*

Speleothem precipitation rates from thin water films open to the cave atmosphere are controlled by three processes (Baker and Smart, 1995; Baker *et al.*, 1998): 1) chemical reactions at the calcite-solution interface as described by the rate equations of Plummer *et al.* (1978) through which precipitation rates can be calculated when the concentrations of reactants are known; 2) mass transport of reactants through the solution towards or away from the speleothem surface; and 3) the rate-limiting reaction $H^+ + HCO_3^- \rightleftharpoons H_2O + CO_2$, through which CO_2 is released into the cave atmosphere. Buhmann and Dreybrodt (1985a,b) have solved the transport equations taking into consideration these three mechanisms in order to obtain precipitation rates. For speleothems, these processes can be approximated within 10% by:

$$\text{Precipitation rate (mmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) = \alpha([\text{Ca}^{2+}] - [\text{Ca}^{2+}]_{\text{equilibrium}})$$

where α is a $p\text{CO}_2$ (cave air)-, dripwater temperature- ($T_{\text{dripwater}}$) and flow characteristic-dependent (mainly film thickness) kinetic rate constant, in $\text{cm} \cdot \text{s}^{-1}$; $[\text{Ca}^{2+}]$ and $[\text{Ca}^{2+}]_{\text{equilibrium}}$ are respectively the actual and equilibrium concentrations of Ca^{2+} ions with respect to calcite, in $\text{mmol} \cdot \text{cm}^{-3}$, in the water film. $[\text{Ca}^{2+}]$ is controlled by the dissolution of the carbonate substrate, determined by the $p\text{CO}_2$ (soil), prior to the solution entering the cave. $[\text{Ca}^{2+}]_{\text{equilibrium}}$ is the equilibrium concentration of Ca^{2+} under atmospheric CO_2 conditions (for 3×10^{-4} atm). This equation can be used in situations where solution flow over the speleothem is high: it has been calculated that high flow rates ($\gg 1 \text{ cm}^3 \cdot \text{s}^{-1}$) should generate sizeable features of at least 2-3 m in diameter (Dreybrodt, 1999), such as the flowstones that are described below. Otherwise, drip rate must be taken into account (Dreybrodt and Franke, 1987; Dreybrodt, 1988). Both the value for α and for $[\text{Ca}^{2+}]_{\text{equilibrium}}$ can be obtained using Buhmann and Dreybrodt (1985a; Table 3.1). For example, under laminar or stagnant flow conditions, values of $6.35 \times 10^{-6} \text{ cm} \cdot \text{s}^{-1}$ and $6.3 \times 10^{-4} \text{ mmol} \cdot \text{cm}^{-3}$ were obtained for α and $[\text{Ca}^{2+}]_{\text{equilibrium}}$ respectively (for $T_{\text{dripwater}} = 10^\circ\text{C}$, water film thickness (d) = 0.01 cm and $p\text{CO}_2$ (cave air) = 3×10^{-4} atm). Within this range, $[\text{Ca}^{2+}]_{\text{equilibrium}}$ as a function of temperature can be summarized by (Dreybrodt, 1988):

$$[\text{Ca}^{2+}]_{\text{equilibrium}} = (-0.01T_{\text{dripwater}} + 0.72)/1000 \text{ mmol} \cdot \text{cm}^{-3}$$

where $T_{\text{dripwater}}$ is the dripwater temperature in $^{\circ}\text{C}$. The use of these two equations to determine growth rates provides estimates for $[\text{Ca}^{2+}] > 1.5 \times 10^{-3} \text{ mmol} \cdot \text{cm}^{-3}$, although inhibition processes might be present close to equilibrium, which may reduce the rates significantly (Dreybrodt *et al.*, 1997).

Figure 3.2 illustrates the response of various parameters to temperature. Figure 3.2a shows the effects of increasing $[\text{Ca}^{2+}]$ on growth rate for various thicknesses (d) of the supersaturated water film, illustrating a slight increase with thickness, although the rate becomes independent of thickness between 0.02 cm and 0.04 cm (Dreybrodt, 1996). One study reports a mean speleothem water film thickness of $7.5 \times 10^{-3} \text{ cm}$, albeit with a $\pm 5.5 \times 10^{-3} \text{ cm}$ 1σ error (Baker and Smart, 1995). Figure 3.2b shows significant increases in precipitation rates for increasing temperature for a given film thickness and $p\text{CO}_2$ (cave air). Figure 3.2c illustrates the effect of $p\text{CO}_2$ (cave air), occasioning a slight reduction in growth rates with increased $p\text{CO}_2$ (cave air). This effect, however, is small. The average atmospheric $p\text{CO}_2$ is $3 \times 10^{-4} \text{ atm}$, which is often taken as the average value for cave air $p\text{CO}_2$, although caves occasionally exhibit much higher values (Ek and Gewelt, 1985). The overall effect of these parameters on the actual value of α is illustrated in Figure 3.2d, showing a marked non-linear increase with temperature. Dreybrodt and Buhmann (1987) have shown that the presence of foreign ions does not affect precipitation rates.

Growth rates can be obtained by converting $\text{mmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ to $\text{mm} \cdot \text{yr}^{-1}$ by multiplying by $1.1677 \times 10^7 \text{ cm}^3 \cdot \text{s} \cdot \text{mmol}^{-1} \cdot \text{yr}^{-1}$, assuming a molecular weight of $100.09 \text{ g} \cdot \text{mol}^{-1}$ for CaCO_3 , a density (ρ) for compact calcite of $\sim 2.7 \text{ g} \cdot \text{cm}^{-3}$ and time conversion factor of

3.156×10^7 s per year (Dreybrodt, 1980). However, spelean calcites with up to 10% porosity have been reported (Genty *et al.*, 1997). Some of this porosity arises from incomplete coalescence of crystallites forming common columnar crystals (Kendall and Broughton, 1978). As well, some types of speleothems with extensive micro-gour development can have high porosities owing to the development of dog-tooth calcite crystals in standing water (Hill and Forti, 1997). Contrary to the speleothems discussed in the study (see Turgeon and Lundberg, in press a), these gour speleothems require high-angle slopes (Hill and Forti, 1997) and are not commonly used in high-resolution paleoclimatic studies. Growth rates can be corrected by determining porosity in samples and adding this volume to the rates obtained from the equations above. Given that porosities are generally small (<10%; Baker *et al.*, 1998), this factor is not significant considering other uncertainties involved in the growth model.

Baker and Smart (1995) presented data calculated for a 50% increase in growth parameters modelled from the means of actual samples (Table 3.1). According to this table, changes in $[Ca^{2+}]$ account for 43% of the variability while 29% is explained by water film thickness, and temperature and CO_2 partial pressure account for 21% and 8% respectively. This is in agreement with Dreybrodt (1988). These data suggest that growth rates are sensitive to temperature variations, with higher growth rates occurring in response to higher temperatures (assuming a constant film thickness d). Overall, this theoretical model has been shown to overestimate the actual growth rate by approximately 2 to 5 times for laminar flow conditions (Baker and Smart, 1995), owing to uncertainties associated with the rate equations of Plummer *et al.* (1978). These

uncertainties could relate to differences in surface roughness between experimental and natural calcites, in addition to seasonal cessation and variations of water supply and soil $p\text{CO}_2$ that have yet to be accounted for and incorporated into this model. Although these parameters are known and can be measured with a satisfying degree of accuracy for present-day speleothem deposition (Baker and Smart, 1995; Baker *et al.*, 1999), the individual effects of these parameters are difficult or impossible to isolate in older cave deposits. However, these theoretical considerations point out that temperature influences most of these parameters and mechanisms, including $p\text{CO}_2$ (soil) (film thickness is often assumed to be constant over stalagmites and flowstones owing to their slopes, hence recharge rates are thought to have little or no effect on the film thickness). This points to the possibility of modelling speleothem growth rates as a function of temperature using well-established paleotemperature proxies (such as $\delta^{18}\text{O}$ and other signatures from marine-, ice-, and other long-term records). Paleotemperature records from speleothems include $\delta^{18}\text{O}$, although the effect of temperature on the proxy needs to be established for each site (Lauritzen and Lundberg, 1999b). The speleothem record can be anchored with whatever U-series dates are available. The growth rate function used to assign ages to the isotopic values can then be optimised so that the peaks and troughs of the speleothem curve conform to those of the well-established paleotemperature proxy. This can be tested first in the well-dated sections of the speleothem and then applied to other sections. Below we present the results of this exercise applied to speleothem samples from Oregon Caves National Monument.

3.4 Study area

Oregon Caves National Monument (OCNM) is located on steep, northwest facing slopes of the Klamath Mountains physiographic province in southwestern Oregon, approximately 65 km inland from the Pacific Ocean (Figure 3.3), from which the cave site's rainfall is derived (transported through westerly winds). The OCNM site is located south of the maximum limit of Pleistocene ice sheets (Figure 3.3), allowing us to rule out advancing continental ice sheets as a non-depositional control on speleothem deposition at OCNM while remaining northward of more evaporative latitudes. The Monument is located at an altitude of approximately 1400 m ASL, covers 1.9 km², and is nested amidst old-growth Douglas- and white firs, providing abundant organic matter to the soils overlying the cave.

OCNM consists of a main dissolutional cave developed in a Triassic marble lens, bounded by pyrite-rich argillites. Cave development is controlled by a NE joint system and high-angle (60° to 85°), N-S trending normal faults within the marble lens, formed in response to tectonic activity during the Miocene (Wells and Heller 1988). These faults and joints allow the deep penetration of water into the subsurface and regulating passage alignment of the cave. The cave contains several subhorizontal levels, representing former water table levels controlled by river down-cutting. The most laterally extensive level, located at approximately 28 m above the main entrance level contains thick, well-developed flowstones, from which most of our samples come. Few speleothems are located in the older, higher levels formed mainly by vadose drawdown shafts.

3.5 Sample description

Two flowstones, one approximately 13 cm thick from the *Exit Tunnel Cave* (ETC) and a 73 cm thick sequence from *Neptune's Grotto* (NG) (Figure 3.4), as well as a 5 cm high stalagmite from the *White Formation Passage* (WFP-2L), were analysed for this study. The NG and WFP-2L samples were taken from areas deep within the cave, away from the present-day main airflow in order to minimise evaporative effects and temperature variations stemming from airflow generated by the two known natural entrances. The ETC flowstone was collected in an isolated chamber discovered during the excavation of a tunnel in the 1930's allowing access to the cave at higher elevations. Since the ETC flowstone was collected from a cave with no known natural entrances, conditions of minimal evaporative and temperature variations are thought to have dominated the cave climate at this site.

In order to establish the depositional history of the speleothems, outcrop-scale features such as discontinuities were mapped. Four discontinuity surfaces were found within the NG flowstone (Figure 3.4). The discontinuities are laterally continuous over the entire outcrop of the specimen sampled. Debris such as broken soda straw and stalactites lying horizontally on these surfaces (Figure 3.4). Although columnar calcite crystals with rhombohedral terminations protrude from these sub-horizontal surfaces, they are generally smooth, and are covered with a thin layer of allogenic brownish detritus of mineral origin.

3.6 Methodology

X-ray diffraction analyses were undertaken on powdered samples of the speleothems, analysed with a Philips PW1730 apparatus at Carleton University, and used in conjunction with thin-section petrography to confirm the mineralogy of the crystals. Speleothem samples were cut parallel to the growth axis. These surfaces were then ground and polished. The speleothems were sampled for stable isotopic analysis along the growth axis of the samples using a 0.6 mm drill bit. Oxygen stable isotope ratio measurements were done every 1 mm for the WFP-2L stalagmite and the lower section of the NG flowstone, while all the other samples were analysed every 2 mm. Standard extraction techniques, using H_3PO_4 digestion, were used to purify and isolate CO_2 , which was analysed for oxygen stable isotopes using a Micromass Siral2 mass spectrometer located in the Earth Sciences Department of the University of Ottawa. The analytical errors on $\delta^{18}\text{O}$ values are $\pm 0.1\%$ and all results are reported as V-PDB.

Chronological control is provided by 14 high-precision thermal ionisation mass spectrometry (TIMS) U-series dates performed at University of Bergen (Norway) on a Finnigan-MAT 262 RPQ solid source mass spectrometer following the analytical procedure described by Lundberg (1997). Owing to low uranium content, ranging from 0.086 to 0.233 ppm (Table 3.2), sample sizes ranged from 1 to 2 g, representing vertical intervals between 2 and 7 mm. Samples were cleaned ultrasonically, ignited to remove organics, and a ^{229}Th - ^{223}U - ^{236}U spike was added. U and Th were separated in anion exchange columns, loaded onto single filaments with silica gel (U fraction) or graphite

(Th fraction) and the isotopic ratios measured in peak switching, ion counting mode. Typical 2σ analytical precisions on isotopic ratios are 0.08% and 0.15% for U and Th respectively.

3.7 Results and discussion

3.7.1 *OCNM cave calcites as paleoenvironmental indicators*

The first step towards utilising speleothem stable isotopes as paleoenvironmental indicators is to establish the primary nature of the calcite crystals comprising the bulk of the speleothems. One such verification involves searching for evidence of recrystallisation within the crystals, given evidence that suggests that some cave calcites are recrystallised from aragonite (Folk and Assereto 1976). Folk and Assereto (1976) proposed petrologic criteria to determine the presence of former aragonitic precursors within speleothems, namely: (i) preservation of the original aragonite crystals; (2) needle-like inclusions from possible surviving aragonite needle ghosts contained within a randomly-oriented recrystallised polycrystalline euhedral calcite mosaic; (3) presence of a randomly-oriented polycrystalline euhedral calcite crystal mosaic; (4) quadratic or feathery crystal termination possibly indicative of a former aragonitic crystal; (5) presence of extensive dissolution possibly occurring in less stable aragonitic layers. No evidence of recrystallisation was observed in the samples according to these criteria, including randomly-oriented equant calcite crystals. In addition, X-ray diffraction data

confirm that no aragonite is present in the samples, indicating that the crystals are primary features and possibly reflect original environmental conditions.

The second step is to establish whether the calcites were deposited in isotopic equilibrium with the waters from which they are derived. During slow degassing, the isotopic fractionation between the aqueous and solid phases is controlled indirectly by cave temperature under equilibrium conditions. However, under an evaporative cave régime or rapid crystallisation, the isotopic fractionation is modulated by kinetic effects which inhibit isotopic equilibrium between the calcite and the dripwaters (Hendy, 1971).

A test for isotopic equilibrium deposition of speleothem calcite has been devised by Hendy (1971) based upon variations in C and O isotope ratio variations along coeval growth layers. Theoretically, $\delta^{13}\text{C}$ values of calcite should become progressively higher with distance from the source of dripwater as $^{12}\text{CO}_2$ is lost by degassing preferentially to $^{13}\text{CO}_2$. The $\delta^{18}\text{O}$ signal should remain constant owing to the relatively large amount of water available. Under evaporative conditions, both $^{12}\text{CO}_2$ and H_2^{16}O molecules are preferentially fractionated as water travels down the speleothem, thereby producing synchronous enrichments of both ^{13}C and ^{18}O in the calcite deposited from solution.

Several drawbacks, however, are associated with the use of the Hendy test. The first concerns the physical sampling of single growth layers, typically only a few tens of microns thick, with drill burs ranging from approximately 0.3 mm up to 1 mm in diameter. This would not only induce an averaging of the isotopic values over the width

of the sample, but also create problems sampling the same group of coeval bands at several locations within a single speleothem, producing false enrichment trends. Secondly, although this test is theoretically sound for stalagmites with smooth surfaces (on which water flow direction is clearly downward), it could prove more difficult to establish the flow direction on flowstones, which typically have subhorizontal surfaces. However, as many dissolutional caves unaffected by air flow have high relative humidity levels (>90%), evaporation is thought to be of minor importance (Hill and Forti, 1997).

In the absence of any alternative, and in spite of the drawbacks enumerated above, Hendy tests were performed on the WFP-2L stalagmite and near the base of the NG flowstone (Figure 3.5). Figure 3.5a illustrates the results for sampling the WFP-2L stalagmite along coeval subsamples. Figure 3.5b illustrates the results for the lower parts of the NG flowstone. Sampling of the ETC flowstone for the Hendy test was not performed due to the lack of clear banding. For both the WFP-2L and the NG speleothem samples (Figure 3.5a and b, left panels), the results show the absence of parallel enrichment of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ along “coeval” growth layers. Furthermore, Figure 3.5a (right panel) shows that there is no synchronous enrichment of the carbon and the oxygen isotopes, although the right panel of Figure 3.5b shows a trend between the isotopes δ values, but this is not considered significant as there are no directional trends over the surface of the flowstone (Figure 3.5b, left panel). This evidence, in conjunction with the physical setting of the samples (in areas with high humidity and away from natural entrance or areas of high air flow), indicates that the stable isotopes potentially contain paleoclimatic information.

The next step is to confirm the presence of paleoclimatic signals in our samples, and to determine the relationship of isotopic trends with climate. Several effects operating within the cave-surface-atmosphere-ocean system control oxygen isotope variations in speleothems. The *cave temperature effect* represents the thermodynamic fractionation of oxygen isotopes between water and calcite during equilibrium precipitation. The *ocean temperature effect* reflects the temperature-dependent fractionation of oxygen isotopes between liquid and vapour phases over ocean surfaces, the source of the atmospheric moisture. The *rainwater composition effect* describes the effect of atmospheric processes on oxygen isotope compositions of vapour and relates to the behaviour of air masses en route towards the site of rainfall in the vicinity of the cave: it is mainly a function of rainout before it reaches the site and relates to storm-tracks and temperature over the precipitation site (Dansgaard, 1964). The *ice-volume effect* represents changes in isotopic composition of ocean waters between glacial and interglacial periods, with seawater becoming enriched in heavy isotopes as ice volume increases (Shackleton and Opdyke, 1973). An example of local effects, soil-water evaporation could cause isotopic enrichment of the dripwaters.

The relative importance of these effects described above depends on the scale of the climatic changes. For example, during glacial-interglacial cycles, the ice-volume effect may be important, while cave temperature or rainout factors can be dominant during periods of less severe environmental changes such as within an interglacial. The overall relationship between climate and oxygen stable isotope ratios must be independently established for each study site and can be summarised using the speleothem delta

function (SDF) as described by Lauritzen and Lundberg (1999b). Generally, the meteoric-dependent isotopic shifts will be greater than the cave temperature effect (Lauritzen and Lundberg, 1999b) so that the oxygen isotopes in the cave calcites will become more enriched as the temperature increases (positive relationship), although inverse correlations have also been established, mostly for cave sites influenced by maritime-derived moisture sources.

3.7.2 *Speleothem geochronology and isotopic signatures*

Fourteen U-series dates were used as the basis for developing a speleothem growth chronology (Table 3.2). These ages ranged from 2.26 ka to 359 ka, while relative 2σ errors were from 0.32 to 2.62% of the actual age, with the greater errors occurring in older samples. All samples are in chronological order, except for two (NG-G and NG-L) that have overlapping 2σ errors. Two dates (NG-D and NG-J), taken from the same interval of overlapping samples within the Neptune's Grotto Section 1, gave overlapping 2σ errors. As well, two samples (ETC-B and ETC-E) presented low (<10) $^{230}\text{Th}/^{232}\text{Th}$ ratios (Table 3.2), which could be indicators of detrital contamination of the samples (Blackwell and Schwarcz, 1995). However, both samples had no visible detrital contamination and their absolute Th concentrations were below 1 ppm (0.66 and 0.77 respectively). These factors, in addition to the high $^{234}\text{U}/^{232}\text{Th}$ activity ratios encountered in these samples (76 and 64), contributed to our decision not to correct for an assumed initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in these samples.

To facilitate preliminary comparisons, we have aligned the dated intervals of our speleothem isotopic records, plotted as distance from the base of the deposit, to the chronology of established global paleoclimatic records (from ice and marine cores) and have assumed linear growth rates between these dated intervals. We utilised the highest resolution paleoclimatic isotopic record for given intervals, although our oldest samples could only be compared to the two longest records available (SPECMAP; Imbrie *et al.*, 1984 and Devils Hole; Winograd *et al.*, 1992).

