VOLATILES ON SOLAR SYSTEM OBJECTS: CARBON DIOXIDE ON IAPETUS
AND AQUEOUS ALTERATION IN CM CHONDRITES

by

Eric Edward Palmer

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF PLANETARY SCIENCES
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA
2009
As members of the Dissertation Committee, we certify that we have read the dissertation prepared by Eric Edward Palmer entitled Volatiles on Solar System Objects: Carbon Dioxide on Iapetus and Aqueous Alteration in CM Chondrites and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

Date: 15 October 2009

Robert H. Brown

Date: 15 October 2009

Dante Lauretta

Date: 15 October 2009

Roger Yelle

Date: 15 October 2009

Jonathan I. Lunine

Date: 15 October 2009

William Boynton

Final approval and acceptance of this dissertation is contingent upon the candidate’s submission of the final copies of the dissertation to the Graduate College. I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Date: 15 October 2009

Dissertation Director: Robert H. Brown
STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at the University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Eric Edward Palmer
ACKNOWLEDGEMENTS

The quest for getting my Ph.D. has been a long one that started shortly after I completed flight training in the United States Air Force. I began the task of getting some necessary background courses in physics, chemistry and geology such that I could apply to the University of Arizona's Planetary Science Program. Dr. Terry Spell, and Dr. Ron Metcalf at the University of Nevada, Las Vegas provided me a great background and insight into geological processes and its application to how the world works. I always had an eye as to how it would apply to planetary science, and they were very accommodating dealing with my questions and my Air Force driven sporadic schedule. Dr. Charles Wood, who was the department head at the University of North Dakota, also had a strong influence during my quest into planetary sciences. He sent me to my first Lunar and Planetary Science Conference and greatly supported me in my quest to get my Ph.D.

To my committee, I’d like to thank them for their support and dedication in developing my professional career. Their tough questions and subsequent discussions proved to be insightful and greatly helped me understand the complex set of relationships that I was investigating. I would like to also thank Dr. H. Jay Melosh and Dr. John S. Lewis, though could not be at my defense, spent many hours helping me and advising me through my journey.

I give my heart felt thanks to Jason Barnes, Nicole Baugh, Brian Jackson, Diana Smith, Jason Soderblom, Kat Volk, and John Weirich. Long hours they have spent on insightful discussions that helped me to clarify my research, its analysis and its presentation. Knowledge, understanding and wisdom are goals we all share and I hope they achieve them.

To all the grads, I thank them all for their support, interest and general discussions that enriched my time at LPL.

I would also like to thank Pam Street, Glinda Davidson, Virginia Pasek, Maria Schuchardt, Brett Lawrie, Bill Verts, Dyer Lytle, John Pursch, Chris Schaller, and Joe Plassman for their help in the non-academic portions of getting my Ph.D.

To thank my parents, Carl Palmer and Wanda Palmer, I’d like to thank for raising me a nurturing environment and a desire to learn.

Finally, I would like to thank my wife, Cristina, and my kids, Jenna, Thomas and Anna who have traveled with me through this quest. Many times they had to give up what they wanted to do because my schedule required it of them. Their patience, humor and support have been essential.
DEDICATION

To humanity

The goal of discovery is one of the most driving forces of man. May we never lose the desire to look over the next ridge, to turn over another rock, to ask the hard questions, and to be amazed at how things were made.
TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. 8
LIST OF TABLES ...................................................................................................................... 10
ABSTRACT .............................................................................................................................. 11
CHAPTER 1 INTRODUCTION ................................................................................................. 13

CHAPTER 2 STABILITY OF CARBON DIOXIDE .................................................................. 16
  2.1 Introduction ....................................................................................................................... 16
  2.2 Model ................................................................................................................................. 17
    2.2.1 Thermal Model ............................................................................................................ 18
    2.2.1.1 Insolation ............................................................................................................... 18
    2.2.1.2 Black Body Radiation ........................................................................................... 22
    2.2.1.3 Latent Heat Transfer ............................................................................................. 22
    2.2.1.4 Thermal Diffusion ................................................................................................. 25
    2.2.2 CO₂ Transport ............................................................................................................ 29
  2.3 Results ............................................................................................................................... 33
    2.3.1 Ablation Rate ............................................................................................................. 33
    2.3.2 Polar Caps .................................................................................................................. 35
    2.3.3 CO₂ Escape Rates ....................................................................................................... 41
    2.3.4 CO₂ Resupply ............................................................................................................ 45
  2.4 Discussion .......................................................................................................................... 47
  2.5 Conclusion ........................................................................................................................ 50

