1991

A study of carbon impurities in magnesium oxide using ultra-high resolution infra-red tunable diode laser spectroscopy

James Patrick Trice
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Trice, James Patrick, "A study of carbon impurities in magnesium oxide using ultra-high resolution infra-red tunable diode laser spectroscopy" (1991). *Master's Theses*. 221.
DOI: <https://doi.org/10.31979/etd.p4cd-pfvu>
https://scholarworks.sjsu.edu/etd_theses/221

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 1345828

**A study of carbon impurities in magnesium oxide using
ultra-high resolution infra-red tunable diode laser spectroscopy**

Trice, James Patrick, M.S.

San Jose State University, 1991

U·M·I

300 N. Zeeb Rd.
Ann Arbor, MI 48106

A STUDY OF CARBON IMPURITIES
IN MAGNESIUM OXIDE USING
ULTRA-HIGH RESOLUTION INFRA-RED
TUNABLE DIODE LASER SPECTROSCOPY

A Thesis
Presented to
The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
James Patrick Trice
August 1991

APPROVED FOR THE DEPARTMENT OF PHYSICS

Dr. Joseph F. Becker
Physics Department,
San Jose State University

Dr. Friedemann Freund
Adjunct Professor, Physics Department,
San Jose State University

Dr. H. Sarma Lakkaraju
Physics Department,
San Jose State University

APPROVED FOR THE UNIVERSITY

ABSTRACT

A STUDY OF CARBON IMPURITIES IN MAGNESIUM OXIDE USING ULTRA-HIGH RESOLUTION INFRA-RED TUNABLE DIODE LASER SPECTROSCOPY

by James Patrick Trice

When MgO crystals grow from a CO/CO₂-saturated melt, they are expected to incorporate carbon as a solute impurity. Upon cooling the carbon segregates towards the surface. Upon reheating the carbon degasses as CO₂ and at the same time diffuses back into the bulk. The kinetic isotope fractionation is modeled for different initial conditions. A time-dependent ¹²C/¹³C oscillation is predicted in the evolved CO₂ gasses that is insensitive to surface contamination. Time-dependent ¹²C/¹³C variations are reported experimentally for CO₂ which evolves isothermally at 390°C from MgO, using a tunable diode laser spectrometer to measure the vibrational lines of ¹²C¹⁶O₂ and ¹³C¹⁶O₂ near 4.3 um. The first results reported here support the proposition that carbon impurities are incorporated in the interior of MgO crystals and that diffusion-controlled degassing occurs out of a pronounced surface segregation profile.

ACKNOWLEDGEMENTS

The author owes a debt of gratitude to several individuals whose assistance has been invaluable to the completion of this Thesis. My special thanks to Professor Friedemann Freund and Professor Joseph F. Becker who with their constant support have gone beyond the role of a Thesis advisor. To them I owe my deepest gratitude. I wish to thank Dr. Todd B. Sauke of the Solar System Exploration Branch, NASA Ames Research Center, for his many contributions and help to improve the project and his immense patience. I also wish to thank Professor H. Sarma Lakkaraju for participating as a member of my graduate committee. Finally, I wish to thank my wife, Jane Trice, for her infinite patience and understanding during those long hours I spent away from home working in the laboratory.

Table of Contents

1	INTRODUCTION	1
2	MAGNESIUM OXIDE	4
2.1	Solute Carbon in Magnesium Oxide	4
2.2	Surface Segregation of Solute Carbon	6
2.3	Diffusion Model of Solute Carbon in MgO Crystals	7
3	EXPERIMENTAL METHODS	20
3.1	Preparation of MgO Sample	20
3.2	Gas Collection at High Temperatures	21
3.3	Laser Spectrometer	24
3.4	Experimental Procedure	31
4	EXPERIMENTAL RESULTS	33
5	CONCLUSIONS	36

6	FIGURES	38
7	REFERENCES	89

Chapter 1

INTRODUCTION

Measurements of stable isotopic ratios are used in many areas of science. In particular, fractionation of carbon isotopes in chemical and biological processes can provide scientists with information regarding the history and origin of carbon-containing materials [1,2]. The primary causes of isotope fractionation are different reaction rates and different equilibrium constants for reactions involving the two isotopes ^{12}C and ^{13}C [3]. For example, during photosynthesis plants tend to fix ^{12}C more readily than ^{13}C thus incorporating 2-3% more ^{12}C than ^{13}C relative to the abundance in the ambient gas phase CO_2 [4]. Variations of up to several tenths of a percent may result from a variety of inorganic reactions. In addition, the measurement of the carbon isotope fractionation plays an important role in identifying the origin of different organic and inorganic carbon reservoirs in the geological environment.

A variety of scientific disciplines has used carbon isotope fractionation as a discriminant technique. Geologists in petroleum exploration have measured carbon isotope ratios to determine the sources of oil and natural gases, and the evolution of global photosynthesis during the Earth's past history has been studied by determining carbon isotope ratios in traces of carbon extractable from sedimentary, metamorphic and igneous rocks dating back 3.7 billion years ago [5,6]. Variations in the CO_2 content and the associated $^{12}\text{C}/^{13}\text{C}$ ratio have been traced in CO_2 recovered from frozen ice cores formed during the past 10,000 - 100,000 years [7]. NASA scientists have studied carbon

compounds in extraterrestrial materials such as meteorites and lunar rocks, and they have now proposed the use of carbon isotope ratio measurements on Mars in the Martian atmosphere and possibly Martian soil samples to trace the possible past existence of life on the red planet [8]. The widespread use and importance of carbon isotope fractionation measurements has created a need for the development of new methods that offer advantages over the well-accepted mass spectrometer.

An approach using a tunable diode laser spectrometer to measure $^{12}\text{C}/^{13}\text{C}$ ratios is being pursued at the NASA Ames Research Center [9,10]. The spectrometer is capable of resolving the complex spectrum of rotational lines within the fundamental C-O stretching vibrations of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$. The instrument emits in the 4.3 μm region of the infrared where the manifold of the $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ spectral lines overlap and have approximately equal absorbances at the isotopic concentrations found on Earth ($^{12}\text{C}:^{13}\text{C} \sim 89:1$). The diode laser is scanned over the wavelength range of interest, producing absorption spectra of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ rotational lines. From these absorption spectra the $^{12}\text{C}/^{13}\text{C}$ ratio can be obtained. The high spectral resolution of the instrument eliminates problems with impurity gases. This represents a major advantage over the more conventional Gas Chromatograph-Mass Spectrometer (GCMS) technique. The often elaborate gas purification procedures required to remove trace gas impurities for GCMS measurements are not needed using the tunable diode laser approach. Near real-time gas collection and absorption spectra can be obtained. At present the instrument has been developed to the point where measurements may be made to an accuracy better than 0.4 % [11].

A novel approach has been put forth to determine whether trace impurities of carbon can be found in MgO. Current scientific thinking is that MgO is free from trace carbon impurities in the crystalline lattice; however, recent evidence lends support to the existence of carbon impurities in MgO. Techniques thus far employed in the determination of trace carbon in MgO include x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), $^{12}\text{C}(\text{d,p})^{13}\text{C}$ nuclear reaction profiling, and GCMS measurements of gases evolved from heated MgO crystals [12-17]. A major problem in these measurements is the potential for contamination in the purification of the gases and surface contamination on the crystal which can effect the results from these measurements, thus making them inconclusive. Owing to the kinetic isotope effect, measurements of the $^{12}\text{C}/^{13}\text{C}$ ratio of CO_2 diffusing out of the MgO crystal lattice at elevated temperatures can separate surface contamination effects from trace carbon within the crystal, thus providing conclusive evidence regarding the existence of carbon impurity elements in the interior of the MgO crystal. Furthermore, by using the laser spectrometer to measure the carbon fractionation during diffusion, the possibility of contamination during gas sample preparation is eliminated. Conclusive evidence of carbon impurities in MgO is an important scientific discovery because the scientific community at large believes this is not the case and trace carbon diffusing out of MgO could be another source for the Earth to produce organic compounds.