Our youngest sample is the WFP-2L stalagmite, with a basal date of 3.88 ± 0.17 ka (WFP-2-A) and a topmost date of 2.26 ± 0.02 ka (WFP-2-B). These dates indicate a mean growth rate of $3.15 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$ during a short growth interval of approximately 1600 years. This growth rate agrees well with interglacial stalagmite growth rates from Norway ($2.0 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$; Linge, 1999), Ireland (2.8 to $3.4 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$; Vesely, 2000), as well as growth rates ($2.79 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$) calculated for the ETC flowstone (Table 3.2). Figure 3.6 illustrates the oxygen isotope record of this sample in relation to the high-resolution ice cores from Greenland (GISP2; Grootes *et al.*, 1993; Meese *et al.*, 1994; Stuiver *et al.*, 1995) and Antarctica (Vostok; Chappellaz and Jouzel, 1992). For both of the ice cores, an isotopic enrichment indicates an increase in global temperature (Grootes *et al.*, 1993). The WFP-2L record seems to indicate a slight positive relationship of isotopic signal and temperatures as the 3rd-order polynomial best-fit lines indicate overall parallel trends. The WFP-2L record also seems to reveal a series of isotopic depletion events occurring about every 200 years. These appear to correlate with similar periodicity events in the GISP2 record (Grootes *et al.*, 1993; Meese *et al.*, 1994; Stuiver

et al., 1995). The resolution of the Vostok ice core is too low to reveal these short-term shifts.

The chronology of deposition for the NG flowstone was established using seven U-series dates (Table 3.2). Figure 3.4 shows the distribution of outcrop-scale discontinuities within the NG flowstone. The top-most growth interval (Section 1; Figure 3.4) is defined by three dates. A mean growth rate of $1.57 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$ was obtained based on the two dates, NG-F and NG-L (given the overlap 2σ overlap of NG-L and NG-G, we chose the U-Th sample that was the farthest away from the basal NG-F U-Th sample along the growth axis). The stable isotopic record for this growth interval is plotted in Figure 3.7. It is compared to the Illinoian to Sangamon glacial-interglacial transition in the GRIP and Vostok ice core records, as well as the SPECMAP marine record. A 3rd-order best-fit polynomial trendline has been added to the NG record in order to better illustrate similarities with the established records. The large-scale variations in data between all three records are strikingly similar in terms of timing of major events within each data set.

Chronologic difference of the timing of peaks and troughs of the statistical trendlines are apparent, with the GRIP record showing its peak at approximately 130 ka, approximately 500 years earlier than on the NG record, and approximately 1 kyr earlier than the Vostok record. These offsets are well within the 2σ ranges and the timing is in good agreement with coral reef data from the Bahamas indicating the high sea-level stand during marine isotope substage 5e occurred between 132 and 129 ka (Chen *et al.*, 1991). The similarity

of the shapes of the paleoclimatic curves suggests that the onset of the climatic amelioration in all three records was about of roughly equal intensity. The trough at ~122 ka on the GRIP and NG records, resulting from a climatic degradation followed by a temperature increase, appears to be absent from the Vostok ice core record. Given the striking correspondence with both ice core records, we conclude that growth of the speleothem occurred during interglacial conditions (early marine isotope stage 5) (Table 3.2) during an interval of approximately 13.4 kyrs. Comparing these records to the marine isotopic record of SPECMAP highlights the differences between the marine record and the ice and terrestrial records. A notable difference is the timing of the Termination II (terminations are defined as the middle of the transition between glacials to interglacial periods) within the records, which are offset by as much as 5000 years (Imbrie *et al.*, 1984; Martinson *et al.*, 1987). This difference is the subject of much on-going controversy, as much of the recently TIMS dated coral reef evidence supporting the earlier date for Termination II is in agreement with the ice core records (Chen *et al.*, 1991; Gallup *et al.*, 1994). In spite of timing differences between events, OCNM speleothem isotopes mirror the ice core and ocean core records for the last interglacial, establishing the positive relationship of speleothem oxygen isotopes and temperature. The rest of the NG record is less well dated or lies beyond the range of U-series dating.

The second interval of the NG flowstone (Section 2) is anchored by a single U-series date (~235 ka). The NG isotope record for this interval has been compared to the GRIP ice core and SPECMAP marine records (Figure 3.8). All three records are similar and the NG and GRIP records show three prominent peaks that can be tentatively correlated,

albeit weakly. However, the GRIP record terminates at 250 ka, leaving a short section of the NG (approximately 4 kyrs) record without any direct comparison to a record of similar resolution (Figure 3.8). Based on the tentative correlation of the NG and the GRIP records, a mean growth rate of $\sim 2.9 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ over a 22.4 kyr period from 253.8 to 231.4 ka have been estimated, indicating relatively slow speleothem growth during the marine oxygen isotope stage (MOIS) 7.

The lowermost of the dated NG intervals (Section 3) is chronologically validated using the mean date provided by the overlapping samples (NG-D and NG-J) indicating MOIS 9 deposition, along with a third date (NG-I) from a lower interval (MOIS 10)(Figure 3.9). These dates provide a mean growth rate of $5.6 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ between these two outcrop-scale discontinuities. Based on the mean growth rate, this interval represents approximately 51 kyrs of growth, possibly from marine isotope stages 9 through 11. Trends, broadly corresponding to the shape of the SPECMAP record, are apparent Figure 3.9). The absence of any indicators of growth stoppage suggests that growth was continuous during the MOIS 10 glacial.

Another example shows the same pattern. Three dates (ETC-C, ETC-A and ETC-D) from the Exit Tunnel Cave flowstone range in age from 116 to 119 ka (isotope substage 5e) and have a high growth rate ($2.79 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$) in the lower section of the flowstone, while two dates (ETC-E and ETC-B) in the upper reaches of the flowstone are clearly late Wisconsinan (MOIS 2) and indicate a growth rate of $7.6 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$. The interval between ETC-D and ETC-E, broadly corresponding to the colder conditions of stages 4

through 2 (and including late 5), therefore represents either severely reduced growth ($\sim 3.0 \times 10^{-4} \text{ mm} \cdot \text{a}^{-1}$) or a pause in deposition of approximately 102 kyrs. No outcrop-scale discontinuity has been observed and no microscopic evidence of precipitation stoppage has been identified, suggesting that growth was continuous throughout the Wisconsin glacial period, although complete growth cessation could have occurred. The ETC isotopes for this section provide few clues into this problem as the $\delta^{18}\text{O}$ values have remained more or less constant between the two dates (ETC-D and ETC-E) constraining stages 4 through 2, a situation similar to Section 3 of the NG flowstone described above. The mean growth rates for the section spanning glacial intervals should therefore be considered minimum growth rates for these intervals.

3.8 Growth modelling

A simple theoretical model to determine growth rates for our interglacial samples can be obtained by using data in Figures 3.1 and 3.2. For example, using an approximate present-day mean annual temperature for OCNM of 7.5°C , a $p\text{CO}_2$ (soil) of 0.015 atm is obtained (Figure 3.1a). This translates into theoretical $[\text{Ca}^{2+}]$ values ranging from 0.75 to $2.3 \text{ mmol} \cdot \text{cm}^{-3}$ for closed and open systems respectively (Figure 3.1b) (preliminary testing of actual cave water at OCNM in 1992 reports mean values of approximately $0.68 \text{ mmol} \cdot \text{cm}^{-3}$, with a $2\sigma = \pm 0.52$ for $n = 27$; OCNM internal document). Thus the $([\text{Ca}^{2+}] - [\text{Ca}^{2+}]_{\text{equilibrium}})$ term, assuming an approximate $[\text{Ca}^{2+}]$ equilibrium value of $0.63 \text{ mmol} \cdot \text{cm}^{-3}$ (Dreybrodt, 1996, although he reports an apparent equilibrium value of $0.72 \text{ mmol} \cdot \text{cm}^{-3}$), becomes 0.15 to $1.7 \text{ mmol} \cdot \text{cm}^{-3}$. Using a α value of 1.0 (from Figure 3.2d,

for $d = 7.5 \times 10^{-3}$ cm and $p\text{CO}_2$ (cave air) = 3×10^{-4} atm), we obtain values ranging from 1.5×10^{-9} to 1.7×10^{-8} mmol · cm⁻² · s⁻¹, translating into growth rates of 1.8×10^{-2} to 0.20 mm a year. The upper limit of 0.2 mm · a⁻¹ should be considered an absolute maximum as no karst system is perfectly “open” (Drake, 1983). Furthermore, the air volume ($\approx$ pores) of soils is restricted with respect to water volume, further reducing the theoretical $[\text{Ca}^{2+}]$ equilibrium at different $p\text{CO}_2$ (soil) (Drake, 1983). The upper values are in excess of the values reported for our samples ranging between 2.86×10^{-3} to 3.15×10^{-2} mm · a⁻¹, although our growth rates generally fall within the 5×-overestimation factor of the theoretical growth model (Baker and Smart, 1995). These rates, however, are better represented by restricted air volume approximations ($V_{\text{air}} = V_{\text{solution}}$). In addition, as mentioned earlier, this simple model does not take into account the seasonality (winter stoppage) of calcite precipitation. As an example, for approximately 8 months of the year temperatures at OCNM, located at an altitude of approximately 1400 m asl, the monthly minimum temperature above the cave is below 0°C (OCNM internal document). This seasonality potentially allows for freezing of the ground above the cave, thereby substantially slowing down or stopping calcite precipitation. Also, long-term climatic variations, which could allow mean annual air temperatures above the cave to hover just above the freezing point, would further reduce the theoretical growth rate to approximately 7.6×10^{-3} mm · a⁻¹ for an open system, hence even at near-freezing temperatures speleothem growth can be significant. Overall, our dated sections generally confirm the validity of this model, although the modelled growth rates obtained show a rather wide range (1.8×10^{-2} up to 0.2 mm · a⁻¹) for end-member dissolution systems. However, these climatic controls

on growth rates might be negligible over significant time periods, as put forth in the next section.

3.8.1 Evidence for linear growth rates

The model suggests that growth should relate strongly to temperature. This glacial-interglacial climate change probably explains the obvious reduction in the growth of ETC during MOIS 4-2. However, within the interglacials, it is apparent from the good fit of the speleothem $\delta^{18}\text{O}$ chronologies presented above with the other proxies that growth rates are linear rather than temperature controlled. Although variations in calcium concentrations over time are not available for the OCNM site, Baker *et al.* (1996) found $[\text{Ca}^{2+}]$ to be generally constant for a given cave site. The models discussed above indicate that most of the growth rate changes ($\approx 42.5\%$) can be attributed to long-term variations in Ca^{2+} concentration (Baker and Smart, 1995; Baker *et al.*, 1996), although other parameters such as thickness of the water film (d) and atmosphere CO_2 also contribute to varying degrees. The assumption that our samples show linear growth between U-series dates is valid over the time scales for which we have chronological controls.

This apparent incompatibility between the theoretical and the empirical data could be reconciled by considering the water film thickness (d), which controls $\approx 29\%$ of the growth variability. In climate systems that show alternating warm-dry and cool-wet periods, speleothem growth might be controlled alternately by the temperature and the

water film thickness. Temperate maritime climates, controlled by depressions related to westerly winds and the polar front, do in fact show these extremes of climate (warm-wet or cool-dry conditions are relatively rare). In another climate system, temperature and water film thickness controls may combine rather than alternate; this is probably true of a well-dated Bahamian speleothem which grew during Termination II with a logarithmic growth increase during the termination (Lundberg, 1997). The glacial to interglacial climate transition here was probably cool-dry to warm-wet.

Other empirical studies have also shown varying degrees of growth linearity for speleothems samples from similar climatic settings to OCNM's, most commonly after a slower growth period during the initial phases (of a few cm) of speleothem development (Hellstrom *et al.*, 1998; Lauritzen and Lundberg, 1999; Linge, 1999). The slower growth during early speleothem development could be associated with initial length-slow calcites representing the initial encrusting of an unconformity (Folk and Assereto, 1976; Dickson, 1978).

Our conclusions from this comparison of the theoretical and empirical is that growth cannot necessarily be simply modelled as a function of temperature, that water film thickness may act as either an alternate or as a complementary control along with temperature, and that the climate system(s) must be known in detail in order to model both controls.

3.8.2 Extending the chronology of the OCNM speleothems

The lower section of the NG flowstone could not be dated by TIMS U-Th dating owing to a generally low U content of the flowstone (Table 3.2). In addition, $^{234}\text{U}/^{238}\text{U}$ dating could not be performed owing to a non-constant initial $^{234}\text{U}/^{238}\text{U}$ content in our samples (Table 3.2). Using the linear growth rate assumption in conjunction with the positive relationship between climate and the oxygen isotope ratios of OCNM speleothems during interglacials, we therefore present peak-matching correlations of the lower sections of the NG flowstone isotopic record (lacking or beyond U-series chronological control) with other records of global paleoclimates such as the SPECMAP curve (Imbrie *et al.*, 1984) and Devils Hole (Winograd *et al.*, 1992). Figure 3.10 illustrates the correlation for NG Section 4. A 3rd-order polynomial best-fit trendline has been added to the NG curve on Figure 3.10. The best correlation between the paleoclimatic records occurs between 393 ka and 443 ka. In this interval, trends within all three records correlate well. This chronology indicates a mean growth rate for this NG interval of $3.24 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$, which is roughly comparable to a rate of $2.05 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ for a well-dated northern Norwegian flowstone from MOIS 11 (Lauritzen and Lundberg, in press) and suggest that our modelling attempt for this section of flowstone is not unreasonable.

Figure 3.11 shows the lowermost NG interval (Section 5), constrained by an outcrop-scale discontinuity at the top and resting directly on the marble bedrock (Figure 3.4). The 3rd-order best-fit polynomial trendline matches the shape of the SPECMAP record well. This indicates a growth period for this interval from c. 519 to c. 462 ka, placing this

deposition at the beginning of MOIS 13. The mean growth rate for this interval is $1.54 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$. The estimated age for the lower part of this interval indicates that initiation of speleothem deposition in this area of the cave probably started around 519 ka. Given that the NG flowstone is located on the most extensive level within the cave, this could be a good age estimate for the beginning of widespread speleothem deposition in the cave.

3.8.3 *Climatic implications of outcrop-scale discontinuities*

Figure 3.12a summarises all our data and the paleoclimatic proxies used for comparisons; the unconformities within the OCNM speleothem are illustrated as grey areas. Through the use of the proposed chronology for the growth intervals of the NG flowstone, and U-series dates when available, we have estimated the time interval represented by the outcrop-scale disconformities to be approximately 14 kyrs (IV), 22 kyrs (III), 63 kyrs (II), and 96 kyrs (I) (Figure 3.4) respectively. These breaks in sedimentation broadly correspond to glacial conditions of MOIS 12, 10, 8, and 6. The ETC flowstone also corroborates this pattern: although no apparent precipitation cessation occurred (Turgeon and Lundberg, in press a), a severe reduction of growth rates between two U-series dates indicates the influence of climate on speleothem growth. This growth rate reduction observed in the ETC flowstone lasted approximately 102 kyrs during late MOIS 5 through MOIS 2.

These isotopic records and unconformities indicate narrow growth intervals during early to mid-interglacial conditions. Although several growth frequency studies show that speleothem deposition occurs mainly during interglacial intervals in high-latitude environments (Gordon *et al.*, 1989; Gascoyne *et al.*, 1983; Gascoyne, 1992; Baker *et al.*, 1993; Lauritzen, 1995), calcite precipitation in these studies was interrupted by continental ice sheet glaciation in most cases. No evidence of continental glaciation has been reported in the immediate vicinity of the study area, although cirque-like structures suggesting alpine-style glaciation have been observed at higher altitudes elsewhere in the Klamath Mountains (John Roth, U.S. Park Service, personal communication, 1994). This suggests that these growth stoppages may be associated with periglacial conditions extending well below the alpine glacier limit. The increasing durations of these hiatuses indicates that precipitation could reflect an interplay between climate and additional effects related to cave development.

Glaciation thresholds in the northwestern United States suggest that climatic gradients during the last glacial maxima were similar to those of today, and that the change in summer temperature was about 5.5 ± 1.5 °C (Porter, 1977; Porter *et al.*, 1983). These glaciation thresholds allowed for changes in mountain snowline altitude (currently at about 3200 m ASL), which was depressed by approximately 1100 m during the last glacial maximum at 42°N, to approximately 700 m above the cave site (Porter, 1977). In addition, Heusser and Heusser (1990) report that sub-alpine vegetation was established at elevations between 1300 and 1800 m lower than present-day conditions (owing to an inferred 5-7 °C temperature depression, in line with Porter's data), further suggesting that

permafrost conditions could have occurred well below the 2100 m snowline during glacial conditions in the study area.

Colman and Pierce (1992) concluded that early Wisconsinan alpine glaciers of the western United States were more extensive than their late Wisconsinan counterparts in some areas, thereby contrasting with marine oxygen-isotope records which suggest that world-wide ice volumes were smaller during MOIS 4 than those in MOIS 2 (Emiliani and Shackleton, 1974; Martinson *et al.*, 1987). This indicates that alpine areas could have responded more rapidly than continental ice sheets to climatic events associated with late MOIS 5 and MOIS 4 growth reduction. This sensitivity to climate change may also have been heightened owing to the location of the cave, which was probably very close to the lower permafrost limit during glacial periods, suggesting that the speleothems are predominantly records of local paleoclimate.

Another feature of the hiatuses is their apparent increase in duration with time, associated with higher growth rates after MOIS 7. This could reflect an increasing intensity of glacial periods over time accompanied by warmer interglacials, although the influence of temperature on growth rates in OCNM speleothems, as shown in this study, is equivocal. This pattern might be linked to the predominance of the eccentricity parameter over the precession and tilt orbital parameters during the later parts of the Pleistocene (Berger and Loutre, 1991). Alternatively, these features could reflect the transition between closed to a more open dissolutional system in response to either a thinning of the overburden through erosional processes above the cave or a greater opening of the cave. Given that

the cave is located in a marble lens of limited extent (and hence thickness), erosion above the cave would expose the cave to progressively shallower pedogenic processes until the marble lens is directly in contact with the soil overlying the cave. This would not only make the cave system more sensitive to environmental changes, it would also create a more open system of carbonate dissolution and precipitation. In addition, a greater number of natural entrances would develop in a shallower and enlarging cave system, creating additional ventilation of the cave thereby potentially lowering the $p\text{CO}_2$ of the cave air. Under these conditions, hiatuses would become progressively longer during glacial stages, while higher growth rates would be expected during interglacials.

3.9 The start-stop model of cave calcite precipitation

The model presented in the first section indicates that growth rates of speleothem calcite should be directly related to temperature. Nevertheless, our results show that growth rates during interglacials can be obtained by linear interpolation between dated sections, indicating little or no net influence of temperature on OCNM speleothem growth rates, but rather a probable interplay between the effects of temperature and film thickness. The precipitation is however influenced by climate on a broader scale. Results for terminations I and II clearly indicate that precipitation is initiated at the very end of a glacial period, while precipitation cessation occurs very early in the climatic deterioration from interglacial to glacial. Therefore, if we assume that all growth intervals follow the same pattern, it is possible to approximate isotopic limitations on these

precipitation/unconformity cycles as well as propagate the model back using established proxies of paleoclimate.

Figure 3.12b plots 11 of the 14 U-series dates obtained on our samples against the SPECMAP marine oxygen isotope curve (Imbrie *et al.*, 1984). These dates cluster into four groups, indicating mean dates around 340 ka, 215 ka (one date only), 120 ka and 13 ka, suggesting that the samples were deposited mainly during interglacials. Using this distribution, we have broadly constrained the lowermost growth interval of our samples by using the lowermost (on the marine isotope curve) point for which we have any chronological control (ETC-E) at 14.3 ka (indicated as “precipitation initiation” line on Figure 3.12b). The upper growth limit (“precipitation cessation” line) can be similarly constrained (Figure 3.12b). In this case, it seems that growth stops shortly after major climatic cooling episodes. Note that owing to the low number of dates from our samples, these lines might not constrain growth perfectly. A major complicating factor is the question of the suitability of marine curves to reflect adequately the paleoclimatic régime of OCNM. The results of this simple model are mixed: while the growth intervals correspond well with growth during terminations (Figure 3.12b), the precipitation initiation and cessation lines are adequate only about half the time: this could be due to generalised paleoclimatic curve (SPECMAP) used, that might not mimic the precise paleotemperature conditions at the OCNM site. In addition, a revision of the SPECMAP chronology could reduce the asymmetry of the start-stop model.

3.10 Conclusions

Cave calcites from Oregon Caves National Monument have been shown to be suitable as an indicator of global paleoclimates. Isotopes from dated interglacial intervals have been shown to record a direct relationship with temperature, controlled mainly by the temperature of the source ocean waters. Correlations with high-frequency Holocene events (~ 200 years) in the GISP2 ice core have been demonstrated, confirming the global nature of the signal.