CHAPTER 3 A POSSIBLE TRACE CO₂ POLAR CAP .......................................................... 52
  3.1 Abstract ............................................................................................................................. 52
  3.2 Introduction ....................................................................................................................... 52
  3.3 Model ................................................................................................................................ 53
  3.4 Results ............................................................................................................................... 54
  3.5 Predictions of a Polar Cap ................................................................................................. 58
  3.6 Conclusion ........................................................................................................................ 66

CHAPTER 4 PRODUCTION OF CARBON DIOXIDE ON IAPETUS ................................. 67
  4.1 Abstract ............................................................................................................................. 67
  4.2 Introduction ....................................................................................................................... 68
  4.3 Method .............................................................................................................................. 70
  4.4 Results ............................................................................................................................... 78
  4.5 Discussion .......................................................................................................................... 85
    4.5.1 Applicability to Iapetus ............................................................................................. 85
    4.5.2 Production of CO₂ on Iapetus ................................................................................... 88
    4.5.3 Quantity of CO₂ on Iapetus ....................................................................................... 92
      4.5.3.1 Dark Material (Leading Side) .............................................................................. 93
      4.5.3.2 Bright Regions (Trailing Side and Poles) ............................................................. 95
TABLE OF CONTENTS - Continued

4.5.3.3 Transition Between Bright and Dark Regions ............................................. 97
4.5.4 UV Photolysis as the Source of CO2 .............................................................. 99
  4.5.4.1 Complexed CO2 ......................................................................................... 99
  4.5.4.2 Photodissociation ...................................................................................... 102
  4.5.4.3 Radiolytic Production .............................................................................. 104
4.6 Conclusion ......................................................................................................... 105

CHAPTER 5 AQUEOUS ALTERATION OF KAMACITE IN CM CHONDRITES 107
  5.1 Abstract .......................................................................................................... 107
  5.2 Introduction ....................................................................................................... 108
    5.2.1 Traditional Alteration Sequence ................................................................. 109
    5.2.2 Location of Alteration .................................................................................. 111
  5.3 Analytical Procedure ......................................................................................... 113
  5.4 Results .............................................................................................................. 116
    5.4.1 Samples ....................................................................................................... 117
    5.4.2 Kamacite ..................................................................................................... 127
    5.4.3 Tochilinite ................................................................................................... 130
    5.4.4 P-rich Sulfide and Accessory Phases in Tochilinite ...................................... 140
    5.4.5 Tochilinite/cronstedtite intergrowth (TCI) .................................................... 150
    5.4.6 Cronstedtite .................................................................................................. 153
    5.4.7 Iron Oxides ................................................................................................. 155
    5.4.8 Troilite ......................................................................................................... 157
  5.5 Discussion ......................................................................................................... 159
    5.5.1 Proposed Alteration Sequence ..................................................................... 159
      5.5.1.1 Alteration Products of Water with S ......................................................... 160
      5.5.1.2 Alteration Products of Water with Si ....................................................... 170
      5.5.1.3 Alteration Products of Water with Limited Reactive Components ......... 171
    5.5.2 Indicators for Post-Accretion Parent-Body Alteration .................................. 175
      5.5.2.1 Tochilinite growth into matrix ................................................................. 175
      5.5.2.2 Regional alteration .................................................................................. 176
    5.5.3 Indicators for Pre-Accretion Parent-Body Alteration ..................................... 183
    5.5.4 Model for alteration ..................................................................................... 189
  5.6 Conclusion ......................................................................................................... 191

CHAPTER 6 CONCLUSION ......................................................................................... 193

APPENDIX A FULL LISTING OF EMPA DATA ...................................................... 195
APPENDIX B SUMMARY OF ALTERATION ......................................................... 221
REFERENCES ........................................................................................................ 224
LIST OF FIGURES