In this thesis, results of an investigation of carbon diffusing out of MgO crystals are presented and compared to theoretical results calculated using a three-dimensional diffusion model. Agreement between theory and experimental results supports the proposition that carbon is in fact present in the interior of MgO crystals.

Chapter 2

MAGNESIUM OXIDE

2.1 Solute Carbon in Magnesium Oxide

Magnesium oxide (MgO), or periclase, is a structurally dense, face-centered cubic, highly ionic crystal with a very high melting temperature around 2800°C. Technical purity grade MgO (>99.5%) is produced in industrial carbon arc-fusion furnaces for many commercial applications. High purity (>99.99%) MgO crystals are produced by basically the same technique in laboratory-size arc furnaces. Due to the CO-CO₂-rich atmosphere associated with the carbon arc, the melt is saturated with these gas species and with traces of H₂O. Traces of dissolved H₂O manifest themselves readily through the presence of OH⁻ impurities in MgO crystals which can be observed by IR spectroscopy [18]. Traces of Fe, Al, In, and Ca have also been observed in MgO crystals [19,20].

Whether or not traces of CO/CO₂ also become structurally incorporated is a contentious question. Recent studies by x-ray photoelectron spectroscopy (XPS) and ¹²C(d,p)¹³C nuclear reaction profiling have shown evidence that solute carbon in MgO exists and strongly segregates towards the surface at room temperature. At elevated temperatures the carbon concentration in the subsurface zone decreases and upon re-cooling the carbon concentration rises in a reversible manner. Studies of freshly cleaved MgO crystals by secondary ion mass spectroscopy (SIMS) have also provided preliminary evidence that carbon impurities do exist in the arc-fusion grown MgO crystals and

segregate to the surface. These techniques, however, are also sensitive to surface contamination by C-bearing molecules from the gas phase. Rigorous contamination control is often difficult to achieve. Hence these surface-sensitive techniques may not easily provide conclusive results.

On the other hand, basic thermodynamic laws applying to gas-solid phase equilibria require that, whenever a solid crystallizes from the melt in the presence of a gas, in particular a reactive gas like CO and/or CO₂, a certain amount of this gas will become incorporated into the growing crystals. The concentration may be small but it never will be zero. The same fundamental laws indicate that the solubility of a structurally misfitting impurity in the solid state decreases with decreasing temperature. In other words, upon cooling the crystal will tend to segregate the impurity. The segregation is a kinetic process which may come to a halt if the time to achieve thermodynamic equilibrium is insufficient.

Figure 1 depicts schematically the phase relations at the MgO-rich end of the MgO-CO₂ phase diagram for a given CO₂ partial pressure [13]. T_m and T_{crys} are the melting point temperature of MgO in the absence of CO₂ and the crystallization temperature of the melt in the presence of CO₂, respectively. The field to the left of the bold curve is the field of MgO-CO₂ solid solution without foresight of the detailed knowledge of the microscopic structure. The bold curve outlines the exponential decrease in equilibrium concentration (∂_{eq}) with decreasing temperature. This decrease in ∂_{eq} requires segregation of carbon and degassing of CO₂ with concomitant adjustment of the point defect stoichiometry. In the ideal case, in the absence of limiting kinetic factors, the carbon segregation-CO₂ degassing (exsolution) point defect adjustment would continue down to $T = 0$ K at which point $\partial_{eq} = 0$. However, in real cases a departure from thermodynamic equilibrium will occur due to

kinetic effects and other limiting factors. T_{crit} is the temperature at which kinetic factors limit the above process, thus causing the MgO-CO₂ solid solution (ss) to turn into a supersaturated solid solution (sss) of MgO-CO₂. In Figure 1 the hatched area between the bold dashed curve and the vertical straight dotted line downwards from T_{crit} to the abscissa at room temperature, RT, outlines this region of the supersaturated solid solution.

2.2 Surface Segregation of Solute Carbon

If supersaturation occurs, equilibrium thermodynamics requires that the solute impurity builds up a concentration profile beneath the surface [21,22]. Surface concentration of calcium impurities in MgO due to segregation has been reported in the literature 1000 times larger than the nominal bulk concentration [23,24]. The segregation profile is formed by the thermodynamic attempt of the non-equilibrium system to approach local equilibrium in the absence of complete exsolution. The shape of the segregation profile is controlled by various coupling parameters related, for instance, to the heat of solution, the structural misfit of the impurity inside the crystal and the elastic relaxation provided by the surface and the subsurface regions.

Figure 2 depicts two segregation profiles which represent local equilibrium states at different temperatures. The segregation profile is more pronounced at the lower temperature when the degree of supersaturation is highest. Note that Figure 1 predicts the solubility in the bulk increases as the temperature is raised. Therefore, if a given sample has equilibrated internally at a relatively low temperature, and if a high temperature is suddenly imposed, the solute impurity has to redistribute in a predictable way. This is applied here to solute carbon. The solute carbon must in part diffuse into the bulk as the

segregation profile adjusts from the lower to higher temperature. This is equivalent to a mass flux of the solute carbon away from the surface. This is called retrodiffusion. However, raising the temperature also means that the exsolution which was kinetically impeded at the lower temperature can start again. Hence, another mass flux will occur directed towards the surface. This is called exodiffusion. Note that Figure 2 only shows the expected equilibrium profiles without degassing.

Thus, basic thermodynamic laws predict two diffusional fluxes occurring simultaneously in opposite directions in the surface/subsurface area. If above a given temperature the retrodiffusion increasingly prevails over exodiffusion, the total amount of gases evolved isothermally must decrease with higher temperature. This leads to a peculiar phenomenon termed "inverse kinetics." Because the ^{12}C and ^{13}C diffusion coefficients differ by a factor proportional to the square roots of the mass, $(12/13)^{1/2}$, both retrodiffusional and exodiffusional fluxes must be endowed with kinetic $^{12}\text{C}/^{13}\text{C}$ fractionation. The gases collected which evolve from the surface at elevated isothermal temperatures will thus have a time-varying $^{12}\text{C}/^{13}\text{C}$ fractionation signature that is insensitive to surface contamination.

2.3 Diffusion Model of Solute Carbon in MgO Crystals

We generated a diffusion model and numerically simulated the diffusion of solute carbon and the resulting time-varying $^{12}\text{C}/^{13}\text{C}$ ratio from carbon evolved at the surface of MgO crystals in the form of CO_2 . The MgO crystal was modeled as a sphere with radius a and an initial solute carbon concentration with a radial only dependence given by $f(r)$. The

solute carbon retrodiffusion and exodiffusion coefficients were assumed to be equal. This is a simplification and in reality the diffusion coefficients may be different. Fick's law of diffusion in spherical coordinates gives:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(Dr^2 \frac{\partial C}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(D \sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \phi^2} \right] \quad (1)$$

Assuming no θ or ϕ dependence for the diffusion coefficient D and concentration distribution C , (1) reduces to:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left[\frac{\partial}{\partial r} \left(Dr^2 \frac{\partial C}{\partial r} \right) \right] = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \quad (2)$$

where $C = C(r,t)$ = concentration at point r inside sphere at time t
 t = time after equilibrium is perturbed
 r = radial position inside sphere
 D = diffusion coefficient

On putting $u = Cr$, we have

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2} \quad \text{for } 0 < r < a \quad (3)$$

Two boundary cases were considered and modeled for various initial concentration profiles. The first case constrained the boundary of the sphere to zero concentration for all time $t > 0$. This is equivalent to infinitely fast desorption or evaporation of CO_2 from the

crystal surface. The second case limits the rate of desorption or evaporation of CO₂ at the surface. The second case approaches the first case in the limit of the evaporation coefficient (h) going to infinity. The mathematical forms of the two cases are now considered.