In this paper we explored techniques for modelling growth for those parts of the record that were not well dated or were beyond the range of dating. According to theoretical modelling of calcite precipitation, growth rates of speleothems should respond mainly to temperature. The growth rates calculated for our speleothem, ranging from a lower value of 1.54×10^{-3} up to $3.15 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$, are broadly within the growth rates predicted by the model (taking into account the 2 to 5 $\times$ overprediction of the model). However, results from dated interglacial sections of our samples from OCNM indicate that precipitation rates are essentially linear on long-term scales ($\sim 10^3$ to 10^4 years). We conclude that for this region, growth modelling simply as a function of temperature does not adequately describe growth, a conclusion that apparently contradicts the theoretical findings. This empirically-defined linear growth can be reconciled with the theoretical findings if both temperature and water film thickness are included. The relative balance of the two controls will depend on the climate system, where a warm-dry episode might produce the

same growth rate as a cool-wet one. Thus film thickness must also be taken into account when attempting to model growth rates and the climate system should be known.

Comparisons with well-established paleoclimatic records show that the speleothems growth started early in the terminations and ended shortly after the onset of climatic deterioration associated with glacial stadials or interstadials. Precipitation cessation, in most cases, is expressed as an outcrop-scale discontinuity within the Neptune's Grotto flowstone. These discontinuities probably reflect growth cessation through groundwater freezing brought about by periglacial conditions owing to the lowering of the alpine glacial limit. Based on established growth rates for various sections, along with associated dates and correlations of their oxygen isotope variations with global paleoclimatic records, these outcrop-scale discontinuities represent depositional breaks ranging from 14 to ~102 kyrs. The hiatuses associated with these unconformities, which get longer with time, are accompanied by an increase in growth rates (also over time). These conditions are probably indicative of an opening of the cave system through enlargement and shallowing of the cave overburden through surficial erosional processes. This would allow not only for greater ventilation of the cave system, but could also shift the dissolutional system from closed (CO_2 source and carbonates separate) towards a more open system (where CO_2 and carbonates are coincident).

A simple growth model, based on minimum isotopic values of SPECMAP before or during terminations and after the beginning of climatic deterioration is presented. This "start-stop" model shows a very good correlation between growth periods and

terminations. The precipitation initiation and cessation lines, however, show mixed results, possibly owing to uncertainties related to global records, which might not be indicative, on sub orbital time-scales, of precise conditions encountered at OCNM.

Although not an aim of the research, it is of interest that the OCNM U-series dates and oxygen isotope data for the period ~135 to 121 ka support the estimates of the timing of Termination II from ice-cores and corals of ~134 to 132 ka rather than the later SPECMAP estimate.

Table 3.1 – Growth rate changes in response to increases in growth parameters.

Parameter	Mean	Modelled increase	Δ growth rate (mm· yr ⁻¹)
[Ca ²⁺]	$2 \times 10^{-3} \text{ mmol} \cdot \text{cm}^{-3} \pm 0.3 (1\sigma)$	$+ 1 \times 10^{-3} \text{ mmol} \cdot \text{cm}^{-3}$	+0.037
d	$0.08 \text{ mm} \pm 0.06 (1\sigma)$	+ 0.04 mm	+0.025
T _{dripwater}	10°C	+ 5°C	+0.018
pCO ₂ (cave air)	$3 \times 10^{-4} \text{ atm}$	$+ 1.5 \times 10^{-4} \text{ atm}$	+0.007

After Baker and Smart (1995).

Table 3.2 – U-series dates for OCNM speleothems.

Sample number	U (ppm)	Th (ppm)	Distance from base (mm)	$^{230}\text{Th}/^{234}\text{U}$ Age ^a (ka)	$^{230}\text{Th}/^{234}\text{U}^b$	$(^{234}\text{U}/^{238}\text{U})_{\text{initial}}^c$	$^{234}\text{U}/^{238}\text{U}^b$	$^{230}\text{Th}/^{232}\text{Th}^b$	$^{234}\text{U}/^{232}\text{Th}^b$
WFP-2-B	0.187	0.06	47-49	2.26 ± 0.02	0.02058 ± 0.00014	1.07468 ± 0.00255	1.07420 ± 0.00255	18.32 ± 0.2	890 ± 11
WFP-2-A	0.233	0.02	1-5	3.88 ± 0.02	0.03508 ± 0.00015	1.07091 ± 0.00198	1.07013 ± 0.00198	134.10 ± 1.2	3822 ± 38
ETC-B	0.168	0.66	127-129	11.98 ± 0.13	0.10450 ± 0.00103	1.12956 ± 0.00163	1.12523 ± 0.00163	7.99 ± 0.1	76 ± 1
ETC-E	0.169	0.77	109-112	14.29 ± 0.05	0.12342 ± 0.00037	1.11867 ± 0.00220	1.11396 ± 0.00219	7.94 ± 0.0	64.3 ± 0.4
ETC-D	0.183	0.53	74-77	116.69 ± 0.45	0.67317 ± 0.00135	1.15919 ± 0.00128	1.11385 ± 0.00123	69.25 ± 0.5	103 ± 1
ETC-A	0.197	0.42	36-38	117.50 ± 0.39	0.66967 ± 0.00114	1.13974 ± 0.00149	1.10015 ± 0.00144	91.66 ± 0.7	137 ± 1
ETC-C	0.189	0.16	1-7	119.25 ± 0.75	0.67487 ± 0.00212	1.13307 ± 0.00315	1.09490 ± 0.00305	224.42 ± 2.3	332 ± 4
NG-L	0.102	0.06	704-706	122.92 ^{+1.01} _{-1.00}	0.68187 ± 0.00288	1.06698 ± 0.00174	1.04727 ± 0.00170	345.5 ± 2.6	507 ± 4
NG-G	0.167	0.05	681-684	122.84 ^{+0.54} _{-0.53}	0.68193 ± 0.00150	1.07120 ± 0.00123	1.05026 ± 0.00121	384.10 ± 5.0	563 ± 7
NG-F	0.136	0.13	574-576	131.22 ± 0.74	0.70513 ± 0.00193	1.05588 ± 0.00126	1.03852 ± 0.00124	123.00 ± 0.8	174 ± 1
NG-E	0.085	0.09	508-511	234.9 ^{+2.9} _{-2.8}	0.89313 ± 0.00289	1.07200 ± 0.00122	1.03699 ± 0.00118	142.70 ± 1.6	160 ± 2
NG-D	0.161	0.38	435-437	315.3 ^{+6.9} _{-6.5}	0.95525 ± 0.00251	1.08543 ± 0.00381	1.03495 ± 0.00364	70.07 ± 0.6	73 ± 1
NG-J	0.169	0.39	435-437	326.6 ^{+8.8} _{-8.0}	0.96462 ± 0.00296	1.11996 ± 0.00425	1.04752 ± 0.00398	115.60 ± 0.6	120 ± 1
NG-I	0.086	1.05	219-221	359.3 ^{+9.8} _{-9.0}	0.97931 ± 0.00313	1.13926 ± 0.00112	1.05029 ± 0.00104	22.21 ± 0.2	22.7 ± 0.2

Note: Errors are quoted as 2σ.

^a Calculated using Kaufman and Broecker's (1965) equation and half-lives of ^{230}Th and ^{234}U of 75 383 and 244 500 years respectively.^b Activity ratio.^c Initial $^{234}\text{U}/^{238}\text{U}$ activity ratio calculated for $^{230}\text{Th}/^{234}\text{U}$ age.

Figure 3.1 CO₂ partial pressure control on carbonate dissolution: A) effect of temperature on biogenic soil pCO₂ and total soil pCO₂; soil pCO₂ is lower than biogenic pCO₂ due to inhibition effects of high CO₂ or low oxygen levels (Drake, 1983); and, B) equilibrium concentrations of Ca²⁺ with respect to calcite for open, closed, and restricted air volume systems ($V_{\text{air}} = V_{\text{solution}}$). The darker shaded area indicates equilibrium pCO₂ values below atmospheric equilibrium, where dissolution occurs (figures modified from Dreybrodt, 1999), while the light grey area shows the upper and lower limits of carbonate precipitation.

Figure 3.2 Effects of different parameters on cave calcite growth rate: A) precipitation rates for various film thicknesses (d in cm; the thicker line represents average film thickness of 7.5 cm^{-3} ; Baker and Smart, 1995) as a function of $[\text{Ca}^{2+}]$ in the water film ($T = 10^\circ \text{C}$, cave $p\text{CO}_2 = 3 \times 10^{-4} \text{ atm}$); B) precipitation rates (with $d = 0.01 \text{ cm}$ and cave $p\text{CO}_2 = 3 \times 10^{-4} \text{ atm}$) for various temperatures (in $^\circ \text{C}$); C) precipitation rates for various cave $p\text{CO}_2$ (in 10^{-3} atm) ($d = 0.005 \text{ cm}$, $T = 10^\circ \text{C}$); D) values of the kinetic constant α as a function of temperature for different film thicknesses (d in cm) (cave $p\text{CO}_2 = 3 \times 10^{-4} \text{ atm}$). All figures after Baker *et al.* (1998).

Figure 3.3 Location map of Oregon Caves National Monument. The lighter grey shades indicate maximum extent of Pleistocene glaciers and continental ice sheets.

Figure 3.4 Cross-section of Neptune's Grotto flowstone (~73 cm thick), unconformably overlying Triassic marble. Black arrows indicate outcrop-scale disconformities (numbered I to IV). Numbered sections on the left correspond to text descriptions. White arrow shows a broken stalactite resting on a disconformity surface. The open triangles indicate stratigraphic locations of U-series samples.

Figure 3.5 Hendy Tests results for two speleothem samples: A) WFP-2L and, B) NG. For the left panel of sample WFP-2L, subsamples were taken at approximately equal intervals from the apex (top) of the growth layer all the way down the side of the stalagmite (one subsample was lost during laboratory analyses). Subsamples for the NG flowstone were taken at equal intervals over the entire width (~3 cm) of the sample. The left panels show the absence of parallel enrichment of $\delta^{13}C$ and $\delta^{18}O$ with distance along coeval samples; the right panels show an absence of strong progressive positive relationship between $\delta^{13}C$ and $\delta^{18}O$ in sequential samples.

Figure 3.6 WFP-2L $\delta^{18}\text{O}$ values compared to the GISP2 and Vostok ice-core records for similar time periods. 3rd-order polynomial best-fit lines are shown for the WFP-2L and Vostok isotope records. A 3-point running mean is shown for the GISP2 record. This reduces the GISP2 record to a resolution similar to the WFP-2L's resolution (WFP-2L has 51 points while the GISP2 record has ≈ 160 points). $\delta^{18}\text{O}$ values are not available for the Vostok record. The speleothem isotopes are plotted relative to distance from base. Bars on the dates represent vertical sampling range and they have been lined up with the compared chronologies. One possible peak-correlation scenario is shown. The GISP2 data are from Grootes *et al.* (1993), Meese *et al.* (1994) and Stuiver *et al.* (1995). The Vostok data is from Chappellaz and Jouzel (1992).

Figure 3.7 NG $\delta^{18}\text{O}$ values compared to the GRIP ice core (Johnsen *et al.*, 1993), Vostok (Chappellaz and Jouzel, 1982), and the SPECMAP (Imbrie *et al.*, 1984) marine record's $\delta^{18}\text{O}$ signatures for the Termination II/5e period. A 3rd-order polynomial best-fit line is shown for the NG record. The speleothem isotopes are plotted relative to distance from base. The dated intervals for NG-L and NG-F have been lined up with the compared chronologies. Bars on the dates represent vertical sampling range. TII bars represent the locations of the MOIS6/5 termination for various records. The marine isotope substage number is indicated on the SPECMAP curve.

Figure 3.8 Tentative correlation of NG $\delta^{18}\text{O}$ values relative to the GRIP ice core (Johnsen *et al.*, 1993) and SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ records for parts of MOIS 7. The speleothem isotopes are plotted relative to distance from base. The dated interval has been lined up with the compared chronology. Bars on the dates represent vertical sampling range. The marine isotope stage number is indicated on the SPECMAP curve.

Figure 3.9 NG $\delta^{18}\text{O}$ values relative to the SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ record for parts of MOIS 11 through 9. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The dated interval has been lined up with the compared chronology. Bars on the dates represent vertical sampling range. The marine isotope stage numbers are indicated on the SPECMAP curve.

Figure 3.10 NG $\delta^{18}\text{O}$ values relative to the Devils Hole (Winograd *et al.*, 1992) and SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ records for parts of MOIS 12 through 11. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The marine isotope stage numbers are indicated on the SPECMAP curve.

Figure 3.11 NG $\delta^{18}\text{O}$ values relative to the SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ record for parts of MOIS 13. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The marine isotope stage number is indicated on the SPECMAP curve.

Figure 3.12 (following page) A) Composite OCNM $\delta^{18}\text{O}$ record compared to the SPECMAP (Imbrie *et al.*, 1984) stacked marine record (with marine isotope stage numbers), Devils Hole (Winograd *et al.*, 1992) $\delta^{18}\text{O}$ record, GRIP (Johnsen *et al.*, 1993) $\delta^{18}\text{O}$ ice core record, Vostok (Chappellaz and Jouzel, 1992) δD ice core record and GISP2 (Grootes *et al.*, 1993; Meese *et al.*, 1994; Stuiver *et al.*, 1995) $\delta^{18}\text{O}$ ice core record; B) southwestern Oregon speleothem growth model. Speleothem growth is indicated by heavy black arrows. The upper and lower dotted lines represent approximate upper and lower thresholds for speleothem precipitation according to the location of U-series dates on the marine curve. U-series dates are plotted against the oxygen isotope data from Imbrie *et al.* (1984). Dashed vertical lines represent location of Terminations. Grey areas represent inferred (outlined) and recorded precipitation cessation intervals (hiatuses).

4.0 A 500 KA TERRESTRIAL STABLE ISOTOPE RECORD OF INTERGLACIALS FROM SOUTHWESTERN OREGON: PALEOCLIMATIC AND PALEOENVIRONMENTAL IMPLICATIONS

4.1 Abstract

Stable isotopes (O and C) signatures were obtained from cave calcites from Oregon Caves National Monument (OCNM). The age model applied to the speleothems is provided by 14 U-Th TIMS dates in conjunction with global paleoclimatic proxies from marine and ice cores for the undated parts of the record. The dates indicate mean growth rates between 5.6 and 27.9 mm/kyr, mostly during early- to mid-interglacial periods. $\delta^{18}\text{O}$ values vary from -6.38 to -16.86‰ (mean = -7.36‰, 1σ = 3.70), while $\delta^{13}\text{C}$ values range from +5.45 to -11.19‰ (mean = -9.84‰, 1σ = 1.84) (V-PDB). Although the O and C records generally parallel each other, the overall correlation coefficient is low (r^2 = 0.29). The relationship between isotopes and temperature was tested for the best-dated part of the record – marine oxygen isotope substage 5e. Both O and C isotopes peak at around ~130 ka, indicating a simple positive relationship of isotopes and temperature, and a direct relationship with global paleotemperatures; they also provide support for the timing of the 5e peak at around ~130 ka. Oxygen isotopic records from the last 6 interglacials show values close to those of modern cave calcites and episodic negative spikes. A short period from isotope stage 11 shows values above modern. For most of the interglacial peaks, carbon isotopic values follow oxygen values. However, prominent positive carbon excursions occur, unmatched to oxygen isotopes, which may be

explained by depression of treeline. Oxygen isotope values reflect glacial to interglacial atmospheric transport processes; carbon isotope values are probably controlled by biomass-water-rock interactions. Outcrop-scale discontinuities, representing periods of prolonged growth stoppage, translate into hiatuses ranging from 14 to 102 kyrs and are presumed to be caused by groundwater freezing during extended periglacial conditions triggered by the lowering of periglacial thresholds by as much as 1800 m during glacial periods.

4.2 Introduction

The use of speleothem stable isotopes as paleotemperature and paleoclimatic indicators was established in the late 1960s (Hendy and Wilson, 1968) and 1970s (Emiliani, 1971; Thompson *et al.*, 1976). Dorale *et al.* (1992) showed that, with improvements in mass spectrometry of the last decade, it is now feasible to use speleothem for high-resolution climate change studies and thus help to fill the huge gap in paleoclimatic evidence from terrestrial records older than the Holocene. Increasing attention is being focused on high-resolution paleoclimatic studies of terrestrial environments in order to establish global teleconnections (Rittenour *et al.*, 2000) and the timing of global events as expressed in land-based environments (Winograd *et al.*, 1992). However, few high-resolution paleoclimatic studies have been done in North American mid-latitude, west coast settings. Such a setting offers a relatively simple climatic system where westerly atmospheric circulation provides a moisture source to coastal environments that emanates unequivocally from the Pacific Ocean. This W-E atmospheric circulation provides a

direct link for transferring global signals from the oceans to the land. Speleothems from areas south of the Pleistocene ice limit, where calcite precipitation may not have been interrupted by frozen groundwater during glacial periods, can provide long-term high-resolution carbon and oxygen isotope records which can be precisely dated using the U-Th method (Edwards *et al.*, 1986; Blackwell *et al.*, 1995 and references therein). In addition, these records can provide information concerning global linkages through direct comparison with well-established $\delta^{18}\text{O}$ records from marine- (Imbrie *et al.*, 1984; Shackleton *et al.*, 1990) and ice cores (Chappellaz and Jouzel, 1992; Grootes *et al.*, 1993a and b; Johnsen *et al.*, 1993; Meese *et al.*, 1994; Stuiver *et al.*, 1995), as well as other terrestrial records such as “vein” calcites (Winograd *et al.*, 1992). In this paper, we present paleoenvironmental trends extracted from the high-resolution isotopic record of speleothem calcites from southwest Oregon and discuss the implications for global paleoenvironmental reconstructions.

4.3 Physical setting

Oregon Caves National Monument (OCNM, 42°05'30" N, 123°24'00" W) is situated on steep westward facing slopes of the Klamath Mountains, 65 km from the Pacific Ocean (Figure 4.1), at an altitude of approximately 1400 m asl in southwestern Oregon. The site is nested amidst an old-growth fir forest providing abundant organic matter to the soils overlying the cave. This site, well south of the maximum limit of Pleistocene ice sheets (Figure 4.1), was chosen in order to minimise the likelihood of ground freezing during glacials and increase the odds of finding a continuous speleothem depositional record

while remaining northward of more evaporative latitudes. In addition, its proximity to a steeply dipping plate margin and windward orientation should minimise glacial-interglacial variations in certain geographic factors that pertain to stable isotopic reconstructions, such as distance of atmospheric moisture travel and rain shadow effects.

Long-term weather data for OCNM are scarce. The closest weather stations to OCNM with reliable weather data are located in Cave Junction, Oregon (21 km WNW, altitude ~390 m), and Happy Camp, California (33 km S, altitude ~341 m). Average annual precipitation at Cave Junction from 1962 to 1993 was 151 cm with average annual temperatures of 11.8°C during the same period, while the average annual precipitation and average annual temperature at Happy Camp from 1931 to 1993 were 141 cm and 13.0°C respectively (National Weather Service website). Precipitation data recorded at OCNM for 1991 indicate 148 cm of total precipitation, with much of this occurring as winter snow (OCNM internal document). Given the high relief of the area, temperatures can vary dramatically over short distances. For example, Grants Pass (altitude ~282 m) and Sexton Summit (altitude $\approx$ 1169 m) weather stations, NNE of OCNM, are only 16 km apart but their average annual temperatures vary considerably (12.6°C and 8.8°C respectively) (US National Weather Service website). The average annual temperature within the cave, thought to reflect mean annual surface temperature (Wigley and Brown, 1976; Harmon *et al.*, 1978), is estimated to be 7°C (Sims, undated). As well, average temperatures at the cave site are below the freezing point for approximately three months of the year (OCNM internal document).

The geological setting of OCNM is part of the Applegate Formation (Triassic) of the Rattlesnake Creek subterranean. This formation is largely composed of volcanic arc basalts (Orr *et al.*, 1992), although most of the Applegate rocks within the boundaries of the Monument are argillites, with small outcrops of metabasalts, serpentine, andesite, chert, talc, as well as a substantial pyrite-rich argillite bounded marble lens in which the cave developed (Orr *et al.*, 1992). OCNM consists of a main dissolutional phreatic cave. Cave development was controlled by a NE-SW joint system and high-angle (60° to 85°) N-S trending normal faults within the marble lens. Most of these joints and faults formed in response to tectonic activity during the Miocene (Wells and Heller, 1988) and allowed penetration of water deep into the subsurface and regulated the alignment of passages in the cave. The cave contains several subhorizontal levels, representing former water table positions controlled by river down-cutting, joined by vadose shafts. The most laterally extensive level, located approximately 28 m above the main entrance, contains thick flowstones that were sampled for this study. The higher levels have few speleothems. The cave is approximately 100 m below the surface and the dripwater route is entirely through marble (Orr *et al.*, 1992).