Figure 2.1: Bond Albedo Map of Iapetus ................................................................................. 20
Figure 2.2: Effective Inclination ............................................................................................... 23
Figure 2.3: Energy Balance and Temperature ............................................................................ 24
Figure 2.4: Buffering Effect of CO$_2$ on Temperature .............................................................. 26
Figure 2.5: Distance of CO$_2$ for a Single Time Step .............................................................. 32
Figure 2.6: Ablation Rate ........................................................................................................ 34
Figure 2.7: Long Term Ablation Rates ...................................................................................... 36
Figure 2.8: Thickness Evolution of a Seasonal Polar Cap ......................................................... 37
Figure 2.9: Long Term Loss Rate of CO$_2$ from Iapetus' Surface ........................................... 43
Figure 2.10: Net CO$_2$ Loss Rate ........................................................................................... 46

Figure 3.1: Iapetus' Temperature Map ..................................................................................... 55
Figure 3.2: Flux of CO$_2$ ...................................................................................................... 61
Figure 3.3: Thickness of Removed CO$_2$ ................................................................................ 62
Figure 3.4: Polar Cap ............................................................................................................ 65

Figure 4.1: Thick Film Cryogenic Sample Chamber ................................................................. 71
Figure 4.2: Sample Images ..................................................................................................... 74
Figure 4.3: Deuterium Bulb UV Flux ....................................................................................... 76
Figure 4.4: CO and CO$_2$ Production, Warm ........................................................................ 80
Figure 4.5: CO and CO$_2$ Production, Cold ........................................................................... 81
Figure 4.6: Volatile Burn-Off .................................................................................................. 82
Figure 4.7: Production Rates vs. Temperature ........................................................................ 84
Figure 4.8: Iapetus' Transition Region ..................................................................................... 91
Figure 4.9: Iapetus' Dark Side and IR Spectrum ...................................................................... 94
Figure 4.10: Spectrum of Iapetus' Bright Terrain ................................................................. 96
Figure 4.11: CO$_2$ Absorption Near Water Sources ............................................................... 98

Figure 5.1: Si/Mg/Fe ternary diagram and phases .................................................................. 111
Figure 5.2: BSE image of Murray sample #1 and the 30 regions studied ....................... 121
Figure 5.3: BSE image of Murray sample #2 and the 11 regions studied ....................... 122
Figure 5.4: BSE image of Murchison and the 13 regions studied .................................. 124
Figure 5.5: BSE image of Cold Bokkeveld and the 9 regions studied ......................... 125
Figure 5.6: BSE image of Nogoya and the two regions studied .................................. 126
Figure 5.7: BSE image of Chondrule A of Cold Bokkeveld .............................................. 128
Figure 5.8: Matrix kamacite grain with schreibersite ......................................................... 129
Figure 5.10: Tochilinite associated with type-I chondrules ................................................. 131
Figure 5.11: Tochilinite boundary ......................................................................................... 132
Figure 5.12: FESEM image of kamacite/tochilinite alteration boundary ..................... 133
Figure 5.13: Advanced tochilinite alteration ...................................................................... 135
| Figure 5.14: | Tochilinite's stoichiometric parameters, x and n | 139 |
| Figure 5.15: | Histogram of the Mg/(Mg+Fe) content of tochilinite | 140 |
| Figure 5.16: | Fractured troilite with embedded P sulfide grains | 141 |
| Figure 5.17: | FESEM of P Sulfide | 143 |
| Figure 5.18: | Murray1, Ch 4 X-ray map BSE | 146 |
| Figure 5.19: | Murray1, Ch 4 X-ray map | 147 |
| Figure 5.20: | Murray1, Ch 4 reflected light | 148 |
| Figure 5.21: | Cr/Mg Phase | 149 |
| Figure 5.22: | FESEM TCI | 151 |
| Figure 5.23: | Si/Mg/Fe ternary plot for TCI grains | 153 |
| Figure 5.24: | Cronstedtite in type II chondrules | 154 |
| Figure 5.25: | Cronstedtite rims on kamacite | 155 |
| Figure 5.26: | Oxidized kamacite | 157 |
| Figure 5.27: | Troilite and tochilinite | 158 |
| Figure 5.28: | Kamacite alteration sequence | 160 |
| Figure 5.29: | Plot of tochilinite and P-rich sulfides in Murray | 163 |
| Figure 5.30: | Line scan through Cold Bokkeveld tochilinite grain | 165 |
| Figure 5.31: | Depleted P-rich sulfide ternary diagrams | 166 |
| Figure 5.32: | Volume and alteration of tochilinite and P-rich sulfides | 168 |
| Figure 5.33: | O/Ni/Fe ternary phase diagram | 172 |
| Figure 5.34: | Magnetite rich dust rim | 174 |
| Figure 5.35: | Indications of parent body alteration | 177 |
| Figure 5.36: | Study Region R8I - Indications of parent body alteration | 178 |
| Figure 5.37: | Breccia clast vs. alteration boundary | 181 |
| Figure 5.38: | Localized parent body alteration | 182 |
| Figure 5.39: | Kamacite near tochilinite | 185 |
| Figure 5.40: | Kamacite and hydrated matrix | 186 |
| Figure 5.41: | Nebular alteration of matrix material | 188 |
LIST OF TABLES