In the first case with the boundary of the sphere ($r=a$) constrained to zero concentration and initial concentration at $t = 0$ given by $f(r)$, equation (3) along with the following boundary equations hold:

$$u = 0, \quad \text{when } r=0 \quad (4a)$$

$$u = 0, \quad \text{when } r = a \quad (4b)$$

$$u = rf(r), \quad \text{when } t = 0 \quad (4c)$$

Assuming a solution of the form:

$$u = e^{(-D\alpha^2 t)} (A \cos \alpha r + B \sin \alpha r) \quad (5)$$

It can be shown that:

$$u = \sum_{n=0}^{\infty} e^{(-D\alpha_n^2 t)} B \sin \alpha_n r \quad (6)$$

where

$$\alpha_n = \frac{n\pi}{a} \quad \text{and} \quad A = 0 \quad (7)$$

The constant B in equation (6) can be solved by expanding $f(r)$ in a Fourier sine series (8a) thus obtaining the solution for u in (9).

$$f(r) = \sum_{n=0}^{\infty} g(n) \sin \frac{n\pi r}{a} \quad (8a)$$

where

$$g(n) = \frac{2}{a} \int_0^a f(r) \sin \frac{n\pi r}{a} dr \quad (8b)$$

$$u = \frac{2}{a} \sum_{n=0}^{\infty} e^{(-D\alpha_n^2 t)} \sin \frac{n\pi r}{a} \int_0^a r' f(r') \sin \frac{n\pi r'}{a} dr' \quad (9)$$

Substituting C back in for u gives:

$$C(r,t) = \frac{2}{ar} \sum_{n=0}^{\infty} e^{(-D\alpha_n^2 t)} \sin \frac{n\pi r}{a} \int_0^a r' f(r') \sin \frac{n\pi r'}{a} dr' \quad (10)$$

Equation (10) is the concentration profile inside a crystal at a given time t . The amount of carbon diffused out of the crystal, ∂C_{out} , between times t_1 and t_2 is given in (11) and is the difference in volume integrals of the concentration profile about the sphere at times t_1 and t_2 . The $^{12}\text{C}/^{13}\text{C}$ ratio observed from gases diffusing out of the crystal is given in (12) and is obtained by calculating (11) for the two diffusion coefficients, and possibly different initial concentration profiles, then dividing the results.

$$\partial C_{\text{out}} = \int_{\text{vol}} [C(r, t_1) - C(r, t_2)] dV \quad (11)$$

$$\frac{{}^{12}\text{C}}{{}^{13}\text{C}} = \frac{\partial {}^{12}\text{C}_{\text{out}}}{\partial {}^{13}\text{C}_{\text{out}}} \quad (12)$$

In the second case with a limiting rate of desorption or evaporation off the surface of the MgO crystal, equation (3) along with the following boundary conditions hold:

$$u = 0, \text{ when } r=0 \quad (13a)$$

$$\frac{\partial C}{\partial r} + hC = 0, \text{ when } r = a \quad (13b)$$

$$u = rf(r), \text{ when } t = 0 \quad (13c)$$

Again, assuming a solution of the form:

$$u = e^{(-D\beta^2 t)} (A \cos \beta r + B \sin \beta r) \quad (14)$$

It can be shown that:

$$u = e^{(-D\beta_n^2 t)} B \sin \beta_n r \quad (15)$$

where β_n are the roots of the equation:

$$\beta_n a \cot \beta_n a + ah - 1 = 0 \quad (16)$$

Note that a series solution for u is not given in equation 15 since the series $\sin(\beta_n r)$ is not an ortho-normal function. A series solution for u can be formed in terms of β_n 's after ortho-normalization of the series $\sin(\beta_n r)$. The constant B can then be solved by expanding $f(r)$ in an ortho-normalized sine series about β_n thus giving the following solution for $C(r,t)$ in equation 17 [25,26].

$$C(r,t) = \frac{2}{ar} \sum_{n=1}^{\infty} e^{(-D\beta_n^2 t)} \frac{a^2 \beta_n^2 + (ah-1)^2}{a^2 \beta_n^2 + ah(ah-1)} \sin \beta_n r \int_0^a r' f(r') \sin \beta_n r' dr' \quad (17)$$

Equation (17) is the concentration profile inside a crystal at a given time t . The amount of carbon diffused out of the crystal and the corresponding $^{12}\text{C}/^{13}\text{C}$ ratio is equivalent to equations (11) and (12), respectively, if the evaporation limiting concentration profile, $C(r,t)$, is substituted for the zero surface boundary condition profile.

The numerical evaluation of $C(r,t)$, ∂C_{out} , and $^{12}\text{C}/^{13}\text{C}$ ratio were performed by computer programs written in the "C" programming language. The programs were run on an IBM compatible computer with a 80386-33 MHz CPU and 80387-33 MHz math co-processor. Program execution time varied from a few hours to 2-3 days depending on the number of iterations (n) used in the series solution, the discrete time increment (time resolution), and the total time period covered during a program run. These three parameters in addition to the diffusion coefficient were judiciously chosen to extract and compare certain aspects of the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of surface condition and initial carbon concentration profile. The volume integral in equation (11) was numerically approximated by the trapezoidal rule for numeric integration using 100 equipartitions. In order to simplify the evaluation of the roots for β_n in equation (16), the radius of the crystal

a multiplied by the evaporation coefficient h was set to a value of one. Thus, if the radius of the crystal is set at 100 μm the evaporation coefficient will be $10,000 \mu\text{m}^{-1}$. Only this evaporation coefficient was modeled to investigate the functional differences between the infinitely fast evaporation condition and a limiting evaporation condition. Other evaporation coefficients may be evaluated with an increase in computation time and program complexity in order to determine the roots of equation 16.

The first profile considered was a constant solute carbon distribution ($f(r) = V$) inside the crystal which is equivalent to zero surface segregation. The sine series integrals in equations (10) and (17) can thus be integrated in closed form to give (18) and (19), respectively.

$$\int_0^a r V \sin \alpha_n r' dr' = \frac{V a}{\alpha_n} (-1)^{n+1} \quad (18)$$

$$\int_0^a r V \sin \beta_n r' dr' = \frac{V}{\beta_n} \left[\frac{1}{\beta_n} \sin \beta_n a - a \cos \beta_n a \right] \quad (19)$$

These expressions were substituted back into (10) and (17) and the results for $C(r,t)$, ∂C_{out} , and $^{12}\text{C}/^{13}\text{C}$ ratio as a function of time were numerically computed with the initial ^{12}C and ^{13}C concentrations, V , equal. Figure 3 is a two dimensional plot of the solute carbon concentration profile inside the sphere, with initially constant concentration for $0 < r < a$, at different time slices with the surface of the crystal constrained to zero concentration. The horizontal axis is the radius from the center of the crystal increasing out to the surface in units of $a/100$ and the vertical axis is the ^{12}C solute carbon concentration. In Figure 4, the evaporation limiting case is shown. Comparison of time slices in Figures

3 and 4 clearly shows the limiting effect on exodiffusion or slowing of exsolution of solute carbon by the evaporation surface condition for an initially constant concentration. This is further exemplified in Figures 5a and 5b where the total amount of carbon diffused out of the crystal as a function of the square root of time for both boundary conditions are shown. Note that Figure 5b is the same as Figure 5a except for a change in time scale to show the long term behavior. The vertical axes in Figures 5a and 5b are the cumulative sum of $\partial^{12}\text{C}_{\text{out}} + \partial^{13}\text{C}_{\text{out}}$ and can be equated with the total amount or cumulative pressure of CO_2 evolved during an experiment. For a zero surface segregation profile the model predicts that the zero surface condition will initially exhibit a parabolic or t^2 behavior in evolved CO_2 gases, whereas the evaporation condition initially exhibits a functional dependance less than t^2 . The $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time for both the zero and evaporation limiting cases are shown in Figure 6a. The horizontal axis is the square root of time in the same time unit as the diffusion coefficient, and the vertical axis is the $^{12}\text{C}/^{13}\text{C}$ ratio in units of mils (per-thousand). At very long times, longer than shown in Figure 6a, the $^{12}\text{C}/^{13}\text{C}$ ratio must become less than one to maintain an isotope balance after depletion of all solute carbon. Figure 6b, equivalent to Figure 6a with a decreased time scale, shows the initial increase in the $^{12}\text{C}/^{13}\text{C}$ ratio followed by the gradual decrease in the $^{12}\text{C}/^{13}\text{C}$ ratio. The first initial peak in the oscillation ($t=2$) is an artifact of the program and will be discussed below. By inspection of equations (18) and (19), a difference in the ^{12}C to ^{13}C initial concentration ratio V would affect the vertical scale on the $^{12}\text{C}/^{13}\text{C}$ ratio graph by a proportional amount, but would not affect the shape or relative deviation in the $^{12}\text{C}/^{13}\text{C}$ ratio.