4.4 Methodology

Three samples were collected for this study: a 5 cm high stalagmite (from the *White Formation Passage*; WFP-2L) and two flowstones (a 73 cm thick flowstone from *Neptune's Grotto* – NG, and a 13 cm thick flowstone from the *Exit Tunnel Cave* – ETC). Figure 4.2 shows a cross-section through the NG flowstone section. In order to avoid

evaporative effects and short-term temperature variations (Harmon *et al.*, 1979), all samples were taken from areas of high humidity and low air flow, deep in the cave and away from natural entrances. Speleothems were cut and ground/polished. Powdered samples for X-ray diffraction were used in conjunction with standard polarised light microscopic observations performed on contiguous thin sections to test for the primary nature of the crystals. Crystal fabric was studied in detail (Turgeon and Lundberg, in press a).

Samples of Triassic marble were analysed for stable isotope ratios in order to qualify water-rock interactions as a control on the isotopic composition of the cave calcites. In order to establish the present-day relationship between dripwaters and modern cave calcite oxygen isotope ratios, twenty-two rainwater samples were collected in October of 1998 and analysed for oxygen isotopes at Geochron Labs in Massachusetts, along with a recent soda straw and a dripwater sample collected in November 1995. The speleothems were sampled for isotopic ratios along visible growth layers in order to rule out non-equilibrium depositional (with respect to dripwaters) controls of stable isotope signatures (Hendy, 1971). This Hendy test was done on the WFP-2L stalagmite and near the base of the NG flowstone. This test was not performed on the ETC flowstone owing to the lack of clear growth banding. The speleothems were then sampled along their growth axes for oxygen and carbon stable isotopic ratios using a 0.6 mm dental burr. Samples were taken every mm for the stalagmite and every 2 mm for the flowstones. CO₂ was obtained through H₃PO₄ digestion and analysed using a Micromass Siral2 mass spectrometer at the University of Ottawa. Analytical errors are $\pm 0.1\%$ and $\pm 0.05\%$ for oxygen and

carbon respectively. Unless otherwise noted, all isotopic results in this paper are expressed in ‰ relative to the Vienna-Pee Dee belemnite (V-PDB) standard.

In order to establish growth mechanisms and depositional history of the speleothems, outcrop-scale features such as discontinuities were mapped. Fourteen high-precision thermal-ionisation mass spectrometry (TIMS) U-series dates were performed at the University of Bergen on a Finnigan-MAT 262 RPQ solid source mass spectrometer. Sample sizes varied from 1 to 2 g, representing 2 to 7 mm vertical thicknesses of the speleothems. Samples were cleaned ultrasonically and ignited to remove organics. A ^{229}Th - ^{223}U - ^{236}U spike was added as a reference. U and Th fractions were separated in anion exchange columns, loaded onto Re filaments with silica gel (U) or graphite (Th). The isotopic ratios were measured in peak switching, ion counting mode. Relative 2σ errors on the calculated ages range from 0.32 to 2.62%, with greater errors occurring on older samples, close to the limit of the dating technique.

Given the high costs associated with this dating technique and also that significant parts of our flowstone sections lie beyond the range of the U-Th dating method, the speleothem isotopic signature chronologies were established using the U-series dates in conjunction with well-established isotopic global paleoclimatic proxies from marine- (SPECMAP; Imbrie *et al.*, 1984) and ice cores (Vostok; Chappellaz and Jouzel, 1992; GISP2; Grootes *et al.*, 1993a and b; Meese *et al.*, 1994; Stuiver *et al.*, 1995; and GRIP; Johnsen *et al.*, 1993), as well as the terrestrial “vein” calcite record from Devils Hole in Nevada (Winograd *et al.*, 1992). The method relies on the relationship between speleothem

oxygen isotopic ratios and global paleoclimatic proxies for well-dated sections; a good correlation has been found for a well-dated speleothem interval from the Sangamon and the growth rate was found to be linear between the dates. This relationship is assumed to be valid for other sections of the speleothem with less reliable dating or lying beyond the range of the U-Th method. Then the age of the best fit proxy is applied to the speleothem isotopic curve. Complete details of the methodology employed are discussed in Turgeon and Lundberg (in press b).

4.5 Results

Average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the Triassic marble are -4.87 and +1.67‰ respectively. The $\delta^{18}\text{O}$ values for the dripwater sample and the tip of the soda straw are -41.14‰ and -8.70‰ respectively. The average isotopic ratio of the October rainwater samples ($\delta^{18}\text{O}_{\text{rain}}$) is -38.7‰ ($1\sigma = \pm 2.5\%$). For comparison, the closest long-term precipitation isotope data hails from Destruction Island off the coast of Washington state (47°40'12" N, 124°28'48" W, altitude = 21 m). Data collected from 1962 to 1966 show a bimodal summer-winter distribution (IAEA/WMO, 1998). These values are summarised in Table 4.1; they are then corrected for the altitudinal difference ($\Delta \approx 1400$ m) between Destruction Island and the cave site following Gat's (1981) factor of -0.33‰/100 m.

Figure 4.3 shows the isotopic data for all three speleothems plotted against distance from their respective bases and the location of the U-series subsamples. The isotopic records (Figure 4.3) show high-variability in both the O and the C records with isotopic values

ranging from +5.45 to -11.19‰ ($\delta^{13}\text{C}$), and -6.38 to -16.86‰ ($\delta^{18}\text{O}$). Mean values are -7.36‰ (1.85 1σ) for $\delta^{13}\text{C}$ and -9.84‰ (0.92 1σ) for $\delta^{18}\text{O}$. The C and O records parallel each other but have a low overall correlation coefficient (r^2) of 0.29, although correlation coefficients for the three samples vary (WFP = 0.62; ETC = 0.44; NG = 0.26). 3rd-order polynomial trendlines show amplitudes up to 1.5‰. Prominent positive carbon excursions, unmatched to oxygen isotope variations, occur within the ETC and NG flowstone records. At least two of these carbon isotope enrichments occur near discontinuities on the NG record (at the top of the flowstone at 715 mm and at 530 mm from the base of the flowstone)(Figure 4.3). General enrichment trends in carbon isotopes can also be observed between 40 and 260 mm from the base of the NG flowstone, as well as between 72 and 130 mm from the base of the ETC flowstone, forming isotopic plateaus. An abrupt $\delta^{13}\text{C}$ depletion occurs within the ETC record between 30 and 50 mm from the base of the flowstone. This corresponds to a similar depletion within the oxygen record, although of lesser magnitude. Several single depletion “spikes” of up to 7‰ in magnitude can be observed within the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ curves. Many (~60%) of these spikes are coincident and these depletion events appear to diminish upwards in the NG flowstone (Figure 4.3). Oxygen isotopes records from the last six interglacials show values close to those of modern cave calcites and episodic negative spikes. Two short periods from isotope stage 11 (at 150 and 180 mm from the base of the NG flowstone) show values rising above the modern cave calcite values modern.

All the TIMS U-series dates are in stratigraphic order, except for two (NG-G and NG-L) that have overlapping 2σ errors (Table 4.1). These ages range from 2.3 ka to 359 ka. Two subsamples (NG-D and NG-J) were taken from the same interval of two overlapping samples within the Neptune's Grotto section and have overlapping 2σ errors. Two samples (ETC-B and ETC-E) have low (<10) $^{230}\text{Th}/^{232}\text{Th}$ ratios (Table 4.2), which could be indicators of detrital contamination of the samples (Blackwell and Schwarcz, 1995). However, both samples had no visible detrital contamination and their absolute Th concentrations are below 1 ppm (0.66 and 0.77 respectively). These factors, in addition to the high $^{234}\text{U}/^{232}\text{Th}$ activity ratios in these samples (76 and 64), and the minor impact of these ages on the final interpretation, contributed to our decision not to correct for an assumed initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in these samples. As well, two dates (NG-A and NG-B) lie beyond the range of TIMS U-Th dating (Table 4.2). The outcome of the speleothem growth modelling is presented in Figure 4.4, the composite growth diagram for all three speleothems analysed. All subsequent graphs of isotopic values against age are based on this model.

4.5.1 WFP stalagmite

The youngest speleothem in our study is the WFP-2L stalagmite, with a basal date of 3.88 ± 0.02 ka (WFP-2-A) and a top date of 2.26 ± 0.02 ka (WFP-2-B), indicating a mean growth rate of $3.2 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$ during a 1600 year growth interval. This growth rate is in good agreement with Norwegian ($2.0 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$; Linge, 1999) and Irish (2.8 to $3.4 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$; Vesely, 2000) interglacial stalagmites and flowstones. In addition, similar

growth rates ($2.8 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$) have been calculated for the ETC flowstone. Figure 4.5 illustrates the isotope record of the WFP-2L stalagmite compared to the high-resolution ice cores from Greenland (GISP2; Grootes *et al.*, 1993a and b; Meese *et al.*, 1994; Stuiver *et al.*, 1995) and Antarctica (Vostok; Chappellaz and Jouzel, 1992). In the ice cores, isotopic enrichments indicate increased global temperatures (Grootes *et al.*, 1993a and b). Although sampled at different resolution, the WFP-2L record shows a series of depletion events occurring approximately every 200 years, which appear to correlate with events of similar periodicity in the GISP2 record (Grootes *et al.*, 1993a and b; Meese *et al.*, 1994; Stuiver *et al.*, 1995). The lower resolution of the Vostok ice core probably obscures these short-term shifts.

4.5.2 ETC flowstone

Three dates (ETC-C, ETC-A and ETC-D) from the Exit Tunnel Cave flowstone ranging from 116.7 ± 0.5 to 119.3 ± 0.8 ka (isotope substage 5e) indicate a high growth rate ($2.8 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$) in the lower section of the flowstone; two dates (ETC-E and ETC-B) in the upper section of the flowstone are clearly late Wisconsinan (MOIS 2) and indicate a growth rate of $7.6 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$. The time scale for the ETC flowstone was established by linear interpolation between the U-Th dates owing to a lack of paleoclimatic proxies of similar resolution. No outcrop-scale discontinuity has been observed and no microscopic evidence of precipitation stoppage has been identified, suggesting that growth was continuous throughout the Wisconsin glacial period (Figure 4.6), although complete growth cessation could have occurred without leaving evidence. The interval between

ETC-D and ETC-E, broadly corresponding to the colder conditions of marine oxygen isotope stages (MOIS) 4 through 2 (and including late 5), therefore represents either severely reduced growth ($\sim 3.0 \times 10^{-4} \text{ mm} \cdot \text{a}^{-1}$) or a break in deposition of approximately 102 kyrs. The isotopes for this section provide few clues into this problem as the $\delta^{18}\text{O}$ values have remained more or less constant between the two dates (ETC-D and ETC-E) constraining stages 4 through 2. The mean growth rates for the section should therefore be considered minimum growth rates. The carbon isotopes display a prominent short-lived (<200 years) depletion around 118 ka, as well as a general enrichment plateau from 117 ka to the top of the flowstone at 11.5 ka.

4.5.3 *NG flowstone*

The depositional history of the NG flowstone was established using seven U-series dates (Table 4.2). Figure 4.3 shows the distribution of four outcrop-scale discontinuities within the NG flowstone with respect to the stable isotopes. Debris such as broken soda straw and stalactites lie horizontally on these surfaces (Figure 4.2). Although columnar calcite crystals with rhombohedral terminations protrude from these sub-horizontal surfaces, they are generally smooth, and are covered with a thin layer of allogenic brownish mineral detritus. A mean growth rate of $1.6 \times 10^{-2} \text{ mm} \cdot \text{a}^{-1}$ was obtained using three U-Th dates from the upper growth interval (Section 1; Figure 4.2).

In Figure 4.7, the NG isotope record is shown plotted against the marine isotope stage 6 to 5 transition in the GRIP and Vostok ice core isotope records, as well as the SPECMAP

marine isotope record. In order to highlight similarities with these records, 3rd-order best-fit polynomial trendlines have been added to the speleothem and the GRIP $\delta^{18}\text{O}$ record. Marine oxygen isotope stage 6 is missing from the NG record; initiation of calcite precipitation coincides with the onset of climatic warming. Although the data trends are similar in all four records, the actual timing of major events is different. Similarities in the relative chronology are apparent: both the GRIP and the NG record reach their peak around 130 ka (based on the trendlines), approximately 1 kyr before the Vostok record. These offsets lie within the 2σ ranges of the dates, indicating that they are indistinguishable from each other. In addition, the peak chronology is in agreement with coral data from the Bahamas that indicate that the high sea-level stand during marine isotope substage 5e occurred between 132 and 129 ka (Chen *et al.*, 1991). For the most part, the carbon isotopic values conform to the oxygen record: the most prominent features for this section are the sharp positive excursions occurring at both ends of the section and lasting between 1 to 2 kyrs each.

The second section of the NG flowstone is anchored by only one U-series date (≈ 235 ka). The NG oxygen isotope record for this section has been compared to the GRIP and SPECMAP records (Figure 4.8). All records are similar and the NG and GRIP records have three peaks that can be tentatively correlated. The GRIP record goes back to 250 ka, thus leaving a section of the NG (approximately 4 kyrs) record without any direct comparison to a high-resolution record. A mean growth rate of $2.9 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ over a 23 kyrs period from 254 to 231 ka has been estimated based on the correlation between records, indicating slow speleothem growth during MOIS 7.

The chronology of the lowermost dated NG interval (Section 3) is validated using the mean date provided by the overlapping samples (NG-D and NG-J) indicating MOIS 9 deposition, along with a third date (NG-I) from a lower interval (MOIS 10)(Figure 4.9). Based on these dates, a mean growth rate of $5.6 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ between these two outcrop-scale discontinuities is calculated. This interval thus represents approximately 51 kyrs of growth, from marine isotope stages 11 through 9. This section of the NG flowstone shows trends within the 3rd-order best-fit polynomial trendline of the calcite $\delta^{18}\text{O}$, broadly correlating in trends in the SPECMAP marine record (Figure 4.9). The record contains several negative spikes and one prominent positive spike rising above the modern calcite $\delta^{18}\text{O}$ value. No prominent trend can be found in the carbon isotopes for this section, although several prominent carbon enrichment peaks occur near the base of this section.

The chronological control for sections 4 and 5 of the NG flowstone (which are lacking or beyond U-series chronological control) has been established using a linear growth rate assumption and peak-matching to other records of global paleoclimates (SPECMAP: Imbrie *et al.*, 1984; Devils Hole: Winograd *et al.*, 1992). Figure 4.10 illustrates the correlation for NG Section 4. The best correlation between the paleoclimatic records occurs between 393 ka and 443 ka, when the shape of the isotopic signatures within all three records correlates. One of the main features of the $\delta^{18}\text{O}$ signatures for this section is a prominent spike rising above the modern $\delta^{18}\text{O}_{\text{calcite}}$ value. Using this chronology, a mean growth rate for this NG interval of $3.2 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ was calculated. This growth

rate is comparable to a rate of $2.1 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$ for a well-dated Norwegian flowstone from MOIS 11 (Lauritzen and Lundberg, in press).

Figure 4.11 shows the lowermost NG interval (Section 5), constrained upwards by an outcrop-scale discontinuity and lying on the marble bedrock (Figure 4.2). The shape of the oxygen isotopic curve matches the SPECMAP record, indicating a growth interval from 519 to 462 ka, placing this deposition at the beginning of MOIS 13. The mean growth rate for this interval is $1.5 \times 10^{-3} \text{ mm} \cdot \text{a}^{-1}$. The estimated age for the lower part of this interval indicates that initiation of speleothem deposition in this area of the cave probably started around 519 ka. The $\delta^{13}\text{C}$ record shows a marked departure from the oxygen record from about 495 ka onward as the $\delta^{13}\text{C}$ values become more positive.

4.6 Discussion

4.6.1 *OCNM isotopes as paleoclimatic indicators*

To use cave calcites as paleoclimatic indicators, the primary nature of the crystals must first be established. According to Folk and Asseretto's (1976) criteria, no clear evidence of recrystallisation, such as randomly-oriented equant calcite crystals, was observed in the samples. The absence of aragonite, from which stable calcite could have recrystallised, is confirmed by powder XRD data. This evidence indicates that the crystals were originally calcite and have not recrystallised. Over 90% of these speleothems consist of columnar calcite crystals; minor fabrics, such as transitional- and

randomly-oriented elongate calcite crystals, are seeded on small discontinuities and detrital layers (reported in detail by Turgeon and Lundberg, in press a).

The second requirement is that the cave calcites must have been deposited in isotopic equilibrium with their dripwaters, as during slow degassing; in this case, the isotopic fractionation between the aqueous and solid phases is controlled (indirectly) by cave temperature. However, under evaporative cave régimes, rapid degassing or rapid crystallisation, the isotopic fractionation is modulated by kinetic effects that inhibit isotopic equilibrium in the calcite-dripwater system (Hendy, 1971). Many dissolutional caves, especially in humid temperate climates, have high relative humidity levels (>90%), an environment in which cave calcites are unlikely to have been deposited through evaporation of the dripwaters. Hendy (1971) has devised a test for isotopic equilibrium deposition of cave calcites. Calcite $\delta^{13}\text{C}$ within a growth layer should progressively enrich away from the dripwater source, as $^{12}\text{CO}_2$ is preferentially lost over $^{13}\text{CO}_2$ under slow degassing conditions. In this scenario, the $\delta^{18}\text{O}$ values along the same growth layer should remain constant given the large volume of water in the system. Under evaporative conditions, however, H_2^{16}O is preferentially lost down-speleothem. This produces a synchronous enrichment of both the O and C isotopes. This test is however hampered by two problems: 1) the sampling of coeval growth layers, typically only a few tens of microns thick, with drill burs of up to 1 mm in diameter can obscure or average the isotopic signatures from several layers to different degrees (remembering that for stalagmites, the growth layers become thinner away from the apex); 2) given that the direction of water flow over the speleothem must be known, establishing this flow

direction over the subhorizontal surfaces typically found on flowstones can prove difficult. In spite of these practical difficulties, the test was still carried out as no practical alternative is yet available.

For both the WFP-2L and the NG speleothem, the results of the Hendy tests show the absence of synchronous enrichment of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values away from the dripwater source (Figure 4.12). Furthermore, the results show no relationship between the C and the O isotopes, which could suggest fractionation controlled by evaporation. These data, taken in conjunction with the physical setting of the samples (from areas of high humidity removed from high air flow and natural entrances), indicates that the calcite crystals were deposited in isotopic equilibrium with their dripwaters.

The third requirement is to establish the link between dripwaters and climate. In temperate climates infiltration occurs year round, in cold climates frozen ground inhibits the infiltration of winter precipitation, and warm and dry climates inhibit the infiltration of summer precipitation. The infiltration waters (cave dripwaters) become integrated over time (Yonge *et al.*, 1985), incorporating infiltration biases, if any. For example, Linge (1999) reports that the $\delta^{18}\text{O}$ of speleothem calcites from northern Norway reflect a bias towards summer rain. For the OCNM speleothems, the link between the dripwaters and climate was tested using a modern soda straw, dripwater and rainfall data. For different $\delta^{18}\text{O}_{\text{dripwater}}$ inputs, the $\delta^{18}\text{O}_{\text{calcite}}$ values were calculated following:

$$\alpha = \frac{\delta^{18}\text{O}_{\text{calcite}} + 1000}{\delta^{18}\text{O}_{\text{dripwater}} + 1000}$$

where α is the fractionation factor between calcite and water. At the mean annual cave temperature of 7°C, α is 1.0331 (O'Neil *et al.*, 1969). The measured $\delta^{18}\text{O}_{\text{calcite}}$ of the soda straw of -8.70‰ represents some tens of years of growth. Long-term $\delta^{18}\text{O}_{\text{dripwater}}$ values are not available; the dripwater sample (-41.14‰) came from a fast drip which responded rapidly to a rainfall event a few days earlier. Rainfall collected in October of 1995 shows a wide range of values (Table 4.1). If these values are used in the equation above, the calculated values for the $\delta^{18}\text{O}_{\text{calcite}}$ are -9.4‰ and -4.3 to -9.5‰ respectively. The calculated $\delta^{18}\text{O}_{\text{calcite}}$ using the translated values from rainwater collected over a four year period at Destruction Island are shown in Table 4.1 and in Figure 4.13, separated according to season. The results using the summer values are closest to the actual $\delta^{18}\text{O}_{\text{calcite}}$ of the soda straw; the winter values are well below it. This implies that winter precipitation does not contribute significantly to the calcite deposition. This is supported by the observation that the average monthly temperatures for December, January and February are below 0°C (OCNM internal document); much of the winter snowfall and spring melt flows overland and does not infiltrate. This indicates that the $\delta^{18}\text{O}_{\text{calcite}}$ values are biased towards spring through autumn rainfall.