Table 2.1: Thermal parameters used in the model .......................................................... 27
Table 2.2: Fraction of CO$_2$ reaching escape velocity as a function of temperature ......... 33
Table 2.3: Sublimation and movement rates for different sized polar caps. .................... 39

Table 3.1: Transport Between Poles of CO$_2$ per Seasonal Cycle. ................................ 57
Table 3.2: Predicted Thickness and Mass of a North Polar Cap as a Function of the Latitude of its Edge. ................................................................................................. 64

Table 4.1: Production Rates ............................................................................................ 79
Table 4.2: Volatile Residence Time.................................................................................. 87
Table 4.3: Optical Constants and Optical Depth .............................................................. 103

Table 5.1: Summary of EMPA data (wt%) .................................................................... 118
Table 5.2: Tochilinite elemental composition (wt%)....................................................... 137
Table 5.3: Empirical formula for tochilinite ................................................................. 138
Table 5.4: Empirical formula for P-rich sulfides .............................................................. 145
Table 5.5: Cr/Mg phase from Murray #1, chondrule 4 (wt%) .......................................... 150
Table 5.6: Tochilinite/Cronstedtite Intergrowths (TCI) chemistry (wt%) ....................... 151
Table 5.7: Iron oxide distribution .................................................................................... 156
Table 5.8: Calculated end members (wt%) for tochilinite and P-rich sulfides .............. 163
Table 5.9: Composition of Cold Bokkeveld tochilinite and P-rich sulfide (wt%) .......... 164
Table 5.10: Mass balance calculations .......................................................................... 168
ABSTRACT

Volatiles are critical in understanding the history of the solar system. We conducted two case studies intended to further this understanding. First, we analyzed the presence of CO$_2$ on Iapetus. Second, we evaluated aqueous alteration in CM chondrites.

We studied the distribution, stability and production of CO$_2$ on Saturn's moon Iapetus. We determined that CO$_2$ is concentrated exclusively on Iapetus' dark material with an effective thickness of 31 nm. The total CO$_2$ on Iapetus' surface is $2.3 \times 10^8$ kg. However, CO$_2$ should not be present because it has a limited residence time on the surface of Iapetus. Our thermal calculations and modeling show that CO$_2$ in the form of frost will not remain on Iapetus' surface beyond a few hundred years. Thus, it must be complexed with dark material. However, photodissociation will destroy the observed inventory in ~1/2 an Earth year.

The lack of thermal and radiolytic stability requires an active source. We conducted experiments showing UV radiation generates CO$_2$ under Iapetus-like conditions. We created a simulated regolith by mixing crushed water ice with isotopically labeled carbon. We then irradiated it with UV light at low temperature and pressure, producing $1.1 \times 10^{15}$ parts m$^{-2}$ s$^{-1}$. Extrapolating to Iapetus, photolysis could generate $8.4 \times 10^7$ kg y$^{-1}$, which makes photolytic production a good candidate for the source of the CO$_2$ detected on Iapetus.