The faster diffusion rate of ^{12}C will produce $^{12}\text{C}/^{13}\text{C}$ isotope fractionation inside the crystal with a $^{12}\text{C}/^{13}\text{C}$ ratio < 1 . Figure 7 is a plot of the $^{12}\text{C}/^{13}\text{C}$ ratio in the interior of

the crystal plotted against radial distance from the center of the crystal at various time slices for the zero surface condition case. Although it would be difficult to devise an experiment to measure the $^{12}\text{C}/^{13}\text{C}$ ratio in the interior of the crystal, the thought of measuring the isotope fractionation wave caused by perturbing equilibrium is provoking.

A brief discussion on the number of series iterations used in the numerical calculations and the effect on the shape of the plots is in order. Figure 8 is the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time with the surface of the crystal constrained to zero concentration. The horizontal axis is the square root of time in the same time unit as the diffusion coefficient, and the vertical axis is the $^{12}\text{C}/^{13}\text{C}$ ratio in units of mils. The three curves on the graph represent the $^{12}\text{C}/^{13}\text{C}$ ratio numerically calculated using 1000, 10000, and 30000 for the number of series iterations, n , in the series solution for $C(r,t)$ given in equation 10. Note that the curves for different values of n converge after some finite time and that the higher value tends to make a smoother initial jump in the $^{12}\text{C}/^{13}\text{C}$ value. The overshoot at smaller values of n is an artifact of the computer program caused by non-infinite number of terms in the series. The series converges and residual errors decrease with increasing values of n such that the $^{12}\text{C}/^{13}\text{C}$ ratio is a smooth curve in the beginning time period. All calculations in this thesis used higher values of n in the beginning time period and lower values at longer times to remove artifacts of the program and keep numerical calculation time to a reasonable value.

A generalized initial concentration profile for evaluating changes in surface segregation profiles was constructed and is shown in Figure 9. This general profile was based in part on an exponential like concentration profile of the surface segregated carbon derived from the XPS data mentioned previously and in part to facilitate the calculation of

the integral in the series solution in closed form. The initial concentration profile (bulk concentration) is constant ($f(r) = V$) from the center of the crystal out to the point cp . Between the points cp and ep the concentration profile increases exponentially to a peak value P at the point ep . From the point ep to a the profile linearly decreases to a nominal surface concentration given by s . Given this initial concentration profile $f(r)$, the sine series integrals in equations (10) and (17) can be integrated in closed form in terms of the variables a, cp, ep, h, V, P , and s . The surface segregation program code was tested and found in agreement with the constant initial profile program code discussed previously by setting the peak concentration P and the surface concentration s equal to the constant concentration V .

The dependence of the time-varying $^{12}\text{C}/^{13}\text{C}$ ratio on peak height P was investigated with the other parameters held constant. The diagram in Figure 10 shows the values of the parameters selected and the three peak heights investigated varying from 2 to 2000 times larger than the bulk concentration. The bulk concentration was set to the same concentration value as the zero segregation case for comparison of results. Figure 11a is a two dimensional plot of the solute carbon concentration in the interior of the crystal at different time slices for the surface of the crystal constrained to zero concentration and the peak height at 2000 times the bulk concentration. The horizontal axis is the interior crystal radius, starting at 75 radial units from the center of the crystal increasing out to the surface in units of $a/100$ and the vertical axis is the ^{12}C concentration. Figure 11a shows the retrodiffusion of carbon towards the interior of the crystal and the decrease in peak height caused by the retrodiffusion and exodiffusion fluxes. Figure 11b is a three dimensional representation of Figure 11a. Figure 12a is a plot of the $^{12}\text{C}/^{13}\text{C}$ ratio in the interior of the

crystal at various time slices for the zero surface condition case and Figure 12b is a three dimensional representation of Figure 12a.

Comparison of Figures 12a and 12b to Figure 7 shows a remarkably different isotope fractionation wave. The $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time using the zero surface boundary condition is shown in Figures 13a and 13b for the three different segregation (peak) heights overlapped with the zero (constant) segregation profile for comparison. Figures 13a and 13b have different time scales to show long term and initial behavior. If solute carbon is present in the interior of the crystal, the model predicts that a time-varying $^{12}\text{C}/^{13}\text{C}$ signature in the gases evolved from the surface will be observed with deviations dependent on whether or not there is segregation and on the height of the segregation profile. The presence of a surface segregation profile induces an oscillation in the $^{12}\text{C}/^{13}\text{C}$ ratio, concomitant with the broadening of the solute carbon profile inside the crystal, not seen in the zero segregation case. Eventually the $^{12}\text{C}/^{13}\text{C}$ ratio from the exponential and zero segregation profiles converge. The greater the surface segregation peak heights, the greater the amplitude of the oscillation and the longer the time for convergence to the zero segregation curve. Figure 14 compares the $^{12}\text{C}/^{13}\text{C}$ ratio for a 2000X segregation height using both the zero surface condition and evaporation condition overlapped with the corresponding zero segregation profiles. The evaporation limiting boundary condition increases the depth of oscillation and shifts the oscillation to longer time in comparison to the zero surface boundary condition.

Next, the dependence of the $^{12}\text{C}/^{13}\text{C}$ ratio on peak widths was investigated with the other parameters held constant. The diagram in Figure 15 shows the values of the parameters selected for three peak widths ranging from 2 to 15 radius units. The peak

heights were selected to be 2000 times the bulk concentration to give a large deviation in the amplitude of the $^{12}\text{C}/^{13}\text{C}$ ratio oscillation. The $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time is shown in Figure 16 using the zero surface boundary condition. The narrower the segregation profile the higher the amplitude of the $^{12}\text{C}/^{13}\text{C}$ oscillation. Additionally, the $^{12}\text{C}/^{13}\text{C}$ oscillation valley and peak shifts slightly to shorter times as the segregation profile narrows, and the time interval between the valley and peak decreases.

By inspection of equations (10) and (17), a change in the diffusion coefficient is equivalent to a change in the time base. The $^{12}\text{C}/^{13}\text{C}$ ratio for two different diffusion coefficients for a zero segregation profile and an exponential segregation profile with a peak height 2000 times the bulk concentration and a width of 5 radius units is shown in Figure 17. A ten fold increase in diffusion coefficient will cause a large (1st order) change in the time interval between valley and peak of the $^{12}\text{C}/^{13}\text{C}$ oscillation, whereas changes in initial peak height or peak width will cause 2nd order changes in the time interval. The diffusion coefficient for carbon impurities in MgO can be estimated by comparison of the time interval between valley and peak of the $^{12}\text{C}/^{13}\text{C}$ oscillation observed in experimental data to that of the model.

The total amount of carbon diffused out of the crystal as a function of the square root of time for the zero surface condition case using various solute carbon profiles mentioned previously is shown in Figures 18a and 18b, using two time scales. The numbers next to each line represent a multiplicative scaling factor used to plot all lines on the same scale. Of particular interest in Figures 18a and 18b are the differences in initial slope and total quantity diffused between the zero surface segregation profile (t^2 behavior) and the exponential surface segregation profile (t^4 behavior). Figure 18c compares the total

amount of carbon diffused out of a crystal for the 2000X zero surface condition and the 2000X evaporation condition.