The fourth requirement is to establish the direction of the relationship between isotopes and temperature. This is done for the well-dated section of MOIS 5e: this part of the NG speleothem record (Figure 4.7) shows a clear direct correlation with the ice record

indicating that elevated $\delta^{18}\text{O}$ values represent warmer conditions, while isotopic depletion occurs during colder phases. The direction of the $\delta^{18}\text{O}$ and temperature relationship is also displayed, albeit weakly, by the late Holocene $\delta^{18}\text{O}$ isotopic record (Figure 4.5). The good correlation between the synchronicity of the trends between the OCNM isotopes and well-established global paleoclimatic signatures from ice- and marine cores indicates that the cave calcites are indicative, at the very least, of some of the same global processes controlling stable isotopes in other records. The linkage between long-term climate variability and speleothem isotopes (both carbon and oxygen) is explored below.

4.6.2 *Fractionation controls on OCNM cave calcite oxygen isotopes*

For OCNM speleothems deposited in isotopic equilibrium with their associated dripwaters, the $\delta^{18}\text{O}$ of the calcite is controlled by (a) ocean surface temperatures and the isotopic value of the northeastern Pacific Ocean, ultimately feeding the clouds that advect over the cave site; (b) the $\delta^{18}\text{O}$ of the dripwaters feeding the speleothems, which is more or less directly related to the $\delta^{18}\text{O}$ of meteoric water and controlled by the mean annual surface temperature above the cave site and taken as a proxy for various geographic factors affecting the air masses such as changes in altitude, degree of rainout, and rehydration of the vapour mass from evapotranspiration of different surface sources (Grootes, 1993); and (c) the temperature of cave, which approximates the mean annual air temperature above the cave (Wigley and Brown, 1976) and governs the thermodynamic fractionation between water and calcite. Table 4.3 provides a summary

of all the fractionation effects controlling the $\delta^{18}\text{O}$ of the cave calcites during glacial/interglacial cycles. Figure 4.14 illustrates the different controls of the oxygen isotopes operating along the ocean-atmosphere-cave system for OCNM as discussed below.

4.6.2.1 Ocean effects

The *ice-volume effect* represents changes in isotopic composition of ocean waters between glacial and interglacial periods, with seawater becoming enriched as ice volume increases (Shackleton and Opdyke, 1973). The $\delta^{18}\text{O}$ value of sea water ($\Delta\delta^{18}\text{O}_{\text{seawater}}$) changed by approximately 1.5‰ during glacial-interglacial transitions (Shackleton, 1968; Shackleton, 1987), indicating that the water removed had an isotopic composition similar to that of the snow in the interior of Antarctica (-45‰ to -50‰) (Emiliani and Shackleton, 1974). The oxygen isotopic values of a marine core from the northeast Pacific Ocean (Y9010002; 41°16' N, 127°01' W) show an average glacial-interglacial $\delta^{18}\text{O}_{\text{V-PDB}}$ difference of approximately 1.6‰ for benthic foraminifera (CLIMAP Project Members, 1981). For this study, these values are taken as a proxy of source water composition (ice-volume effect) affecting the vapour above the ocean (Curve a in Figure 4.14).

The *ocean surface temperature effect* reflects the temperature-dependent fractionation between liquid and vapour phases over ocean surfaces, the source of the atmospheric moisture. As temperatures decrease during glacials, fractionation increases. Table 4.4 gives a list of marine cores from the northeastern Pacific Ocean located at approximately

the same latitude as OCNM for which sea surface temperature (SST) reconstructions have been done for full glacial conditions at 18 ka (Moore *et al.*, 1980). The two cores closest to our site (Y6604-10 and Y6609-10) show that SSTs during the last glacial were approximately 10.5°C on average, while present-day SSTs range from 11 to 15.5°C (average of approximately 14°C for the area), indicating that temperatures during glacials were approximately 3.5°C cooler than present-day conditions. Given that Ruddiman (1984) has shown that temperatures were 1.5°C higher at this site during isotope substage 5e, the maximum glacial-interglacial SST difference is approximately 5°C.

The combination of ice volume and ocean surface temperature allow us to approximate vapour conditions above the ocean that will eventually affect the precipitation over the study area. Between glacials (10.5°C; $\alpha = 1.01067$) and interglacials (15.5°C; $\alpha = 1.01018$), the oxygen isotopic fractionation during evaporation at the sea surface causes a slight depletion of the vapour phase. Correcting for the ice volume effect and assuming an interglacial/glacial $\delta^{18}\text{O}$ range of 0 to +1.6‰ (CLIMAP Project Members, 1981), the resulting vapour would follow a quasi-linear depletion from interglacials to glacials of approximately 0.2‰ per °C, from -8.97 to -10.08‰, following Horita and Wesolowski's equation (1994) (Curve b in Figure 4.14). The varying SST thus reduces the effect of the ice volume component by approximately 60%, following a gradient of about -0.1‰ per °C. Combined, these two fractionation mechanisms produce a net depletion in the vapour phase from glacials to interglacials on the order of 0.1‰ per °C. This atmospheric vapour is then transported towards the rainout site over the cave by Westerlies (during interglacials at least).

4.6.2.2 Meteoric water effects

The *meteoric water effect* relates to the modification of air masses en route towards the site of rainfall in the vicinity of the cave: it is a function of rainout before it reaches the site and relates to storm-tracks, evapotranspiration en route, re-evaporation of rain droplets and surface water, altitude changes and temperature over the precipitation site (Dansgaard, 1964; Grootes, 1993). During glacials, fractionation increases because of the lower temperatures causing an increase in rainout, producing isotopically depleted rain over the cave site compared to interglacial rainwater values. This transport follows finite reservoir depletion patterns according to Rayleigh distillation models (Broecker and Oversby, 1971) that cannot easily be modelled directly. However, for this particular site, two assumptions can be made that help to circumvent this difficulty: (i) present-day storm tracks follow westerly winds bringing vapour from the Pacific Ocean and this is likely to have remained true during glacials because of the latitudinal position of OCNM (Kutzbach *et al.*, 1993); and (ii) owing to OCNM's proximity to the steeply dipping coast, the variation in distance between the vapour source and the cave site (rainout) are assumed to be negligible.

Given present-day values for the seawater, the vapour over the ocean, and cave calcites, we can model the vapour over the cave site and the dripwater values for today. However, for glacial times these cannot be modelled because Rayleigh distillation effects cannot be calculated directly; land temperatures (taken as proxy for cloud-base temperatures) and other controls on rainout are poorly known. In order to estimate the values for the vapour

and rainwater/dripwater of the cave site (Curves c and d in Figure 4.14), we have to work back from the empirical calcite isotopic values in glacial conditions. The actual $\delta^{18}\text{O}_{\text{calcite}}$ values vary from -12.94‰ during glacials to -7.72‰ during interglacials after 3-point smoothing of the raw data, indicating a glacial-interglacial difference of at least 5.22‰ (Curve e in Figure 4.14). These values are not commonly affected by dissolution of the marble because the impact of water/rock interaction on dripwater oxygen isotopes is generally low, and hence the isotopic signal from the rainwater is unlikely to be affected by the marble values.

Three components are required to estimate the dripwater values: the empirical values for the calcites; the fractionation factors for oxygen between calcite and water; and the altitudinal effect. The second component is governed by the cave temperature effect explained below.

4.6.2.3 Cave temperature effect

Isotopic fractionation of oxygen between dripwaters, assumed to represent meteoric waters (Yonge *et al.*, 1985) over the cave site, and cave calcite is dictated by cave temperature. The present-day cave air temperature averages about 7°C, and varies within narrow limits following the seasons (Sims, undated). The outcrop-scale discontinuities are likely caused by sub-zero temperatures for extended periods of time during glacial intervals (Turgeon and Lundberg, in press a and b). This evidence indicates a glacial-interglacial range of at least 0 to 7°C, although the maximum interglacial temperatures

were probably a little higher than today (5e: Ruddiman, 1984; 11: Howard, 1997). The fractionation factor (α) of oxygen between calcite and water varies from 1.0350 at 0°C to 1.0331 at 7°C. The lowermost limit constitutes a maximum glacial temperature as ground- and vadose water freezes and stops carbonate deposition within caves at sub-freezing temperatures. Given this temperature range, the empirical $\delta^{18}\text{O}_{\text{calcite}}$ values indicate a glacial to interglacial difference of +0.73‰/°C.

The altitudinal effect can be estimated as sea level dropped by approximately 120 m during glacial periods (Emiliani and Shackleton, 1974), translating into an average decrease of $\delta^{18}\text{O}$ in the order of 0.39‰ (0.15 to 0.5‰, or approximately -0.33‰/100 m; Gat, 1981), relative to present-day conditions. We can directly estimate the value of $\delta^{18}\text{O}_{\text{rain}}$ over the cave site as dripwaters approximate rainwater (albeit with a summer and/or evaporative bias). Thus the dripwater/rain $\delta^{18}\text{O}$ values would vary from -46.3‰ during glacials to -39.4‰ during interglacials (Curve d in Figure 4.14). From these values, the vapour over the cave site is estimated using the temperature dependent fractionation of oxygen between water and vapour (Curve c in Figure 4.14).

4.6.3 Overall $\partial\delta^{18}\text{O}_{\text{calcite}}/\partial T$ in OCNM speleothem

Figure 4.13 shows that in this cave situation, the meteoric signal is dominant and $\delta^{18}\text{O}$ becomes depleted during glacials. For each cave situation, the relative importance of these effects depends on the scale of climatic changes. For example, during glacial-interglacial cycles, the ice-volume effect may be important, while cave temperature or rainout factors

can be dominant during periods of less severe environmental changes such as within an interglacial. Generally, as is true at OCNM, the meteoric-dependent (rainout) isotopic shifts will be greater than the cave temperature effect (Lauritzen and Lundberg, 1999a and b) so that the isotopes in the cave calcites will become more enriched as the temperature increases (positive relationship). Inverse correlations have also been established, mostly for coastal speleothems, which are thought to reflect the effects of ocean temperatures during glacial to interglacial cycles (Frumkin *et al.*, 1999; Hendy and Wilson, 1968; Hellstrom *et al.*, 1998; Holmgren *et al.*, 1995), although this relationship for New Zealand speleothems is being reevaluated in light of new data (Williams *et al.*, 1999).

A maximum $\partial\delta^{18}\text{O}_{\text{calcite}}/\partial T$ of approximately $+0.73\text{‰}/^{\circ}\text{C}$ for the cave site over glacial-interglacials cycles has been obtained. As seen on Figure 4.14, the main control on the isotopic values of the cave calcites over glacial-interglacial cycles are the factors related to vapour transport, which is a function of long-term degree of rainout variations and atmospheric variability of precipitation and rehydration of the air mass from ground evaporation and transpiration. During glacials, colder temperatures would induce greater rainout closer to the source thereby depleting the vapour source and overwhelming the ocean surface temperature effect as well as ice-volume effect.

4.6.4 Fractionation controls on OCNM cave calcite carbon isotopes

Although the overall correlation coefficient between the oxygen and the carbon isotopes from the cave calcites is relatively low, there is a general agreement between the data sets

as to the direction of the relationship between them; more positive ratios of oxygen are generally mimicked by similar increases in the carbon isotope ratios. Given that more positive $\delta^{18}\text{O}$ values indicate greater temperatures, higher $\delta^{13}\text{C}$ values should have a similar relationship to temperature ($\partial\delta^{13}\text{C}/T > 0$). The other feature of the carbon record that needs to be explained is the positive excursions.

As rain travels through the biosphere-soil system, soil water isotopic composition may be modified. Most of the processes controlling the $\delta^{13}\text{C}$ values are only indirectly controlled by temperature and are poorly understood. These processes include the effects of the isotopic composition of soil CO_2 (relating to biological activity), water-rock ratio, photosynthetic pathways, the rainfall intensity and the drip rate effect (Dorale *et al.*, 1992; Denniston *et al.*, 1999; Lauritzen and Lundberg, 1999a).

4.6.4.1 Isotopic composition of soil CO_2

This effect relates to the proportion of atmospheric CO_2 ($\delta^{13}\text{C} \approx -7\text{‰}$; Dole *et al.*, 1954) to plant-derived CO_2 ($\delta^{13}\text{C}$ values ranging from -32 to -9‰, average = -25‰). In cold environments where low biomass and low respiration rates predominate, soil $\delta^{13}\text{C}$ values are high and close to atmospheric values; the soil $\delta^{13}\text{C}$ values are lower in warm environments in direct proportion to the respiration rate. Indeed, short-term variations in some speleothem $\delta^{13}\text{C}$ during times of stable vegetation conditions appear to be related to changes in atmospheric $\delta^{13}\text{C}$ (Baskaran and Krishnamurty, 1993). Soil $p\text{CO}_2$ varies

annually, increasing at the onset of the growth season, with $\delta^{13}\text{C}$ values shifting concomitantly to biogenic values (Rightmire, 1978). Thus higher $\delta^{13}\text{C}$ values are associated with colder temperatures. This is usually an important control on $\delta^{13}\text{C}$ of calcites. However, the small-scale $\delta^{13}\text{C}$ variations in OCNM speleothem that parallel the $\delta^{18}\text{O}$ values in a positive relationship with temperature appear not to be governed by this effect. However, the prominent $\delta^{13}\text{C}$ excursions could be controlled by this effect: a reduction in biological activity would cause a shift to more positive values. One possible mechanism for this reduction in biological activity could be an altitudinal lowering of the treeline during colder conditions.

4.6.4.2 Water-rock interaction

The carbon in cave calcites is derived from varying proportions of CO_2 and bedrock CaCO_3 (Baskaran and Krishnamurty, 1993). These proportions are largely controlled by the volume and aggressivity of the percolating dripwaters dissolving the bedrock according to complex climatically-controlled parameters (Dreybrodt, 1999) and possibly changing dripwater paths. Higher temperatures increase the $p\text{CO}_2$ levels in groundwater, thereby dissolving greater amounts of bedrock. Therefore at higher temperatures, the isotopic composition of the cave calcite should become more enriched under constant dripwater flow. Shopov *et al.* (1997) have postulated that this *water-rock interaction* effect may explain most variations in cave calcite carbon isotopes. In the case of OCNM, this effect could also contribute to the carbon excursions that tend towards the values of the OCNM marble $\delta^{13}\text{C}$ values ($\approx +1.67\text{‰}$) in the isotopic excursions and plateaus.

4.6.4.3 Photosynthetic pathway effect

Plant carbohydrates are depleted relative to atmospheric CO₂, owing to the selective removal of lighter carbon isotopes during carboxylation. The actual depletion is dependant on the mode of atmospheric CO₂ fixation, which is in turn controlled by the photosynthetic pathway of the plant. The CO₂ fixation in most temperate and broadleaved plants is controlled by the Calvin cycle (C3 pathway), and are highly depleted, with $\delta^{13}\text{C}$ values ranging from -32 to -20‰ (Boutton, 1991). Several desert plants and tropical grasses, however, utilise the Hatch-Slack pathway (C4 pathway). These $\delta^{13}\text{C}$ in these plants are less depleted than their C3 pathway counterparts, with $\delta^{13}\text{C}$ values varying from -19 to -9‰ (Boutton, 1991). Respiratory degradation, transforming plant carbohydrates to soil CO₂ has only a minor effect on isotopic values. In the case of OCNM, given that higher $\delta^{13}\text{C}$ values are associated with warmer temperatures, the $\delta^{13}\text{C}$ values of the speleothems could indicate a transition from C3 to C4 vegetation, which seems unlikely given current interglacial-type vegetation over the cave site. Also, the high humidity along the west coast of North America would favour the establishment of C3 pathway plants during interglacial, as opposed to C4 vegetation mainly indicative of arid conditions. It appears therefore that this control on $\delta^{13}\text{C}$ values is not dominant for our study area.

4.6.4.4 Rainfall effect

Heavy rain can leach biogenically-derived soil CO₂, when several months may be required for the soil atmosphere to recover (Rightmire, 1978). For soils with lower respiration rates such as those found in mid-latitudes, soil CO₂ levels could remain low, thereby increasing the isotopic $\delta^{13}\text{C}$ values of the soil and subsequent cave calcite deposition. As several studies suggest that many localities experienced increased humidity during MOIS 11 (Poore *et al.*, 1997), this mechanism could account for the increase in $\delta^{13}\text{C}$ values as seen during stage 11 in the cave calcites (Figure 4.10).

4.6.4.5 Drip rate effect

The drip rate effect relates to slow drip rates and/or dryer conditions, where there is little mixing between successive drips, allowing each drip the time to deposit calcite through saturation under closed conditions. This creates an increasing trend in $\delta^{13}\text{C}$ downflow (down speleothem). This, however, is not the case in flowstone deposition as flow rates are much greater (Dreybrodt, 1999).

4.6.5 Periglacial control on speleothem precipitation

Figure 4.15 summarises all our cave calcite isotopic data; the growth pauses within the OCNM speleothem are illustrated as grey areas. Through the use of the proposed chronology for the growth intervals of the NG flowstone, and U-series dates when

available, we have estimated the time interval represented by the outcrop-scale disconformities to be approximately 14 kyrs (IV), 22 kyrs (III), 63 kyrs (II), and 96 kyrs (I) (Figure 4.2) respectively. These unconformities broadly correspond to glacial conditions of MOIS 12, 10, 8, and 6. The ETC flowstone also corroborates this pattern: although no apparent precipitation cessation occurred, a severe reduction of growth rates between two U-series dates indicates the influence of climate on speleothem growth. This growth rate reduction observed in the ETC flowstone lasted approximately 102 kyrs during late MOIS 5 through MOIS 2.

These isotopic records and unconformities indicate narrow growth intervals during early to mid-interglacial conditions. Although several growth frequency studies show that speleothem deposition occurs mainly during interglacial intervals in high-latitude environments (Gascoyne *et al.*, 1983; Gascoyne, 1992; Baker *et al.*, 1993; Lauritzen, 1995), calcite precipitation in these studies was interrupted by continental ice sheet glaciation. No evidence of continental glaciation has been reported in the immediate vicinity of the study area, although cirque-like structures suggesting alpine-style glaciation have been observed at higher altitudes elsewhere in the Klamath Mountains (John Roth, U.S. Park Service, personal communication, 1994). This suggests that these growth stoppages may be associated with periglacial conditions extending well below the alpine glacier limit. The increasing durations of the hiatuses associated with the unconformities indicates that precipitation could reflect an interplay between climate and additional effects related to cave development.

Glaciation thresholds in the northwestern United States suggest that climatic gradients during the last glacial maxima were similar to those of today, and that the change in summer temperature was about 5.5 ± 1.5 °C (Porter, 1977; Porter *et al.*, 1983). These glaciation thresholds allowed for changes in mountain snowline altitude (currently at about 3200 m ASL), which was depressed by approximately 1100 m during the last glacial maximum at 42°N, to approximately 700 m above the cave site (Porter, 1977). In addition, Heusser and Heusser (1990) report that sub-alpine vegetation was established at elevations between 1300 and 1800 m lower than present-day conditions (owing to an inferred 5-7°C temperature depression, in line with Porter's data), further suggesting that permafrost conditions could have occurred well below the 2100 m snowline during glacial conditions in the study area. We also postulate that the prominent excursions in our $\delta^{13}\text{C}$ values, occurring near discontinuities, were caused by a shift in treeline below the cave site, leaving the water-rock interactions a prominent sole control on carbon isotopes during these times. In the absence of organic matter, the $\delta^{13}\text{C}$ values would tend towards the value of the host marble, which is in line with the observed ratios.

Colman and Pierce (1992) concluded that early Wisconsinan alpine glaciers of the western United States were more extensive than their late Wisconsinan counterparts in some areas, thereby contrasting with marine oxygen-isotope records which suggest that world-wide ice volumes were smaller during MOIS 4 than those in MOIS 2 (Emiliani and Shackleton, 1974; Martinson *et al.*, 1987). This indicates that alpine areas could have responded more rapidly than continental ice sheets to climatic events associated with late MOIS 5 and MOIS 4 growth reduction. This sensitivity to climate change may also have

been heightened owing to the location of the cave, which was probably very close to the lower permafrost limit during glacial periods.