We also studied the aqueous alteration of metal-bearing assemblages in CM chondrites. We examined Murchison, Cold Bokkeveld, Nogoya, and Murray using
microscopy, electron microprobe analysis and scanning electron microscopy. Alteration on CM meteorites occurred within at least three microchemical environments: S-rich water, Si-rich water and water without substantial reactive components. Kamacite alters into tochilinite, cronstedtite, or magnetite. Sulfur associated alteration can form accessory minerals: P-rich sulfides, eskolaite and schreibersite.

Additionally, we determined that there were two alteration events for some CM chondrites. The first formed a hydrated matrix prior to accretion, indicated by unaltered kamacite surrounded by a hydrated matrix. The second occurred after parent body formation. This event is indicated by large regions with consistent alteration features, surrounded by other regions of less altered material.
CHAPTER 1 INTRODUCTION

The 2006 NASA Strategic Plan identified as the goal for Planetary Science to "advance scientific knowledge of the origin and history of the solar system…" In this work we present two case studies that focus on the history and interactions of volatiles on solar system objects. Ultimately, we attempt to answer the questions of what these objects were like when they formed, and what processes made them like what we see today.

Our first case study evaluated the presence of CO$_2$ on Iapetus. Cassini's Visual and Infrared Mapping Spectrometer (VIMS) detected CO$_2$ on Iapetus’ dark side, its leading hemisphere (Buratti et al. 2005). VIMS detected an absorption feature centered at 4.267 um (2343 cm$^{-1}$), which corresponds to the ν3 fundamental asymmetric stretch of CO$_2$ (Sandford and Allamandola 1990a). Preliminary analysis of VIMS data from the Dec 2004 flyby indicated that some CO$_2$ might be in the form of CO$_2$ frost, something not expected.

Previous work on the stability of volatiles showed CO$_2$ to be unstable over the age of the solar system at Saturn’s distance from the Sun (Watson et al. 1963; Lebofsky 1975). Lebofsky predicted a rate of loss between 10 and 50 mm year$^{-1}$ at 0° latitude and between 0.1 and 5 mm year$^{-1}$ at 60° latitude (1975) for a slow rotating body. However, not only has CO$_2$ been detected on Iapetus, but it has also been detected on other Saturnian satellites: Phoebe (Clark et al. 2005); Hyperion (Cruikshank et al. 2007); Enceladus (Brown et al. 2006); and Tethys, Mimas, Dione, and Rhea (Clark et al. 2008).
To address the presence of CO$_2$ in the Saturnian system, we focused on the stability and formation of CO$_2$ on Iapetus. Chapters 2 and 3 describe how long CO$_2$ can reside on the surface of Iapetus before being lost from the system. We expanded the previous studies of the thermal volatility of CO$_2$ by including the effect of gravitational binding energy and Iapetus' obliquity in hopes that it would explain the Cassini observations. We established the effective sublimation rates of CO$_2$, as well as the loss of CO$_2$ due to transport and sequestration in seasonal polar cold traps.

Chapter 4 considers the possibility of photolytic production of CO$_2$ from water ice and carbon-rich material. We report the results of laboratory experiments that simulate conditions on Iapetus. We then evaluate the distribution of detected CO$_2$ on Iapetus to constrain production mechanisms. Finally, we calculate the photodissociation rate of CO$_2$ by UV radiation as it relates to the long-term stability of complexed CO$_2$.

The second case study evaluates the history of aqueous alteration in the meteorite class CM chondrites. Chapter 5 centers around two major questions of aqueous alteration. First, what are the reactions and products of aqueous alteration? Second, when and where did this alteration occur?

We studied four different CM chondrites with different levels of alteration. Meteorites with slight alteration provided a better description of the alteration processes within the early Solar System. We based our study on kamacite, an alloy of 95% Fe and 5% Ni that is very susceptible to alteration by interactions with water. This enabled us to identify regions with limited alteration, identify alteration products, and establish a sequence of alteration.
Additionally, we reviewed the distribution and extent of alteration to constrain the history of each meteorite. There are two major regimes where aqueous alteration could occur: pre-accretion and post-accretion. Pre-accreational theories assume that meteoritic materials experienced aqueous alteration in the solar nebula before they accreted into the parent body. Post-accreational theories assume that the aqueous alteration occurred on the parent body with water that accreted concurrently. Our final area of study was to evaluate the extent of alteration in a large number of mineral assemblages in order to determine the applicability of each alteration theory.