Contamination on the exterior of the crystal will produce, in the absence of carbon in the interior of the crystal, a constant $^{12}\text{C}/^{13}\text{C}$ ratio if the rate of desorption of ^{12}C and ^{13}C contaminants are equal. In a more elaborate model where the ^{12}C and ^{13}C contaminants exhibit different desorption rates from the surface, in particular desorption of $^{12}\text{C}/^{13}\text{C}$ equal to $(12/13)^{1/2}$, an initial jump followed by a slowly decreasing offset with time of the $^{12}\text{C}/^{13}\text{C}$ ratio will be seen as shown schematically in Figure 19. This might make it hard to distinguish surface contaminants from a zero (constant) segregation distribution. However, the $^{12}\text{C}/^{13}\text{C}$ oscillation from a highly built-up exponential surface segregation distribution is expected to be clearly distinguishable. The presence of contamination on the surface will decrease the amplitude of the $^{12}\text{C}/^{13}\text{C}$ oscillation produced by exodiffusion of solute carbon in the interior of the crystal.

In the next chapter we will discuss the experimental methods and experimental procedures developed for this thesis. This includes the preparation and handling of the MgO sample, gas collection at high isothermal temperatures. A description of the laser spectrometer and of the theory of its operation is included.

Chapter 3

EXPERIMENTAL METHODS

3.1 Preparation of MgO Sample

We performed two series of experiments, series 1 and series 2, using the same MgO crystals but different preparation processes to elucidate various aspects of the diffusion process. The MgO used in these experiments were arc-fused technical purity grade MgO single crystals, designated as EM3 (Dynamit-Nobel AG, Troisdorf, West Germany), produced in blocks of 18 tons. The stated purity of the EM3-grade MgO is 98.5% with approximately 1% secondary phases, mostly forsterite and monticellite. For the series 1 experiments, large lumps of the arc-fused MgO, consisting of millimeter to centimeter sized single crystals, were extracted from the interior parts of the 18-ton industrial production block while still hot (400°C). The lumps were placed in clean, airtight metal containers. Within one hour they were crushed in air in a laboratory jaw crusher and sieved through stainless steel sieves to separate the 75-150 μm grain size fraction. This coarse powder was then packed and stored in glass jars since 1984. The 7 years between crushing the powder and starting the experiment is vastly sufficient time to allow solute carbon contained in the MgO crystal to segregate to the surface. For all series 1 experiments, 6g of MgO was removed from the glass jar and placed into a glass bulb made of standard laboratory glass. The glass bulb was attached to the gas collection system, described later, and slowly pumped down to < 1 mTorr. The glass bulb and sample were then placed in a temperature bath and the experiment started.

For the series 2 experiments, a large cylinder of MgO, roughly 10 cm by 40 cm, was extracted from the interior parts of the same industrial production block of MgO used in series 1, and was stored in open air since 1984. Pieces of the MgO were chipped away from the interior of the cylinder and were immediately crushed in air, using a clean agate mortar, and then sieved through stainless steel sieves to separate the 75-150 μm grain size fraction. A mass of 40g MgO was placed in a glass bulb, then attached to the gas collection system and pumped down to < 1 mTorr. The bulb was placed in a temperature bath and the experiment started. The time from chipping away the MgO from the cylinder to starting the experiment was as short as possible, typically on the order of 1 hour. We did this so that the solute carbon would not have time enough to segregate to the new grain surface, hence giving MgO crystals with a constant initial distribution of carbon impurities.

3.2 Gas Collection at High Temperature

The gas collection apparatus is used to heat the sample to an elevated isothermal temperature, collect in discrete time increments gases evolved from the sample, and transfer the gas from the collection traps to the measurement cell (sample cell) in the laser spectrometer. Figure 20 is a diagram of the gas collection and handling system. We used standard laboratory glass for the tubing. The O-rings on the stop-cock type valves were lubricated with a small amount of silicon grease. The vacuum was generated by a mechanical type pump, capable of < 1 mTorr vacuum, with a LN_2 trap between the pump and gas collection system. A capacitance type pressure gauge (model 600A-10T-R12-H21X-4, Serial Number 709-2977, Datametrics, Wilmington, MA 01887) was used to record the gas pressure in the sample or reference cells. The leak rate into the evacuated

system with the vacuum pump valved closed was < 2 mTorr/min. A gas input to load in the standard reference gas to either the sample or reference cells was provided and operated by one of the stop-cock valves.

The glass bulb containing the sample MgO was placed in a large heat bath containing 20 kg of molten solder (Pb-Sn) contained in a stainless steel container sitting on a hot plate which provided the basic heat load. The sides of the stainless steel container were wrapped with a heating tape and surrounded by thermal insulation. A Nichrome (K-type) thermocouple, embedded in a glass tube, was immersed in the liquid solder, the output of which was attached to a time proportional type temperature controller (model 6001A, Omega, Stamford, CT 06907). The output of the hot plate was set such that the temperature bath would stabilize out at approximately 20°C below the desired temperature when the heating tape was deactivated. The temperature controller would cycle on and off a Variac attached to the heating tape, regulating the temperature of the solder bath to within $\pm 1^{\circ}\text{C}$. The output setting of the Variac was typically set at 50% during an experimental run. In the beginning of an experiment, the Variac output would be increased momentarily to 100% to compensate for the lowering of the bath temperature by about $5\text{--}6^{\circ}\text{C}$ due to the latent heat of mass of the glass bulb and sample. The first gas sample was collected between the time the glass bulb was immersed and the temperature bath re-stabilized to the desired temperature (typically 2 minutes). A second thermocouple was also immersed in the temperature bath and the output periodically monitored to insure the primary temperature controller was operating correctly.

Prior to starting an experiment, the entire gas collection system including the glass bulb (sample) and and spectrometer measurement cells were evacuated to < 1 mTorr. The

gases evolved from the sample under test were collected sequentially in the six gas collection traps after passing through a dry ice/methanol (-80°C) trap to remove water. The trap currently collecting gases was open on the MgO sample side and immersed in a LN_2 dewar, thus cryo-pumping and trapping the CO_2 gases evolved from the sample. After a set period of time this collection trap was closed and another collection trap opened to cryo-pump and trap the evolved gases. Control experiments indicated there was no measurable $^{12}\text{C}/^{13}\text{C}$ isotope fractionation due to cryo-pumping. Prior to removing the LN_2 dewar from a collection trap, the trap was opened to the spectrometer side of the gas collection system, with the sample cell closed and tubing evacuated, to measure the pressure of non-condensable gases. Before closing the cell, the cell and tubing were pumped down < 1 mTorr to remove the non-condensable gases from the collection trap. The LN_2 dewar was removed and the trap allowed to warm up to room temperature. A slight deviation from the procedure was used in the series 2 experiments to minimize the effects of the relatively large amount of non-condensable gases evolved from the series 2 prepared samples. The non-condensable gases were periodically bled off, at a slow rate, through the collection cell currently collecting the gases by opening the spectrometer end of the cell to the vacuum pump.

Prior to the start of an experiment, the standard reference gas was pre-loaded into the reference cell at a pressure of 500 mTorr and the sample cell evacuated and closed off. The collection trap containing the gas to be analyzed was open and the CO_2 gas pressure was recorded. The sample cell was then opened and the gas pressure again recorded. If the pressure in the sample cell was above 500 mTorr, the cell was slowly pumped down to 500 mTorr to match the pressure of the standard reference gas in the reference cell. The sample cell was then closed and spectra recorded by the spectrometer. If the gas in the

sample cell was less than 500 mTorr, the sample cell was closed off and the reference cell and tubing evacuated. The reference cell was then reloaded with the standard reference gas at the same pressure as the sample gas contained in the sample cell. The reference cell was then closed and the spectra recorded by the spectrometer. Calibration spectra were periodically obtained by appropriately evacuating and re-loading the sample and reference cells.