Another feature of the unconformities is their apparent increase in duration with time, associated with higher growth rates after MOIS 7. This could reflect an increasing intensity of glacial periods over time accompanied by warmer interglacials, although the influence of temperature on growth rates in OCNM speleothems, as shown in this study, is equivocal. These features could reflect the transition between closed to a more open dissolutional system in response to either a thinning of the overburden through erosional processes above the cave or a greater opening of the cave. Given that the cave is located in a marble lens of limited extent (and hence thickness), erosion above the cave would expose the cave to progressively shallower pedogenic processes until the marble lens is directly in contact with the soil overlying the cave. This would not only make the cave system more sensitive to environmental changes, it would also create a more open system of carbonate dissolution and precipitation. In addition, a greater number of natural entrances would develop in a shallower and enlarging cave system, creating additional ventilation of the cave thereby potentially lowering the $p\text{CO}_2$ of the cave air. Under these conditions, hiatuses would become progressively longer during glacial stages, while higher growth rates would be expected during interglacials.

4.7 Conclusions

Stable isotopes (O and C) signatures extracted from Oregon Caves National Monument (OCNM) cave calcites contain paleoenvironmental information related to global paleoclimates, although their interpretation is not straightforward. The chronology of speleothem growth is provided by 14 U-Th TIMS dates. They indicate mean growth rates of 5.6 to 27.9 mm/kyr during interglacial periods. The growth of the speleothems was modelled by comparing the oxygen isotope curve with well-established paleoclimatic proxies from marine- and ice-cores, as well as from terrestrial “vein” calcites. This comparison showed that the speleothems growth started early in the terminations and ended shortly after the onset of climatic deterioration associated with glacial stadials or interstadials.

The O and C records closely parallel each other, although the overall correlation coefficient is low. $\delta^{18}\text{O}$ values varied from -6.38 to -16.86‰, while $\delta^{13}\text{C}$ values range from +5.45 to -11.19‰ (V-PDB). The oxygen isotopes from interglacial intervals show direct relationships with global paleotemperatures, and seem to correlate with high-frequency Holocene events (~200 years) in the GISP2 ice core, as well as to curve peaks of established paleoclimatic proxies, thereby confirming the global nature of the signal. In addition, they also provide support for the timing of the 5e peak at around ~130 ka. Prominent positive carbon excursions, unmatched to oxygen isotope variations, occur within the ETC and NG flowstone records. While the oxygen isotope ratios in the cave calcites reflect glacial to interglacial atmospheric transport processes, the carbon isotopes

are thought to be controlled by varying water-rock ratios, as well as shifting treelines towards the beginning and the end of interglacials. Shorter-term fluctuations, such as the individual negative spikes seen in both the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records, are difficult to interpret adequately given current knowledge of short- to mid-term climatic events in this region as well as to a lack of adequate paleoclimatic proxies with which to compare them to.

Precipitation cessation, in most cases, is expressed as an outcrop-scale discontinuity within the Neptune's Grotto flowstone. These discontinuities represent pauses in precipitation ranging from 14 to 102 kyrs, mainly during glacial intervals and decrease with age. Given the lack of evidence for direct continental or alpine-style glaciation in the study area, and the sensitivity to alpine regions to climatic change, it is assumed that extended periglacial conditions, triggered by the lowering of glaciation thresholds by as much as 1800 m during glacial intervals, are responsible for the cessation of calcite precipitation through groundwater freezing.

Table 4.1 – Isotopic rain- and dripwater data and calculated $\delta^{18}\text{O}_{\text{cave calcite}}$ values.

Component	Destruction Island $\delta^{18}\text{O}$ (range in ‰)	OCNM $\delta^{18}\text{O}$ (range in ‰)	Calculated $\delta^{18}\text{O}_{\text{cave calcite}}$ (‰)
Annual rain	-36.75* (-39.29 to -43.45)	-41.35* (-39.29 to -43.45) [†]	-7.52 to -11.82
Summer rain	-34 to -36	-38.6 to -40.6 [†]	-6.80 to -8.88
Winter rain	-39 to -40	-43.6 to -44.6 [†]	-11.98 to -13.01
October rain		-38.7 (-36.2 to -41.2)	-6.91 (-4.32 to -9.47)
November dripwater		-41.14	-9.40

* Average values.

[†] Translated using Gat's (1981) factor of -0.33‰/100 m.

Table 4.2 – U-series dates for OCNM speleothem samples.

Sample number	U (ppm)	Th (ppm)	Distance from base (mm)	$^{230}\text{Th}/^{234}\text{U}$ Age* (ka)	$^{230}\text{Th}/^{234}\text{U}^\dagger$	$(^{234}\text{U}/^{238}\text{U})_{\text{initial}}^\S$	$^{234}\text{U}/^{238}\text{U}^\dagger$	$^{230}\text{Th}/^{232}\text{Th}^\dagger$	$^{234}\text{U}/^{232}\text{Th}^\dagger$
WFP-2-B	0.187	0.06	47-49	2.26 ± 0.02	0.0206 ± 0.0001	1.0747 ± 0.0026	1.0742 ± 0.0026	18.3 ± 0.2	890 ± 11
WFP-2-A	0.233	0.02	1-5	3.88 ± 0.02	0.0351 ± 0.0002	1.0709 ± 0.0020	1.0701 ± 0.0020	134.1 ± 1.2	3822 ± 38
ETC-B	0.168	0.66	127-129	11.98 ± 0.13	0.1045 ± 0.0010	1.1296 ± 0.0016	1.1252 ± 0.0016	8.0 ± 0.1	76 ± 1
ETC-E	0.169	0.77	109-112	14.29 ± 0.05	0.1234 ± 0.0004	1.1187 ± 0.0022	1.1140 ± 0.0022	7.9 ± 0.0	64.3 ± 0.4
ETC-D	0.183	0.53	74-77	116.7 ± 0.5	0.6732 ± 0.0014	1.1592 ± 0.0013	1.1139 ± 0.0012	69.3 ± 0.5	103 ± 1
ETC-A	0.197	0.42	36-38	117.5 ± 0.4	0.6697 ± 0.0012	1.1397 ± 0.0015	1.1002 ± 0.0014	91.7 ± 0.7	137 ± 1
ETC-C	0.189	0.16	1-7	119.3 ± 0.8	0.6749 ± 0.0021	1.1331 ± 0.0032	1.0949 ± 0.0031	224.4 ± 2.3	332 ± 4
NG-L	0.102	0.06	704-706	122.9 ± 1.0	0.6819 ± 0.0029	1.0670 ± 0.0018	1.0473 ± 0.0017	345.5 ± 2.6	507 ± 4
NG-G	0.167	0.05	681-684	122.8 ± 0.5	0.6819 ± 0.0015	1.0712 ± 0.0013	1.0503 ± 0.0012	384.1 ± 5.0	563 ± 7
NG-F	0.136	0.13	574-576	131.2 ± 0.7	0.7051 ± 0.0019	1.0559 ± 0.0013	1.0385 ± 0.0012	123.0 ± 0.8	174 ± 1
NG-E	0.085	0.09	508-511	235 ± 3	0.8931 ± 0.0029	1.0720 ± 0.0012	1.0370 ± 0.0012	142.7 ± 1.6	160 ± 2
NG-D	0.161	0.38	435-437	315 ⁺⁷ ₋₆	0.9553 ± 0.0025	1.0854 ± 0.0038	1.0350 ± 0.0036	70.1 ± 0.6	73 ± 1
NG-J	0.169	0.39	435-437	327 ⁺⁹ ₋₈	0.9646 ± 0.0030	1.1200 ± 0.0043	1.0475 ± 0.0040	115.6 ± 0.6	120 ± 1
NG-I	0.086	1.05	219-221	359 ⁺¹⁰ ₋₉	0.9793 ± 0.0031	1.1393 ± 0.0011	1.0503 ± 0.0010	22.2 ± 0.2	22.7 ± 0.2
NG-B	0.036	0.84	121.122	∞	1.0536 ± 0.0047	na	1.0005 ± 0.0034	12.1 ± 0.1	11.5 ± 0.1
NG-A	0.056	0.95	32-34	∞	1.0377 ± 0.0041	na	0.9949 ± 0.0033	16.3 ± 0.2	15.7 ± 0.2

Note: Errors are quoted as 2σ .* Calculated using Kaufman and Broecker (1965) equation and half-lives of ^{230}Th and ^{234}U of 75 383 and 244 500 years respectively.

† Activity ratio.

§ Initial $^{234}\text{U}/^{238}\text{U}$ activity ratio calculated for $^{230}\text{Th}/^{234}\text{U}$ age.

Table 4.3 – Summary of fractionation effects on the composition of cave calcite during glacial/interglacial cycles.

System component	Glacials	Interglacials
$\delta^{18}\text{O}_{\text{sea water}}$ (ice volume)	↑ Heavier	↓ Lighter
$\delta^{18}\text{O}_{\text{vapour}}$ ($T_{\text{evaporation}}$)	↓ Lighter	↑ Heavier
Atmospheric processes ($\Delta T, \text{ETP}, P, \text{altitude}$)	↓ Lighter	↑ Heavier
$\delta^{18}\text{O}_{\text{drip waters}}$ (T)	↑ Heavier	↓ Lighter
Cave temperature	↑ Heavier	↓ Lighter

Table 4.4 – Estimated sea surface temperature (SST) at 18 ka for various Northeastern Pacific Ocean sites located at approximately the same latitude as Oregon Caves National Monument.

Core	Latitude (N)	Longitude (W)	T _{summer} (°C)	T _{winter} (°C)
Y6604-10	43°16'	126°24'	13.5	8.1
Y6904-10	41°16'	127°01'	14.1	5.9
RC12-176	43°00'	157°50'	12.5	8.6
V20-85	44°54'	143°37'	14.2	6.2
V20-107	43°24'	178°52'	13.4	4.6
V21-173	44°22'	163°33'	11.1	3.6
V21-174	40°08'	162°30'	21.4	10.8

From Moore *et al.* (1980).

Figure 4.1 Location map of the study area showing maximum extent of Pleistocene glaciations.

Figure 4.2 Cross-section of Neptune's Grotto flowstone (~73 cm thick), unconformably overlying Triassic marble. Black arrows indicate outcrop-scale disconformities (numbered I to IV). Numbered sections on the left correspond to text descriptions. White arrow shows a broken stalactite resting on a disconformity surface. The open triangles indicate stratigraphic locations of U-series samples.

Figure 4.3 (following page) Raw $\delta^{13}\text{C}$ (dotted lines) and $\delta^{18}\text{O}$ (solid lines) values for OCNM samples: A) White Formation Passage stalagmite; B) Exit Tunnel Cave flowstone, and; C) Neptune's Grotto flowstone. Dashed lines represent $\delta^{18}\text{O}$ values for modern cave calcite. Outcrop-scale discontinuities within the NG record are identified by roman numeral (I to IV) corresponding to Figure 4.2. All distance and isotopic ratios axes are to scale with respect to each other to facilitate inter-sample comparison. The various are expanded in subsequent figures.

Figure 4.4 (following page) Composite stacked age versus depth relationships for the OCNM speleothems. The sampling intervals and 2σ errors of the U-Th dates are shown to scale. Circled numbers indicate numbered sections belonging to the NG flowstone described in the text. Outcrop-scale discontinuities within the NG flowstone are identified by roman numerals (I to IV) corresponding to Figure 4.2. The marine isotope stratigraphy is based on the time-scale of Shackleton and Opdyke (1976).

Figure 4.5 WFP-2L $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotope values compared to the GISP2 and Vostok ice-core records for similar time periods. 3rd-order polynomial best-fit lines are shown for the WFP-2L and Vostok isotope records. A 3-point running mean is shown for the GISP2 record. This reduces the GISP2 record to a resolution similar to the WFP-2L's resolution (WFP-2L has 51 points while the GISP2 record has ~160 points). $\delta^{18}\text{O}$ values are not available for the Vostok record. The speleothem isotopes are plotted relative to distance from base. Bars on the dates represent vertical sampling range and they have been lined up with the compared chronologies. One potential correlation scenario between the records is presented with the dotted lines. The GISP2 data are from Grootes *et al.* (1993a and b), Meese *et al.* (1994) and Stuiver *et al.* (1995). The Vostok data is from Chappellaz and Jouzel (1992).

Figure 4.6 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ isotopic values for the ETC flowstone section. The time scale was established using linear interpolation between the dates.

Figure 4.7 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values compared to the GRIP ice core (Johnsen *et al.*, 1993), Vostok (Chappellaz and Jouzel, 1982), and the SPECMAP (Imbrie *et al.*, 1984) marine record's $\delta^{18}\text{O}$ signatures for the Termination II/5e period. A 3rd-order polynomial best-fit line is shown for the NG record as well as the GRIP curve. The speleothem isotopes are plotted relative to distance from base. The dated intervals have been lined up with the compared chronologies. Bars on the dates represent vertical sampling range. TII bars represent the locations of the MOIS6/5 termination for various records. The marine isotope substage number is indicated on the SPECMAP curve.

Figure 4.8 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to the GRIP ice core (Johnsen *et al.*, 1993) and SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ records for parts of MOIS 7. The speleothem isotopes are plotted relative to distance from base. The dated interval has been lined up with the compared chronology. Bars on the dates represent vertical sampling range. The marine isotope stage number is indicated on the SPECMAP curve.

Figure 4.9 NG $\delta^{18}O$ and $\delta^{13}C$ values relative to the SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}O$ record for parts of MOIS 11 through 9. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The dated interval has been lined up with the compared chronology. Bars on the dates represent vertical sampling range. The marine isotope stage numbers are indicated on the SPECMAP curve.

Figure 4.10 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to the Devils Hole (Winograd *et al.*, 1992) and SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ records for parts of MOIS 12 through 11. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The marine isotope stage numbers are indicated on the SPECMAP curve.

Figure 4.11 NG $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values relative to the SPECMAP (Imbrie *et al.*, 1984) stacked marine $\delta^{18}\text{O}$ record for parts of MOIS 13. A 3rd-order polynomial best-fit line is shown for the NG isotopes. The speleothem isotopes are plotted relative to distance from base. The marine isotope stage number is indicated on the SPECMAP curve.

Figure 4.12 Hendy Tests results for two speleothem samples: A) WFP-2L and, B) NG. For the left panel of sample WFP-2L, subsamples were taken at approximately equal intervals from the apex (top) of the growth layer all the way down the side of the stalagmite (one subsample was lost during laboratory analyses). Subsamples for the NG flowstone were taken at equal intervals over the entire width (~3 cm) of the sample. The left panels show the absence of parallel enrichment of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ with distance along coeval samples; the right panels show an absence of strong progressive positive relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in sequential samples.

Figure 4.13 Calculated $\delta^{18}\text{O}_{\text{calcite}}$ values for translated Destruction Island rainwater data using $\alpha = 1.0331$ for oxygen between water and calcite.

Figure 4.14 Summary of controls on oxygen isotopes.

Figure 4.15 OCNM $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records. Grey areas represent inferred (outlined) and recorded precipitation cessation intervals (hiatuses).

5.0 GENERAL CONCLUSIONS

Speleothems from OCNM are mainly composed of primary columnar calcite crystals and represent fast growth during stable, wet interglacial conditions. Vertical linear inclusion horizons represent inter-crystallite voids stemming from the incomplete coalescence of syntaxial overgrowths. As most OCNM speleothems grow under stable hydrodynamic conditions, variations in fabric indicate changing environmental conditions influencing the cave system, such as increased rainfall or runoff. Transitional calcites develop under turbulent flow and crystallise on discontinuities. Over time, these length-slow calcites are overridden by length-fast palisade crystals owing to their more favourable orientation and faster growth. Minor fabrics include: randomly oriented elongate calcites, growing in isolated pools; pillar-like structures; and zoned equant calcites.

Numerous discontinuities and contaminants punctuate these cave deposits. Evidence suggests that the events that generated these features were of short duration (probably <100 years) (presumably they relate to environmental events, but do not appear to correlate with the calcite isotopic records). Large (~750 μm) crystal terminations represent growth under increased accommodation space resulting from an increase in the thickness of the water film.

The chronology of speleothem growth was provided by 14 U-Th TIMS dates. They indicate mean growth rates of 5.6 to 27.9 mm/kyr during interglacial periods. The growth of the speleothems was modelled by comparing the oxygen isotope curve with

well-established paleoclimatic proxies from marine- and ice-cores, as well as from terrestrial “vein” calcites. This comparison showed that the speleothems growth started early in the terminations and ended shortly after the onset of climatic deterioration associated with glacial stadials or interstadials.

A growth model, based on minimum isotopic values of SPECMAP before or during terminations and after the beginning of climatic deterioration is presented and discussed. This “start-stop” model shows a very good correlation between growth periods and terminations, although uncertainties may be related to global records, which are not indicative of local conditions at OCNM. It also provides a way to model growth for sections lacking dating control. According to theoretical modelling of calcite precipitation, growth rates of speleothems should respond mainly to temperature. Results indicate that precipitation rates are essentially linear on long-term scales ($\sim 10^3$ to 10^4 years). It should be noted that while a lot of effort has been put into finding the best-fit relationship between the undated parts of the OCNM speleothem record and the well-established SPECMAP curve, there remains a possibility that the selected matches are incorrect. This would not concern any of the interpretations relating to speleothem sections anchored by U-series dates, but would affect some of the conclusions offered by Chapter 3 regarding the long-term shift from a closed to an open dissolutional system. As well, the conclusion regarding the shallowing of the cave system, resting on the lengthening of the hiatuses over the course of the Quaternary, would also require revision should the curve-matching exercise be proven wrong. There is also a “problem” in attempting to date a paleoclimatic record using an established record that has itself been

dated indirectly. This circularity is acknowledged, although very few solutions to this “problem” exist and this practice has been widely used in the Quaternary climate change literature.

The OCNM cave calcites have also been shown to be global paleoclimate indicators: isotopes from dated interglacial intervals have been shown to record a direct relationship with temperature, controlled mainly by glacial-interglacial variations in atmospheric processes, and seem to correlate with peaks of established paleoclimatic proxies such as Vostok and GISP2, thereby confirming the global nature of the signal. In addition, the cave calcites also provide support for the timing of the 5e peak at around ~130 ka. The O and C records closely parallel each other, although the overall correlation is low. Prominent positive carbon excursions, unmatched to oxygen isotope variations, occur within the ETC and NG flowstone records. Shorter-term fluctuations, such as individual depletion events are difficult to interpret owing to a lack of understanding of short- to mid-term climatic patterns and events in this region and adequate paleoclimatic proxies.

While the oxygen isotope ratios in the cave calcites reflect glacial to interglacial atmospheric transport processes, the carbon isotopes are thought to be controlled by varying water-rock ratios, as well as shifting treelines towards the beginning and the end of interglacials.

The outcrop-scale discontinuities probably reflect growth cessation through groundwater freezing brought about by periglacial conditions owing to the lowering of the alpine

glacial limit. Based on established growth rates for various sections, along with associated dates and correlations of their oxygen isotope variations with global paleoclimatic records, these outcrop-scale discontinuities represent hiatuses ranging from 14 to ~102 kyrs. These hiatuses, which get longer with time, are accompanied by an increase in growth rates (also over time). These conditions are probably indicative of an opening of the cave system through enlargement and shallowing of the cave overburden through surficial erosional processes. This would allow not only for greater ventilation of the cave system, but could also shift the dissolutional system from closed (CO_2 source and carbonates separate) towards a more open system (where CO_2 and carbonates are coincident).

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Appendices

Appendix 1 – OCNM cave survey.

OREGON CAVES

PART 4 SOUTH END

BRUNTON & TAPE SURVEYS: 1970-1974
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OREGON CAVES

LOWER CAVE PROFILE AT
AZIMUTH 135° MAGNETIC

BRUNTON & TAPE SURVEYS: 1970-1974
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OREGON CAVES

MIDDLE CAVE PROFILE AT
AZIMUTH 135° MAGNETIC
BRUNTON & TAPE SURVEYS 1970-1974
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OREGON CAVES

GHOST ROOM PROFILE AT
AZIMUTH 180° MAGNETIC

BRUNTON & TAPE SURVEYS: 1970-1974
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Appendix 2 – Microscopic petrology of OCNM samples.

CM = "coconut meat"
 CTL = crystal termination layer
 Dis = discontinuity
 DL = detrital layer
 IH = inclusion horizon

NP = non-palisade
 OL = organic layer
 SER = small equant rhombs
 SS = broken soda straw

CM = "coconut meat"
 CTL = crystal termination layer
 Dis = discontinuity
 DL = detrital layer
 IH = inclusion horizon

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CM	= "coconut meat"	NP	= non-palisade
CTL	= crystal termination layer	OL	= organic layer
Dis	= discontinuity	SER	= small equant rhombs
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DL	= detrital layer	SS	= broken soda straw
IH	= inclusion horizon		

Appendix 3 – X-ray diffraction results.