3.3 Laser Spectrometer

The tunable diode laser spectrometer records the spectra of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ absorption lines in CO_2 gases, namely a sample and standard reference gases, thus determining the $^{12}\text{C}/^{13}\text{C}$ isotopic ratio of the sample gas compared to the reference gas. The technique employs the use of absorption lines of $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ in the 4.3 μm vibrational bands [27]. In the spectral region where the ν_3 bands of the two CO_2 isotopes overlap, certain closely spaced $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ rotational spectral lines have approximately equal absorbances at the isotopic concentrations found on Earth as shown in Figures 21a and 21b. The R(10) line of $^{13}\text{C}^{16}\text{O}_2$ at 2291.6809 cm^{-1} and the P(60) line of $^{12}\text{C}^{16}\text{O}_2$ at 2291.5422 cm^{-1} , both in the ν_3 fundamental band region of CO_2 , were selected for use due to the close separation of 0.139 cm^{-1} between the lines. The narrow emission line width of the semiconductor laser, on the order of 0.0003 cm^{-1} , easily resolves these lines. A very weak absorption hot band P(40) line of $^{12}\text{C}^{16}\text{O}_2$ at 2291.5861 cm^{-1} lies between the R(10) and P(60) spectral lines as shown in Figure 22. At the high spectral resolution obtainable by using the semiconductor diode laser, absorption lines of trace impurity gases such as NO_2 , CH_4 , and H_2O are far from the narrow and closely spaced

$^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ rotational absorption lines and pose no interference problems.

Comparing the absorbances of the R(10) and P(60) line pair yields a measure of the $^{12}\text{C}/^{13}\text{C}$ isotopic ratio.

For this project, the tunable diode laser spectrometer used is a modified model LS-3 (Laser Photonics, Analytics Division, Bedford, MA 01730) and is shown in Figure 23. The diode laser (model L5621-2290-2305, Serial number 18-18, Laser Photonics, Analytics Division, Bedford, MA 01730) used in the spectrometer is a lead sulfide buried heterostructure type device capable of operation up to 120K. The particular diode laser used has a single mode emission and can be temperature tuned between 2290 cm^{-1} and 2305 cm^{-1} and injection current tuned over a 5 cm^{-1} band. The diode laser was mounted under vacuum in a liquid nitrogen dewar with an integral resistance heater and thermocouple. The laser temperature is controlled to within $\pm 0.003\text{K}$ of the set point by a proportional control system closed looped around the thermocouple and resistance heating device. Prior to starting an experiment, the laser temperature set point is adjusted to select an appropriate lasing mode and the injection current minimum and maximum values are selected so the laser output scans across the spectral region of interest. The scan is accomplished by linearly ramping the diode laser injection current between the minimum and maximum values as shown in Figure 24. At the beginning of the injection current ramp, a blanking pulse (current below threshold) turns off the laser providing a zero signal level. The blanking pulse and current ramp are repeated at a fixed frequency of 50 Hz with one period termed a *sweep*.

The diode laser emission is collimated by a one inch focal length barium fluoride lens and is then passed through a 0.5 meter Czerny-Turner grating monochromator to

insure isolation of a single laser mode. The laser beam is split with a pellicle beamsplitter and the two beams are directed through identical reference and sample gas cells, with 15% and 85% of the light passing through each cell, respectively. The cells have a 16 cm pathlength and barium fluoride windows tilted at a slight angle relative to the laser beam propagation direction to minimize the coupling of back reflections with the diode laser. The detectors, operated in a photo-voltaic mode, are fabricated out of indium antimonide (model IS-2, InfraRed Associates, Cranbury, NJ 08512) and are mounted under vacuum in a liquid nitrogen dewar with a sapphire window. The photo-voltaic currents from the detectors are DC-coupled into a transimpedance preamplifier and subsequently sampled and digitized by a 12 bit analog-to-digital (A/D) convertor (model DAS-16F, Metrabyte Corp., Taunton, MA 02780) at a 100 kHz rate. The A/D converter, with built-in timing/synchronization and direct memory access (DMA) circuitry, is installed in an IBM PC-XT compatible computer with a CPU running at 8 MHz. The PC controls all data acquisition and synchronization with the 50 Hz injection current frequency through the A/D converter, obtaining 2000 data points or channels per sweep. The acquired data (spectra and blanking pulse) are stored in computer memory, in the form of channel number vs detector output, via the A/D DMA capability. The spectrometer is fitted with a cover to allow purging of the laser beam path with a nonabsorbing gas in the spectral region of interest, such as nitrogen.

Figure 25 depicts a flow diagram of the data analysis and reduction to obtain the $^{12}\text{C}/^{13}\text{C}$ isotopic ratio of a gas in the sample cell. The dotted boxes are functions not used in the experiments reported in this paper, but are suggestions to improve the system, and will be discussed later. The dotted line shows a partition between functions performed on the PC-XT computer, in BASIC or assembly language, and functions performed on a DEC

Microvax in the Interactive Data Language (IDL). In addition to recording the spectra of the sample gas and standard reference gas, three types of calibration spectra are required to remove systematic instrument errors. The calibration spectra are taken for both the sample and reference cell laser beam paths, and are composed of an evacuated cell, evacuated cell with etalon in the laser beam path, and saturated (~ 100 Torr CO_2 pressure) cell using the standard reference gas.

Multiple sample or reference cell spectra sweeps are co-added to increase the signal to noise ratio. The co-adding is accomplished by a technique known as sweep integration and is performed by assembly language routines in the PC ^[27]. The sample cell and reference cell sweeps to be co-added are acquired alternately (within 100 ms), rather than simultaneously. Since 512 individual sweeps are co-added over the data collection period, the sample and reference data are collected essentially simultaneously. The time to acquire, add, and store 512 spectra sweeps (~ 40 seconds) is a limiting factor in the sample measurement throughput time. The final spectra from the sample or reference cell is transferred to a DEC Microvax for further processing.

The first step after obtaining the final spectra was to convert the channel number to wavenumber scale for each of the spectral scans. A 25.4 mm germanium etalon (free spectral range = 0.04864 cm in the spectral region near 2290 cm^{-1} at room temperature) was inserted into a collimated portion of the laser beam path and the resulting interference spectra recorded. This is the etalon calibration spectra mention previously. The sample and reference cells were evacuated for this measurement. The free spectral range of the etalon divided by the number of data channels between successive interference maxima yields the number of wavenumbers per channel as a conversion factor. A slight non-

linearity in the conversion factor from the beginning to the end of the spectrum is observed, and is compensated for by fitting a polynomial which is then used to convert the data channel numbers to their corrected wavenumber value for all spectra recorded. A typical etalon spectra is shown in Figure 26 with the horizontal axis the channel number and the vertical axis the unnormalized transmission.

The evacuated cell calibration spectra were recorded to determine the 100% transmission as a function of wavenumber. The sample gas, reference gas, and saturated gases spectra are divided by and normalized to the evacuated cell spectra. The zero percent transmission level is estimated by the depth of the blanking pulse section (laser turned off) of the sweep. The normalized saturation spectra is subtracted from the sample and reference gas spectra to correct for a small over estimation of the zero transmission level by the blanking pulse. Figure 27 shows typical raw spectra covering the region of the $^{13}\text{C}^{16}\text{O}_2$ R(10) and $^{12}\text{C}^{16}\text{O}_2$ P(60) spectral lines for an evacuated cell, saturated cell and spectrum of CO_2 lines at 770 mTorr.

The sample and reference gas spectra are fit in transmission space to a mathematical model which consists of Voigt functions $K(\nu)$ that have been transformed from absorption space to transmission space. The Voigt function (equation 20) in absorption space is the convolution of the Doppler-broadened Gaussian line shape and the natural and collision-broadened Lorentzian line shapes ^[29]. The parameters in each spectral line that are fit to the Voigt function are the slope and intercept of the 100% transmission base of the spectra, location of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ absorption peaks, line strength, Lorentz width and Gaussian width. The technique to find the best fit in this multi-dimension space is similar to the Marquardt-Levenberg non-linear regression algorithm ^[30]. Figure 28 shows a typical

calibration-corrected spectrum overlaid with a plot of the Voigt function fit to the data. The horizontal axis is in wavenumbers and the vertical axis is in normalized transmission (1 = 100% transmission). No error in the Voigt fit to the data is perceivable to the eye. The residual (data minus fit) times 10 is plotted below the spectra. Verification of spectroscopic line identity was made by comparing measured spectral parameters with corresponding parameters from the HITRAN data base ^[31]. The normalized ¹²C/¹³C isotopic ratio for the sample gas is determined by dividing the relative line strengths of the ¹²CO₂ and ¹³CO₂ absorption lines in the sample gas by the relative line strengths of the standard reference gas. If the isotopic composition of the standard reference gas is known, the actual, as opposed to the relative, carbon isotope ratio of the sample gas can be determined. For this experiment, we wish to know only the relative change in isotopic ratio for multiple gas samples, hence the standard gas was not analyzed for exact composition.

$$K(\nu) = \frac{Y_C}{\pi Y_D} (\ln 2)^{1/2} \int_0^\infty \frac{\exp(-y^2)}{\left(\frac{Y_C}{Y_D}\right)^2 \ln 2 + \left(\frac{(\nu - \nu_0)}{Y_D} (\ln 2)^{1/2} - y\right)^2} dy \quad (20)$$

where Y_C = Lorentzian line width
 Y_D = Gaussian line width
 ν_0 = wavenumber of line center
 ν = wavenumber

Preliminary tests of the laser spectrometer were made to determine system precision and pressure dependence. Additionally, prior to each experimental run, the ¹²C/¹³C ratio of the standard gas loaded into both the sample and reference cells was determined for

numerous measurements to insure proper operation of the spectrometer. Figure 29 is a plot of the $^{12}\text{C}/^{13}\text{C}$ ratio and Figure 30 the same plot using a 5 point average or smoothing, with standard gas in both sample and reference cells, for one of the experimental runs using calibration spectra taken before and after the string of measurements. The vertical axis is the normalized $^{12}\text{C}/^{13}\text{C}$ ratio in units of mils (parts per thousand) and the horizontal axis is the measurement number taken in sequential order over a time span of 30 minutes. A DC offset between the ideal value of 1 for the isotopic ratio and the two calibration spectra is evident on these plots. Typically the DC offset resulting from different calibration spectra was 1 mil. Based on precision tests of the laser spectrometer, we decided to measure five spectra and average the resulting $^{12}\text{C}/^{13}\text{C}$ ratios for each gas sample to improve measurement accuracy. Furthermore, the averaged $^{12}\text{C}/^{13}\text{C}$ ratios were averaged from calibration spectra taken before and after a string of measurements. Figure 31 shows the pressure dependence of the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of sample cell pressure with the reference cell kept at 500 mTorr. The same dependence exists for other reference cell pressures. Based on this series of tests, we decided to keep the sample cell pressure to within ± 5 mTorr of the reference cell. Figure 32 shows the $^{12}\text{C}/^{13}\text{C}$ ratio of a $\text{CO}_2\text{-N}_2$ gas mixture in the sample cell as a function of percent N_2 in the CO_2 with the reference and sample cells kept at 500 mTorr. Based on this test, we decided to remove non-condensable gases such as CO or CH_4 from a sample before analyzing the gas.

Occasionally the diode laser will "hop" to another mode and return to the original mode within a period of several sweeps. Spectra recorded during a mode hop would give invalid results. Typically, the mode hop is clearly visible in the recorded spectra and the measurement would be rejected. Data were rejected on the basis of a relatively large

residual error (2-3 times greater than the nominal residual error) or from the sample and reference cell pressures not matched within ± 5 mTorr.

3.4 Experimental Procedure

The flowchart in Figure 33 shows the basic procedure followed in an experimental run. The following steps give a brief summary of the procedure involved:

1. Stabilize temperature bath to desired temperature.
2. Prepare sample, put in glass bulb and slowly evacuate.
3. Acquire a set of calibration spectra leaving 500 mTorr standard gas in reference and sample cell.
4. Acquire 20 spectra and resulting $^{12}\text{C}/^{13}\text{C}$ ratio of 500 mTorr standard gas in sample cell.
5. Acquire a set of calibration spectra leaving 500 mTorr standard gas in reference cell and evacuating sample cell.
6. Place bulb in solder bath and start collecting first sample. The Variac controlling the heating tape is increased to 100% output until temperature re-stabilizes at the desired temperature, then reduce back to original setting.
7. Stop collecting the first sample and start collecting the second sample when the temperature bath stabilizes.
8. Use the pressure readings from past measurements to estimate when to stop collecting in a trap and start collecting in another trap. After the gas in a collection trap is loaded into a sample cell and the trap evacuated, the trap can be reused.
9. Analyze gas collected in traps as efficiently as possible to increase throughput time. Always take a minimum of 5 spectra per sample.

10. Periodically (60 minutes) take a new set of calibration spectra. Analyze sample and reference spectra with the closest calibration spectra taken before and after spectral measurements.

Steps 8-10 are repeated as required. Only six collection traps were available for gas collection making it is necessary to process gas samples as efficiently as possible. In the beginning of experiments the traps were quickly filled necessitating longer collection times to allow the gas in a trap to be loaded into the sample cell and the trap evacuated. The average throughput time per sample was about 7 minutes due in part to spectrometer measurement time (3-4 minutes), gas handling and evacuation time (2-3 minutes), and the periodically required calibration spectra.

Chapter 4

EXPERIMENTAL RESULTS

The primary temperature selected for the series 1 (segregated) and series 2 (freshly crushed) experiments was 390°C based on degassing experiments of MgO performed in 1983.^[32] At that time it was observed that an increasing degassing rate was produced with increasing temperature to 400°C, a decreasing degassing rate was produced with increasing temperature between 400°C and 600°C, and an increasing degassing rate was produced with increasing temperature above a temperature of 600°C. Preliminary series 1 experiments were also performed at 350°C, 380°C, and 440°C but were not repeated. Higher temperatures could not be evaluated because of the limited temperature range of the temperature bath (300-450°C).

Figure 34 is a plot of the cumulative pressure of evolved CO₂ from the MgO sample vs square root of time for the 390°C experiments. The plots have been corrected in two instances due to inadvertent loss of gases during the experiments. Differences in cumulative pressure between the two series of experiments are evident, with the series 1 degassing at a far greater rate than the series 2. The series 1 experiments have in effect an even greater degassing rate since the series 1 experiments were performed with 6g MgO powder and the series 2 with 40g of MgO powder. The increased degassing rate for the series 1 experiments relative to the series 2 experiments and the t^2 behavior of the series 2 experiments (zero segregation) was predicted by the model. The series 1 experiments shows a very weak t^4 behavior suggesting a small segregation height (20-200 x Bulk) or an

evaporation limiting condition at the surface when compared to the modeling results. One additional phenomenon recorded was the large (1-2 orders of magnitude) degassing rate of non-condensable gas out of the series 2 experiments relative to the series 1 experiments.

Figure 35 shows the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time at 390°C for two reproduced runs of the series 1 (segregated) and series 2 (freshly crushed) experiments. Five independent spectra for each data point were taken and the resulting $^{12}\text{C}/^{13}\text{C}$ ratios averaged together. Error bars, in the range of 3-5 mils depending on data point, have been omitted for clarity. Figure 36 is a plot of the same data in Figure 35 using a 3 point smooth. The series 1 (segregated) experiments show the predicted oscillation from the modeling results for the carbon surface segregation profile. The series 2 experiments have a different $^{12}\text{C}/^{13}\text{C}$ ratio signature from the series 1 experiments and tend to approach those predicted in the modeling for a zero (constant) segregation profile. The offset between $^{12}\text{C}/^{13}\text{C}$ ratios in the series 1 and series 2 experiments is most likely due to a long term drift (1-2 months) in the day to day operation of the laser spectrometer. The series 1 and series 2 experiments were performed about 6 weeks apart with the inter-series (reproduced) experiments performed 1 week apart. The functional time-dependence of the $^{12}\text{C}/^{13}\text{C}$ ratio is still valid. More experiments, preferably at a shorter time resolution and increased measurement precision, need to be performed at 390°C to provide conclusive evidence of solute carbon impurities in MgO.