XRD PROFILE FOR OCNM-NG-5C2 **XRD PROFILE FOR OCNM-NG-6** **XRD PROFILE FOR OCNM-WFP-1**

Appendix 4 – Microprobe results expressed as weight %. Values above the detection limit are shaded in grey.

Sample	Number	X (μm)	Y (μm)	Ca	Fe	Mg	Sr	Ba	Mn	Na	Si	S	O	Total
ETC-1C2B	1	45631	17642	40.279	0.023	0.006	0.000	0.000	0.022	0.000	0.003	0.000	59.665	100.000
	2	45631	18092	40.171	0.000	0.007	0.000	0.031	0.013	0.006	0.004	0.002	59.766	100.000
	3	45631	18445	39.409	0.019	0.010	0.000	0.000	0.009	0.003	0.002	0.007	60.541	100.000
	4	45606	18809	40.018	0.021	0.006	0.000	0.000	0.000	0.003	0.005	0.006	59.941	100.000
	5	45654	20053	40.228	0.010	0.006	0.000	0.017	0.004	0.000	0.010	0.003	59.723	100.001
	6	45654	20307	39.962	0.001	0.007	0.003	0.000	0.000	0.001	0.013	0.000	60.013	100.000
	7	45654	20790	40.364	0.000	0.005	0.000	0.001	0.000	0.001	0.000	0.005	59.623	99.999
	8	45615	21362	39.657	0.014	0.006	0.000	0.000	0.009	0.000	0.013	0.008	60.293	100.000
	9	45660	21988	40.100	0.004	0.002	0.008	0.010	0.000	0.004	0.000	0.001	59.870	99.999
	10	45689	22499	39.852	0.013	0.002	0.000	0.000	0.000	0.000	0.001	0.007	60.124	99.999
NG-3A21	1	42151	10178	40.086	0.000	0.000	0.000	0.000	0.009	0.003	0.000	0.001	59.902	100.001
	2	42160	10694	39.878	0.012	0.000	0.000	0.000	0.002	0.003	0.003	0.009	60.094	100.001
	3	42169	11210	39.489	0.000	0.003	0.000	0.000	0.000	0.000	0.000	0.001	60.507	100.000
	4	42178	11726	40.278	0.064	0.032	0.165	0.002	0.000	0.012	0.004	0.002	59.443	100.002
	5	42187	12242	39.103	0.004	0.018	0.001	0.027	0.001	0.013	0.043	0.017	60.772	99.999
	6	42196	12758	40.367	0.003	0.003	0.002	0.016	0.014	0.005	0.003	0.005	59.582	100.000
	7	42205	13274	39.862	0.000	0.005	0.016	0.000	0.018	0.000	0.007	0.003	60.089	100.000
	8	42214	13790	39.662	0.000	0.008	0.010	0.013	0.011	0.012	0.000	0.007	60.277	100.000
	9	42223	14306	39.730	0.003	0.008	0.000	0.011	0.000	0.000	0.001	0.003	60.245	100.001
	10	42232	14822	39.629	0.003	0.008	0.000	0.000	0.013	0.000	0.007	0.005	60.334	99.999
	11	42242	15338	39.928	0.015	0.008	0.000	0.000	0.000	0.005	0.000	0.010	60.035	100.001
	12	42251	15854	39.695	0.000	0.009	0.000	0.000	0.000	0.006	0.000	0.001	60.289	100.000
	13	42260	16370	39.794	0.000	0.006	0.000	0.004	0.009	0.000	0.002	0.000	60.184	99.999
	14	42269	16886	24.297	0.008	0.000	0.000	0.005	0.000	0.001	0.000	0.000	75.689	100.000
	15	42278	17402	39.466	0.011	0.006	0.000	0.001	0.001	0.008	0.000	0.009	60.498	100.000
	16	42287	17918	39.589	0.005	0.008	0.000	0.000	0.000	0.000	0.003	0.005	60.390	100.000
	17	42296	18434	36.960	0.375	0.041	0.000	0.000	0.000	0.000	0.377	0.011	62.237	100.001
	18	42305	18950	39.974	0.006	0.005	0.000	0.000	0.000	0.000	0.000	0.005	60.009	99.999
	19	42314	19466	38.695	0.151	0.269	0.000	0.000	0.000	0.005	0.394	0.010	60.476	100.000
	20	42323	19981	39.731	0.005	0.008	0.000	0.003	0.000	0.006	0.002	0.002	60.243	100.000
	21	42332	20497	0.184	0.000	0.001	0.008	0.002	0.003	0.011	0.003	0.095	99.693	100.000
	22	42341	21013	39.556	0.007	0.006	0.009	0.000	0.008	0.007	0.000	0.004	60.403	100.000
	23	42350	21529	39.359	0.000	0.007	0.000	0.000	0.008	0.001	0.004	0.000	60.621	100.000
	24	42359	22045	39.538	0.000	0.003	0.000	0.000	0.000	0.006	0.004	0.000	60.448	99.999
	25	42368	22561	39.333	0.000	0.011	0.000	0.000	0.006	0.008	0.000	0.004	60.639	100.001
	26	42377	23077	39.626	0.000	0.006	0.000	0.003	0.008	0.006	0.000	0.007	60.344	100.000
	27	42386	23593	39.621	0.000	0.002	0.000	0.011	0.007	0.000	0.005	0.008	60.347	100.001
	28	42395	24109	39.224	0.000	0.004	0.000	0.020	0.000	0.000	0.003	0.007	60.742	100.000
	29	42405	24625	39.414	0.000	0.004	0.000	0.002	0.000	0.002	0.009	0.010	60.560	100.001
	30	42414	25141	39.610	0.004	0.007	0.000	0.000	0.000	0.000	0.003	0.003	60.374	100.001
	31	42423	25657	39.909	0.000	0.006	0.000	0.000	0.012	0.005	0.002	0.013	60.053	100.000
	32	42432	26173	39.792	0.011	0.009	0.001	0.000	0.014	0.000	0.000	0.012	60.161	100.000
	33	42441	26689	40.188	0.003	0.008	0.000	0.000	0.000	0.005	0.001	0.006	59.789	100.000
	34	42450	27205	40.010	0.000	0.005	0.000	0.005	0.007	0.000	0.004	0.000	59.969	100.000
	35	42459	27721	39.791	0.000	0.004	0.000	0.005	0.001	0.000	0.002	0.003	60.194	100.000
	36	42468	28237	39.334	0.000	0.012	0.000	0.002	0.000	0.005	0.000	0.008	60.639	100.000
	37	42477	28753	38.847	0.000	0.009	0.000	0.000	0.010	0.010	0.008	0.005	61.112	100.001
	38	42486	29269	38.102	0.019	0.010	0.000	0.003	0.001	0.000	0.011	0.011	61.843	100.000

Appendix 5 – Oxide (weight %) and elemental data (ppm) obtained by XRF analyses for two OCNM samples.

	Oxide/element	Base of NG flowstone	Top of NG flowstone
Oxides (weight %)	SiO ₂	2.30	<0.5
	TiO ₂	0.09	<0.02
	Al ₂ O ₃	0.60	<0.2
	Fe ₂ O ₃ (total)	0.70	0.50
	Fe ₂ O ₃	0.3	
	FeO	0.4	
	MnO	<0.01	<0.01
	MgO	0.37	0.05
	CaO	53.6	54.8
	Na ₂ O	<0.03	<0.03
	K ₂ O	0.06	<0.05
	H ₂ O _(total)	0.9	0.5
	CO ₂ (total)	40.1	42.0
	CO ₂ ²⁻		
	C		
	P ₂ O ₅	0.22	0.28
	S _(total)	<0.02	<0.02
Elements (ppm)	Ba	40	40
	Be	<0.5	<0.5
	Co	<5	<5
	Cr	17	<10
	Cu	10	<10
	La	<10	<10
	Nb	<100	<100
	Ni	<10	<10
	Rb	<100	<100
	Sc	<0.05	<0.5
	Sr	35	31
	V	12	5
	Y	7	<5
	Yb	<0.5	<0.5
	Zn	<5	<5
	Zr	<100	<100
Σ (%)		98.9	98.5
Loss on ignition (%)		24.6	28.1

Appendix 6 – Trace- and rare earth elemental data obtained by ICP-MS for two OCNM samples.

		Base of NG flowstone	Top of NG flowstone
Element		(ppm)	(ppm)
Trace element	Ag	0.5	0.4
	Bi	<0.5	<0.5
	Cd	1.2	<0.2
	Cs	0.14	0.02
	Ga	1.0	0.3
	Hf	0.31	0.05
	In	0.06	<0.05
	Mo	<0.2	0.2
	Nb	2.4	2.2
	Pb	<2	2
	Rb	2.8	0.29
	Ta	0.3	0.5
	Th	0.30	0.04
	Tl	<0.02	<0.02
	U	0.24	0.19
	Zr	14	2.2
REE	Ce	4.4	0.2
	Dy	0.76	<0.02
	Er	0.49	<0.02
	Eu	0.22	<0.02
	Gd	0.80	0.02
	Ho	0.19	<0.02
	La	4.3	0.3
	Lu	0.07	<0.02
	Nd	4.0	0.4
	Pr	0.98	0.08
	Sm	0.71	0.06
	Tb	0.12	<0.02
	Tm	0.07	<0.02
	Y	9.5	0.29
	Yb	0.45	<0.05

Appendix 7 – OCNM stable isotopes and growth model ages.

Sample	Lab series	Lab number	Distance from base (mm)	Age (ka)	$\delta^{18}\text{O}_{\text{V-PDB}}$ (‰)	$\delta^{13}\text{C}_{\text{V-PDB}}$ (‰)	Comments & location of dates
NG-3A1L	97-31	1	1	519.000	-9.86	-8.26	
	97-31	2	2	518.352	-9.90	-8.93	
	97-31	3	3	517.705	-10.12	-8.55	
	97-31	4	4	517.057	-9.83	-8.05	
	97-31	5	5	516.409	-9.50	-8.18	
	97-31	6	6	515.761	-10.27	-8.58	
	97-31	7	7	515.114	-10.15	-8.81	
	97-31	8	8	514.466	-9.56	-8.35	
	97-31	9	9	513.818	-9.56	-8.38	
	97-31	10	10	513.170	-9.43	-8.13	
	97-31	11	11	512.523	-10.02	-7.98	
	97-31	12	12	511.875	-9.80	-7.52	
	97-31	13	13	511.227	-9.54	-8.24	
	97-31	14	14	510.580	-9.35	-8.66	
	97-31	15	15	509.932	-10.43	-8.97	
	97-31	16	16	509.284	-10.04	-9.29	
	97-31	17	17	508.636	-10.57	-8.93	
	97-31	18	18	507.989	-10.42	-8.90	
	97-31	19	19	507.341	-10.18	-9.26	
	97-31	20	20	506.693	-9.28	-8.55	
NG-3A2L	97-31	1	21	506.045	-10.26	-9.02	
	97-31	2	22	505.398	-11.33	-10.47	
	97-31	3	23	504.750	-10.61	-10.09	
	97-31	4	24	504.102	-9.80	-9.34	
	97-31	5	25	503.455	-9.97	-8.91	
	97-31	6	26	502.807	-10.22	-9.17	
	97-31	7	27	502.159	-10.03	-9.86	
	97-31	8	28	501.511	-10.13	-9.39	
	97-31	9	29	500.864	-9.39	-8.30	
	97-31	10	30	500.216	-9.66	-8.95	
	97-31	11	31	499.568	-9.83	-9.45	
	97-31	12	32	498.920	-9.56	-8.79	U-Series NG-A
	97-31	13	33	498.273	-10.34	-9.18	U-Series NG-A
	97-31	14	34	497.625	-9.75	-9.37	U-Series NG-A
	97-31	15	35	496.977	-9.80	-9.06	
	97-31	16	36	496.330	-9.67	-8.81	
	97-31	17	37	495.682	-9.37	-9.43	
	97-31	18	38	495.034	-9.61	-9.61	
	97-31	19	39	494.386	-9.66	-9.33	

NG-3BL	97-31	20	40	493.739	-12.95	-10.89
	97-31	21	41	493.091	-9.61	-8.09
	97-31	22	42	492.443	-9.12	-6.37
	97-31	23	43	491.795	-9.39	-7.71
	97-31	24	44	491.148	-9.27	-6.47
	97-31	25	45	490.500	-9.29	-6.92
	97-31	26	46	489.852	-9.32	-7.33
	97-31	27	47	489.205	-9.71	-6.98
	97-31	28	48	488.557	-9.41	-6.60
	97-31	29	49	487.909	-9.48	-7.64
	97-31	30	50	487.261	-9.32	-7.50
	97-31	1	51	486.614	-9.71	-6.59
	97-31	2	52	485.966	-9.57	-6.35
	97-31	3	53	485.318	-9.55	-6.13
	97-31	4	54	484.670	-10.01	-4.74
	97-31	5	55	484.023	-10.89	-5.62
	97-31	6	56	483.375	-10.73	-7.02
	97-31	7	57	482.727	-10.48	-8.54
	97-31	8	58	482.080	-12.02	-10.63
	97-31	9	59	481.432	-10.05	-8.33
	97-31	10	60	480.784	-10.41	-8.06
	97-31	11	61	480.136	-11.74	-8.84
	97-31	12	62	479.489	-10.19	-8.23
	97-31	13	63	478.841	-9.59	-7.34
	97-31	14	64	478.193	-10.26	-7.03
	97-31	15	65	477.545	-10.09	-6.85
	97-31	16	66	476.898	-10.24	-7.75
	97-31	17	67	476.250	-10.60	-7.59
	97-31	18	68	475.602	-12.06	-8.47
	97-31	19	69	474.955	-11.25	-7.90
	97-31	20	70	474.307	-11.72	-7.04
	97-31	21	71	473.659	-11.22	-7.43
	97-31	22	72	473.011	-11.96	-7.57
	97-31	23	73	472.364		Lost in preparation
	97-31	24	74	471.716	-10.86	-7.57
	97-31	25	75	471.068	-10.94	-7.25
	97-31	26	76	470.420	-11.66	-8.12
	97-31	27	77	469.773	-11.08	-5.85
	97-31	28	78	469.125	-10.85	-5.54
	97-31	29	79	468.477	-12.98	-5.26
	97-31	29A	80	467.830	-10.89	-4.44
	97-31	30A	81	467.182	-11.00	-3.36
	97-31	31A	82	466.534	-9.96	-3.63
	97-31	32A	83	465.886	-11.45	-4.03
	97-31	33A	84	465.239	-14.11	-4.70

	97-31	34A	85	464.591	-9.60	-5.44
	97-31	35	86	463.943	-11.53	-5.10
	97-31	36	87	463.295	-10.08	-4.24
	97-31	37	88	462.648	-10.47	-5.65
	97-31	38	89	462.000	-9.82	-5.76
		39	90	461.352		Missing
		40	91	460.705		Missing
		41	92	460.057		Missing
		42	93	459.409		Missing
	Unconformity		94			
NG-4BL	97-56	2	96	443.100	-9.70	-3.48
	97-56	4	98	441.594	-10.21	-5.02
	97-56	6	100	440.088	-9.46	-4.36
	97-56	8	102	438.582	-10.09	-6.14
	97-56	10	104	437.076	-9.47	-5.14
	97-56	12	106	435.570	-9.76	-4.93
	97-56	14	108	434.064	-9.11	-4.65
	97-56	16	110	432.558	-9.40	-6.36
	97-56	18	112	431.052	-9.72	-6.66
	97-56	20	114	429.545	-10.23	-6.50
	97-56	22	116	428.039	-10.02	-6.62
	97-56	24	118	426.533	-13.64	-8.91
	97-56	26	120	425.027	-9.57	-6.71
	97-56	28	122	423.521	-9.91	-7.60 U-Series NG-B
	97-56	30	124	422.015	-9.51	-6.34
	97-56	32	126	420.509	-9.70	-6.28
	97-56	34	128	419.003	-9.44	-5.97
	97-56	36	130	417.497	-10.10	-6.07
	97-56	38	132	415.991	-9.20	-5.24
	97-56	40	134	414.485	-9.36	-4.64
	97-56	42	136	412.979	-9.11	-5.21
	97-56	44	138	411.473	-9.11	-5.11
	97-56	46	140	409.967	-8.79	-4.88
	97-56	48	142	408.461	-9.11	-5.72
	97-56	50	144	406.955	-8.98	-5.20
	97-56	52	146	405.448	-9.91	-2.71
	97-56	54	149	403.189	-7.52	-1.15
	97-56	56	151	401.683	-7.71	-1.28
	97-56	58	153	400.177	-9.90	-4.68
	97-56	60	155	398.671	-8.72	-2.10
	97-56	62	157	397.165	-9.03	-3.57
	97-56	64	159	395.659	-11.94	-6.12
	97-56	66	161	394.153	-9.72	-7.28
	97-56	68	163	392.647	-10.22	-7.31
		69	164	391.894		Missing

		70	165	391.141		Missing
	Unconformity		166			
NG-4C1L	97-56	1	167	368.718	-10.01	-3.37
	97-56	3	169	368.363	-8.81	0.03
	97-56	5	171	368.007	-9.02	-3.04
	97-56	7	173	367.652	-9.15	-5.04
	97-56	9	175	367.296	-9.99	-6.09
	97-56	11	177	366.941	-8.65	-4.73
	97-56	13	179	366.586	-8.12	-2.41
	97-56	15	181	366.230	-6.38	5.45
	97-56	17	183	365.875	-9.04	-2.74
	97-56	19	185	365.520	-9.05	-4.90
	97-56	21	187	365.164	-9.10	-4.99
	97-56	23	189	364.809	-9.25	-5.40
	97-56	25	191	364.453		Lost in preparation
	97-56	27	193	364.098	-11.37	-6.86
	97-56	29	195	363.743	-9.42	-5.94
	97-56	31	197	363.387	-9.87	-5.92
	97-56	33	199	363.032	-9.65	-6.83
	97-56	35	201	362.677		Lost in preparation
	97-56	37	203	362.321	-11.19	-7.67
	97-56	39	205	361.966	-9.75	-7.43
	97-56	41	207	361.610	-9.55	-7.40
NG-4C2L	97-56	43	209	361.255	-9.62	-7.07
	97-56	45	211	360.900	-10.13	-7.67
	97-56	47	213	360.544	-9.93	-7.25
	97-56	49	215	360.189	-9.29	-5.59
	97-56	51	217	359.834	-10.60	-4.46
	97-56	53	219	359.478	-9.58	-4.44 U-Series NG-I
	97-56	55	221	359.123	-9.90	-5.07 U-Series NG-I
	97-56	57	223	358.767	-10.02	-5.76
	97-56	59	225	358.412	-9.81	-6.03
	97-56	61	227	358.057	-10.06	-5.08
	97-56	63	229	357.701	-11.27	-8.10
	97-56	65	231	357.346	-9.64	-7.44
	97-56	67	233	356.990	-9.66	-6.29
	97-56	69	235	356.635	-9.61	-6.81
	97-56	71	237	356.280	-9.64	-7.05
	97-56	73	239	355.924	-9.39	-6.47
	97-56	75	241	355.569	-10.89	-7.01
	97-56	77	243	355.214	-16.86	-9.79
	97-56	79	245	354.858	-11.06	-7.25
	97-56	81	247	354.503	-9.88	-7.50
	97-56	83	249	354.147	-9.80	-7.77
	97-56	85	251	353.792	-10.27	-7.68

NG-4C3L	97-56	87	253	353.437	-10.84	-8.50
	97-56	89	255	353.081	-11.00	-8.50
	97-56	91	257	352.726	-10.47	-8.18
	97-56	93	259	352.371	-10.55	-8.37
	97-56	95	261	352.015	-10.64	-8.52
	97-56	97	263	351.660	-10.42	-8.51
	97-56	99	265	351.304	-10.50	-8.21
	97-56	101	267	350.949	-9.98	-7.75
	97-56	103	269	350.594	-9.75	-8.70
	97-56	105	271	350.238	-9.47	-8.23
	97-56	107	273	349.883	-10.45	-8.71
	97-56	109	275	349.528		Lost in preparation
	97-56	111	277	349.172	-10.35	-8.32
	97-56	113	279	348.817	-9.92	-8.71
	97-56	115	281	348.461	-10.21	-8.28
	97-56	117	283	348.106	-10.56	-8.55
	97-56	119	285	347.751	-9.71	-8.85
	97-56	121	287	347.395	-9.60	-8.52
	97-56	123	289	347.040	-13.30	-10.44
	97-56	125	291	346.684	-10.95	-9.51
	97-56	127	293	346.329	-10.00	-9.03
	97-56	129	295	345.974	-9.58	-8.45
	97-56	131	297	345.618	-10.25	-8.39
	97-56	133	299	345.263	-10.75	-8.91
	97-56	135	301	344.908	-9.63	-7.74
	97-56	137	303	344.552	-10.05	-7.74
	97-56	139	305	344.197	-10.35	-7.93
	97-56	141	307	343.841	-9.03	-7.61
	97-56	143	309	343.486	-9.13	-7.55
	97-56	145	311	343.131	-9.19	-7.61
	97-56	147	313	342.775	-11.34	-8.94
	97-56	149	315	342.420	-9.44	-7.68
	97-56	151	317	342.065	-9.28	-8.44
	97-56	153	319	341.709	-9.22	-7.84
	97-56	155	321	341.354	-12.40	-9.79
	97-56	157	323	340.998	-10.11	-8.74
	97-56	159	325	340.643	-10.22	-8.76
	97-56	161	327	340.288	-10.21	-8.74
	97-56	163	329	339.932	-9.93	-8.34
	97-56	165	331	339.577	-9.09	-8.46
	97-56	167	333	339.221	-10.45	-8.99
	97-56	169	335	338.866	-9.94	-8.97
	97-56	171	337	338.511	-9.68	-8.86
	97-56	173	339	338.155	-9.31	-8.73
	97-56	175	341	337.800	-9.04	-8.59

NG-4D1L	97-56	177	343	337.445	-9.28	-8.76
	97-56	179	345	337.089	-9.27	-9.23
	97-56	2	347	336.734	-9.50	-8.68
	97-56	4	349	336.378	-9.10	-8.91
	97-56	6	351	336.023	-11.27	-10.12
	97-56	8	353	335.668	-9.98	-9.28
	97-56	10	355	335.312	-9.14	-8.70
	97-56	12	357	334.957	-9.22	-8.69
	97-56	14	359	334.602	-9.96	-9.27
	97-56	16	361	334.246	-9.75	-9.04
	97-56	18	363	333.891	-9.24	-9.12
	97-56	20	365	333.535	-9.70	-8.49
	97-56	22	367	333.180	-9.10	-8.21
	97-56	24	369	332.825	-9.98	-8.44
	97-56	26	371	332.469	-9.59	-7.96
	97-56	28	373	332.114	-8.94	-8.38
	97-56	30	375	331.759	-8.89	-7.65
	97-56	32	377	331.403	-9.47	-8.24
	97-56	34	379	331.048	-9.68	-8.77
	97-56	36	381	330.692	-10.00	-7.45
	97-56	38	383	330.337	-10.54	-7.36
	97-56	40	385	329.982	-9.78	-7.40
	97-56	42	387	329.626	-14.31	-10.09
	97-56	44	389	329.271	-9.69	-7.50
	97-56	46	391	328.915	-10.02	-7.41
	97-56	48	393	328.560	-9.53	-7.73
NG-4D2L	97-56	50	395	328.205	-10.01	-6.97
	97-56	52	397	327.849	-9.53	-7.42
	97-56	54	399	327.494	-11.18	-9.10
	97-56	56	401	327.139	-9.08	-8.19
	97-56	58	403	326.783	-9.17	-8.48
	97-56	60	405	326.428	-9.54	-7.96
	97-56	62	407	326.072	-9.21	-8.06
	97-56	64	409	325.717	-8.82	-7.45
	97-56	66	411	325.362	-10.23	-8.05
	97-56	68	413	325.006	-9.74	-7.45
	97-56	70	415	324.651	-8.69	-7.76
	97-56	72	417	324.296	-9.88	-8.27
	97-56	74	419	323.940	-10.28	-7.82
	97-56	76	421	323.585	-9.64	-8.30
	97-56	78	423	323.229	-9.06	-7.97
	97-56	80	425	322.874	-9.36	-8.00
	97-56	82	427	322.519	-9.54	-7.38
	97-56	84	429	322.163	-9.08	-7.43
	97-56	86	431	321.808	-10.84	-8.72

	97-56	88	433	321.453	-9.51	-7.38
	97-56	90	435	321.097	-8.64	-8.50 U-Series NG-D/NG-J
	97-56	92	437	320.742	-9.50	-8.68 U-Series NG-D/NG-J
	97-56	94	439	320.386	-9.70	-8.69
	97-56	96	441	320.031	-9.34	-7.12
	97-56	98A	443	319.676	-9.30	-7.37
	97-56	100	445	319.320	-10.50	-8.96
	97-56	102	447	318.965	-9.08	-8.03
	97-56	104	449	318.609	-8.89	-8.16
	97-56	106	451	318.254	-8.98	-8.76
	97-56	108	453	317.899	-9.09	-7.75
	Unconformity		455			
NG-5BL	98-24	2	457	253.800	-9.37	-9.53
	98-24	4	459	253.088	-10.34	-9.41
	98-24	6	461	252.376	-9.23	-9.10
	98-24	8	463	251.664	-9.75	-9.44
	98-24	10	465	250.952	-9.44	-9.20
	98-24	12	467	250.239	-9.41	-8.78
	98-24	14	469	249.527	-9.52	-8.81
	98-24	16	471	248.815	-9.24	-8.33
	98-24	18	473	248.103		Lost in preparation
	98-24	20	475	247.391	-11.77	-10.15
	98-24	22	477	246.679	-10.35	-8.63
	98-24	24	479	245.967	-9.22	-6.06
	98-24	26	481	245.255	-11.15	-10.09
	98-24	28	483	244.543	-10.28	-9.28
	98-24	30	485	243.830	-9.80	-8.52
	98-24	32	487	243.118	-9.75	-8.42
	98-24	34	489	242.406	-9.22	-6.29
	98-24	36	491	241.694	-9.55	-7.55
	98-24	38	493	240.982	-9.39	-6.91
	98-24	40	495	240.270	-10.51	-9.00
	98-24	42	497	239.558	-9.85	-8.91
	98-24	44	499	238.846	-9.94	-8.54
	98-24	46	501	238.134	-9.78	-9.05
	98-24	48	503	237.421	-9.93	-8.55
	98-24	50	505	236.709	-9.98	-8.77
	98-24	52	507	235.997	-10.45	-8.58
	98-24	54	509	235.285	-10.48	-9.28 U-Series NG-E
	98-24	56	511	234.573	-10.18	-8.18 U-Series NG-E
	98-24	58	513	233.861	-10.35	-8.38
	98-24	60	515	233.149	-10.12	-8.95
	98-24	62	517	232.437	-9.30	-8.09
	98-24	64	519	231.724	-10.23	-8.96
	Unconformity		521			

NG-5C1L		522	135.012		Missing
98-24	1	523	134.940	-10.18	-3.22
98-24	3	525	134.797	-10.01	-3.31
98-24	5	527	134.654	-9.56	-1.93
98-24	7	529	134.511	-9.64	-3.24
98-24	9	531	134.368	-9.94	-1.95
98-24	11	533	134.225	-9.66	-0.97
98-24	13	535	134.082	-10.80	-2.87
98-24	15	537	133.938	-9.80	-2.71
98-24	17	539	133.795	-10.01	-4.27
98-24	19	541	133.652	-9.63	-6.61
98-24	21	543	133.509	-9.70	-7.60
98-24	23	545	133.366	-9.88	-7.63
98-24	25	547	133.223	-9.53	-8.37
98-24	27	549	133.080	-9.20	-7.72
98-24	29	551	132.936	-9.47	-8.23
98-24	31	553	132.793	-9.42	-8.07
98-24	33	555	132.650	-9.47	-7.94
98-24	35	557	132.507	-9.63	-7.48
98-24	37	559	132.364	-9.50	-7.86
98-24	39	561	132.221	-9.61	-8.14
98-24	41	563	132.078	-9.62	-7.87
98-24	43	565	131.935	-9.06	-8.23
98-24	45	567	131.791		Lost in preparation
98-24	47	569	131.648		Lost in preparation
98-24	49	571	131.505	-9.43	-8.82
98-24	51	573	131.362	-9.08	-8.82
98-24	53	575	131.219	-8.99	-8.62 U-Series NG-F
98-24	55	577	131.076	-10.07	-9.20
98-24	57	579	130.933	-8.99	-8.60
98-24	59	581	130.790	-9.00	-8.24
98-24	61	583	130.646	-8.88	-8.02
98-24	63	585	130.503	-9.04	-7.96
98-24	65	587	130.360	-9.98	-7.95
98-24	67	589	130.217	-8.97	-6.21
98-24	69	591	130.074	-9.20	-7.79
98-24	71	593	129.931	-8.95	-7.24
98-24	73	595	129.788	-8.22	-7.75
98-24	75	597	129.644	-9.23	-7.61
98-24	77	599	129.501	-9.05	-7.75
98-24	79	601	129.358	-9.50	-8.37
98-24	81	603	129.215	-9.97	-8.88
98-24	83	605	129.072	-8.81	-6.27
98-24	85	607	128.929	-8.74	-7.52
98-24	87	609	128.786	-9.26	-6.84

NG-5C2L	98-24	89	611	128.643	-9.44	-8.51
	98-24	91	613	128.499	-9.65	-9.01
	98-24	93	615	128.356	-9.05	-7.85
	98-24	95	617	128.213	-9.26	-8.21
	98-24	97	619	128.070	-9.01	-7.20
	98-24	99	621	127.927	-8.90	-6.81
	98-24	101	623	127.784	-8.64	-7.00
	98-24	103	625	127.641	-9.75	-8.16
	98-24	105	627	127.497	-9.20	-8.14
	98-24	107	629	127.354	-8.77	-7.38
	98-24	109	631	127.211	-8.94	-7.53
	98-24	111	633	127.068	-9.39	-7.81
	98-24	113	635	126.925	-8.84	-8.27
	98-24	115	637	126.782	-8.88	-8.14
	98-24	117	639	126.639	-8.62	-7.70
	98-24	119	641	126.495	-9.16	-7.48
	98-24	121	643	126.352	-8.95	-7.48
	98-24	123	645	126.209	-9.20	-7.81
	98-24	125	647	126.066	-9.35	-6.84
	98-24	127	649	125.923	-9.20	-7.62
	98-24	129	651	125.780	-10.14	-7.66
	98-24	131	653	125.637	-8.84	-7.67
	98-24	133	655	125.493	-9.41	-7.95
	98-24	135	657	125.350	-9.23	-7.86
	98-24	137	659	125.207	-8.81	-7.86
	98-24	139	661	125.064	-8.96	-7.01
	98-24	141	663	124.921	-9.38	-8.56
	98-24	143	665	124.778	-9.49	-8.06
	98-24	145	667	124.635	-9.87	-7.91
	98-24	147	669	124.491	-8.82	-7.95
	98-24	149	671	124.348	-9.47	-8.90
	98-24	151	673	124.205	-9.85	-8.32
	98-24	153	675	124.062	-9.69	-9.73
	98-24	155	677	123.919	-9.43	-8.65
	98-24	157	679	123.776	-9.33	-8.15
	98-24	159	681	123.633	-9.35	-8.13 U-Series NG-G
	98-24	161	683	123.490	-9.20	-8.49 U-Series NG-G
	98-24	163	685	123.346	-9.57	-8.71
	98-24	165	687	123.203	-10.81	-10.02
	98-24	167	689	123.060	-9.06	-7.92
	98-24	169	691	122.917	-8.81	-7.91
	98-24	171	693	122.774	-9.72	-8.02
	98-24	173	695	122.631	-9.45	-8.29
	98-24	175	697	122.488	-10.01	-9.30
	98-24	177	699	122.344	-9.93	-9.09

NG-6L	98-24	179	701	122.201	-9.09	-9.43	
	98-24	181	703	122.058	-8.81	-6.87	
	98-046	77	704	121.987	-9.17	-7.99	U-Series NG-L
	98-046	79	706	121.843	-9.04	-7.63	U-Series NG-L
	98-046	81	708	121.700	-10.06	-5.04	
	98-046	83	710	121.557	-10.23	-5.84	
	98-046	85	712	121.414	-9.65	-2.45	
	98-046	87	714	121.271	-9.35	-1.39	
	98-046	89	716	121.128	-8.98	-2.42	
	98-046	91	718	120.985	-9.66	-4.59	
	98-046	93	720	120.841	-9.31	-5.02	
	98-046	95	722	120.698	-9.80	-4.63	
	98-046	97	724	120.555	-9.45	-8.00	
	98-046	99	726	120.412	-9.27	-5.99	
	98-046	101	728	120.269	-8.84	-6.88	
	98-046	103	730	120.126	-9.25	-6.96	
			731	120.054			Missing
ETC-1C1	98-075	1	1	119.361	-10.22	-8.71	U-Series ETC-C
	98-075	2	3	119.289	-9.18	-8.44	U-Series ETC-C
	98-075	3	5	119.218	-9.91	-8.33	U-Series ETC-C
	98-075	4	7	119.146	-9.80	-8.39	U-Series ETC-C
	98-075	5	9	119.074	-9.41	-8.66	
	98-075	6	11	119.003	-9.61	-8.55	
	98-075	7	13	118.931	-9.23	-8.04	
	98-075	8	15	118.859	-9.01	-8.92	
	98-075	9	17	118.788	-9.49	-8.51	
	98-075	10	19	118.716	-9.68	-8.39	
	98-075	11	21	118.644	-9.88	-8.50	
	98-075	12	23	118.573	-10.17	-8.33	
	98-075	14	27	118.429	-9.34	-8.37	
	98-075	15	29	118.358	-8.97	-7.84	
	98-075	16	31	118.286	-11.72	-11.19	
	98-075	17	33	118.214	-10.12	-10.16	
	98-075	18	35	118.143	-11.56	-9.86	
	98-075	19	37	118.071	-9.98	-9.92	U-Series ETC-A
	98-075	20	39	117.999	-10.25	-10.05	
	98-075	21	41	117.928	-10.07	-9.88	
	98-075	22	43	117.856	-10.50	-9.62	
	98-075	23	45	117.784	-9.77	-9.68	
	98-075	24	47	117.713	-10.42	-9.83	
	98-075	25	49	117.641	-9.64	-9.95	
	98-075	26	51	117.569	-8.78	-3.61	
	98-075	28	55	117.426	-9.35	-3.41	
	98-075	29	57	117.354	-8.58	-4.33	

ETC-1C2A	98-075	30	59	117.283	-8.59	-4.06
	98-075	31	61	117.211	-8.89	-5.68
	98-075	32	63	117.139	-8.88	-4.85
	98-075	33	65	117.068	-10.03	-5.29
	98-075	34	67	116.996	-9.16	-5.48
	98-075	35	69	116.924	-10.52	-7.22
	98-075	36	71	116.853	-9.20	-5.11
	98-075	37	73	116.781	-11.31	-6.69
	98-075	38	75	116.709	-9.01	-4.86 U-Series ETC-D
	98-075	39	77	116.638	-9.51	-6.19 U-Series ETC-D
ETC-1C2B	98-075	40	79	107.489	-9.75	-6.80
	98-075	41	81	101.572	-10.19	-7.61
	98-075	42	83	95.655	-9.14	-6.91
	98-075	43	85	89.738	-8.95	-5.15
	98-075	45	89	77.903	-9.72	-6.00
	98-075	46	91	71.986	-9.83	-5.40
	98-075	47	93	66.069	-9.42	-6.65
	98-075	48	95	60.152	-9.73	-6.24
	98-075	50	97	54.235	-8.63	-6.03
	98-075	51	99	48.318	-9.39	-6.06
	98-075	52	101	42.400	-9.67	-6.35
	98-075	53	103	36.483	-9.15	-5.62
	98-075	54	105	30.566	-9.39	-6.73
	98-075	55	107	24.649	-9.61	-5.64
	98-075	56	109	14.492	-9.24	-5.67 U-Series ETC-E
	98-075	57	111	14.228	-9.25	-5.81 U-Series ETC-E
	98-075	58	113	13.963	-9.62	-6.93
	98-075	59	115	13.699	-9.04	-6.97
	98-075	60	117	13.435	-9.91	-7.27
	98-075	61	119	13.170	-9.90	-6.70
	98-075	62	121	12.906	-10.03	-6.33
	98-075	63	123	12.641	-11.97	-7.95
	98-075	64	125	12.377	-9.71	-6.77
	98-075	65	127	12.112	-12.84	-6.63 U-Series ETC-B
	98-075	66	129	11.848	-11.00	-5.63 U-Series ETC-B
	98-075	67	131	11.583	-9.49	-5.26
WFP-2L	97-8	12	1	3.954	-10.83	-8.70 U-Series WFP-2-A
	97-8	13	2	3.918	-12.50	-9.69 U-Series WFP-2-A
	97-8	14	3	3.882	-10.50	-7.11 U-Series WFP-2-A
	97-8	15	4	3.846	-9.87	-7.00 U-Series WFP-2-A
	97-8	16	5	3.810	-9.74	-7.82 U-Series WFP-2-A
	97-8	17	6	3.774	-10.90	-7.63
	97-8	18	7	3.738	-12.55	-8.99
	97-8	19	8	3.702	-10.00	-8.10

97-8	20	9	3.666	-9.84	-8.16
97-8	21	10	3.630	-10.43	-7.65
97-8	22	11	3.594	-10.12	-7.65
97-8	23	12	3.558	-9.91	-7.88
97-8	24	13	3.522	-9.61	-7.93
97-8	25	14	3.486	-11.73	-9.01
97-8	26	15	3.450	-10.01	-8.49
97-8	27	16	3.414	-9.76	-7.37
97-8	28	17	3.378	-9.67	-7.10
97-8	29	18	3.342	-10.04	-6.54
97-8	30	19	3.306	-10.86	-7.14
97-8	31	20	3.270	-9.11	-6.79
97-8	32	21	3.234	-9.26	-7.55
97-8	33	22	3.198	-9.69	-7.14
97-8	34	23	3.162	-9.53	-7.57
97-8	35	24	3.126	-12.85	-8.37
97-8	36	25	3.090	-9.40	-4.49
97-8	37	26	3.053	-12.44	-8.26
97-8	38	27	3.017	-9.40	-6.41
97-8	39	28	2.981	-9.80	-5.99
97-8	40	29	2.945	-9.07	-5.80
97-8	41	30	2.909	-9.88	-6.99
97-8	42	31	2.873	-9.90	-7.97
97-8	43	32	2.837	-10.00	-7.12
97-8	44	33	2.801	-9.91	-8.04
97-8	45	34	2.765	-9.76	-8.05
97-8	46	35	2.729	-9.60	-7.21
97-8	47	36	2.693	-9.95	-7.45
97-8	48	37	2.657	-9.55	-8.12
97-8	49	38	2.621	-9.31	-7.27
97-8	50	39	2.585	-9.62	-6.84
97-8	51	40	2.549		Lost in preparation
97-8	52	41	2.513	-11.55	-8.37
97-8	53	42	2.477	-9.87	-6.53
97-8	54	43	2.441	-10.12	-7.43
97-8	55	44	2.405	-9.59	-7.85
97-8	56	45	2.369	-9.52	-7.13
97-8	57	46	2.333	-10.16	-8.07
97-8	58	47	2.297	-9.30	-4.53 U-Series WFP-2-B
97-8	59	48	2.261	-9.51	-7.17 U-Series WFP-2-B
97-8	60	49	2.225	-9.17	-5.62 U-Series WFP-2-B
97-8	61	50	2.189	-9.77	-7.04

Appendix 8 – Rainwater isotope data for OCNM.

Sample	Lab	number (XXXXXX)	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$
			V-SMOW (‰)	V-PDB (‰)
RW-1	OR	99359	-8.1	-37.8
RW-2	OR	99360	-8.3	-38.0
RW-3	OR	99361	-8.2	-37.9
RW-4	OR	99362	-8.3	-38.0
RW-5	OR	99363	-8.2	-37.9
RW-6	OR	99364	-8.4	-38.1
RW-7	OR	99365	-8.3	-38.0
RW-8	OR	99366	-8.9	-38.6
RW-9	OR	99367	-8.9	-38.6
RW-10	OR	99368	-9.1	-38.8
RW-11	OR	99369	-9.0	-38.7
RW-12	OR	99370	-7.3	-37.0
RW-13	OR	99371	-3.6	-33.4
RW-14	OR	99372	-16.0	-45.4
RW-15	OR	99373	-16.2	-45.6
RW-16	OR	99374	-7.8	-37.5
RW-17	OR	99375	-8.9	-38.6
RW-18	OR	99376	-8.7	-38.4
RW-19	OR	99377	-9.0	-38.7
RW-20	OR	99378	-9.0	-38.7
RW-21	OR	99379	-9.1	-38.8
RW-22	OR	99380	-9.1	-38.8