The diffusion coefficient of ^{12}C was estimated at 390°C by comparing the peak and valley time interval in the experimental data against the modeling results. Figure 37a and 37b are plots of the $^{12}\text{C}/^{13}\text{C}$ ratio for the series 1 experimental results overlaid with the modeling result giving the best fit for the zero surface condition (using 2000X segregation

height) and evaporation surface condition (using 20X segregation height) cases. This gives a diffusion coefficient of $0.01 (a/100)^{-2}/\text{min}$ in both cases. Note that the time interval between peak and valley was the parameter fit for this estimate, hence the modeling data were shifted slightly to the right in time to align the valley. Figures 37c and 37d compares the experimental data for an order of magnitude change in diffusion coefficient, relative to Figures 37a and 37b. A nominal radius for the sieved MgO powder is 50 μm thus giving a diffusion coefficient of $2.5 \times 10^{-11} \text{ cm}^2/\text{minute} \pm$ one order of magnitude. More experimental data needs to be obtained to confirm this result.

If the diffusion rate doubles for every 10°C change in temperature, then the period of the oscillation for $\pm 10^\circ\text{C}$ change in temperature from the 390°C data presented above may be either too short for the temporal resolution of the experimental apparatus or too long to fit in the same time scale as the 390°C data. Experiments ran at 350°C , 380°C and 440°C tend to support this contention. Figure 38 shows the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of the square root of time for series 1 experiments at 350°C , 380°C , and 440°C and Figure 39 shows the cumulative pressure (corrected in one instance). The $^{12}\text{C}/^{13}\text{C}$ ratio in Figure 38 is a 3 point smooth of the data points and the curves for the 380°C and 440°C experiments have 5 mils and 10 mils offsets added, respectively, to separate the lines for ease of viewing. These experiments were not repeated and more work needs to be done at these and different temperatures to confirm the results.

Chapter 5

CONCLUSIONS

We have modeled isotope fractionation of solute carbon evolved from MgO crystals at elevated temperatures assuming the retrodiffusion and exodiffusion coefficients are equal for surface segregation and zero segregation (constant) impurity distributions. In reality, the diffusion coefficients will not be equal and different diffusion mechanisms such as diffusion along subgrain boundaries or dislocation sites may cause localized changes in the diffusion coefficient. Nevertheless, the model gives insight into the functional shape and dependence of the experimentally measured parameters. The model predicts a distinct signature for the $^{12}\text{C}/^{13}\text{C}$ ratio, insensitive to surface contamination, assuming surface segregated impurities are present in the crystal. The amplitude and period of the oscillation is dependent on the segregation height and width, evaporation coefficient and diffusion coefficient. The experimental results at 390°C show the same functional dependence predicted by the aforementioned model for solute carbon exhibiting surface segregation in the series 1 experiments and for solute carbon exhibiting zero segregation distribution in the series 2 experiments. The time-varying $^{12}\text{C}/^{13}\text{C}$ ratio as well as the functional time dependence of evolved CO_2 (pressure data) support the proposition that solute carbon exists in the *interior* of MgO crystals. Additional data needs to be obtained at 390°C and other temperatures to provide conclusive evidence of solute carbon in MgO.

The technique for measuring the time-varying $^{12}\text{C}/^{13}\text{C}$ ratio in MgO can be improved in two ways. The first is to increase the time resolution of the measurement. We have outlined an approach that would use a continuous flow system for the sample cell in

the spectrometer instead of the six discrete collection traps. Gases evolved from the sample would flow into a measurement cell while older gases further downstream are bled off to maintain a nominal pressure (500 mTorr). This has the potential of increasing the time resolution down to 30 seconds from the current 3-7 minutes. The second improvement is to increase the precision of the laser spectrometer. Since the experiments have been performed, two improvements in the system have already been incorporated by Dr. Todd Sauke of NASA Ames Research Center. The dotted boxes in Figure 25 shows the two processing functions added to increase precision: 1) the tracking function removes a small shifting or drift of the absorption peaks between co-added sweeps due to minute changes in laser diode temperature and injection current noise and drifts; 2) the effect of the instrument response function has been incorporated into the data analysis program to correct for the non-ideal instrument response of the laser spectrometer that tends to broaden the spectral lines. On-going work on the laser spectrometer shows promise of the system reaching the goal of 0.1% measurement accuracy.

The use of isotope fractionation measurements might be useful in many areas of science including the time-varying isotopic ratio of CO₂ gases evolved from various synthetic oxides and natural rocks formed at high pressures in carbon-rich atmosphere in the interior of the Earth. The model developed can easily be extrapolated to other host/impurity systems such as ¹⁴N and ¹⁵N found in crystals. The capability of the diode laser spectrometer to measure other isotope ratios is currently under investigation. Isotope fractionation measurements by diode laser spectroscopy will lead to a better understanding of geologic and biologic processes that took place during early stages of solar system and planetary formation.

Chapter 6

FIGURES

Figure 1. MgO-rich end of the MgO-CO₂ phase diagram for a given CO₂ partial pressure.

Figure 2. Two segregation profiles at local equilibrium states at different temperatures.

Figure 3. Concentration profile time slices inside crystal for constant initial profile using zero surface condition

Figure 4. Concentration profile time slices inside crystal for constant initial profile using evaporation surface condition

Figure 5a. Cumulative (Total) carbon evolved from crystal for constant initial profile.

Figure 5b. Same as Figure 5a except change in time scale.

Figure 6a. $^{12}\text{C}/^{13}\text{C}$ ratio for constant initial profile plotted for zero surface condition and evaporation surface condition.

Figure 6b. Same as Figure 6a using different time scale.

Figure 7. $^{12}\text{C}/^{13}\text{C}$ ratio time slices inside crystal for constant initial profile for zero surface condition.

Figure 8. $^{12}\text{C}/^{13}\text{C}$ ratio for constant initial profile using 1000, 10000 and 30000 terms for number (n) of iterations in series solution.

Figure 9. Generalized concentration profile for solute carbon in MgO.

Figure 10. Three exponential peak heights and corresponding widths used in modeling results of peak height effects on $^{12}\text{C}/^{13}\text{C}$ ratio.

Figure 11a. Concentration profile time slices inside crystal for 2000X peak height using zero surface condition.

Figure 11b. Same as Figure 11a plotted in three dimensions.

Isotopic Ratio vs Radial Distance from Center of
Crystal as a Function of Time

Figure 12a. Isotopic ratio time slices inside crystal for 2000X peak height
using zero surface condition.

Isotopic Ratio vs Radial Distance from Center of
Crystal as a Function of Time

Figure 12b. Same as Figure 12a plotted in three dimensions.

Isotopic Ratio vs Time

Figure 13a. Long term $^{12}\text{C}/^{13}\text{C}$ ratio for three peak heights and same segregation widths using zero surface condition. Plot of zero segregation (constant) profile included for comparison.

Isotopic Ratio vs Time

Figure 13b. Same as Figure 13a except time scale is changed to show initial behavior of $^{12}\text{C}/^{13}\text{C}$ ratio.

Isotopic Ratio vs Time

Figure 14. $^{12}\text{C}/^{13}\text{C}$ ratio for 2000X peak heights using zero surface condition and evaporation surface condition. Plots of zero segregation (constant) profile included for comparison.

Figure 15. Three profile used to determine functional dependence on segregation widths. This leads to 15, 5 and 2 peak widths in Figure 16.

Figure 16. $^{12}\text{C}/^{13}\text{C}$ ratio for 3 peak widths (2000X peak heights) using zero surface condition.

Isotopic Ratio vs Time

Figure 17. $^{12}\text{C}/^{13}\text{C}$ ratio for two diffusion coefficients for zero segregation profiles and exponential segregation profiles with a 2000X peak height and a width of 5 radius units. The numbers next to each line is the relative diffusion coefficient.

Figure 18a. Cumulative (Total) carbon evolved from crystal for various initial carbon profiles. Number at end of each curve is multiplicative scaling factor to plot all curves on same scale.

Figure 18b. Same as Figure 18a except change in time scale to show long term behavior.

Cumulative (Total) Carbon vs Time

Figure 18c. Cumulative (Total) carbon evolved from crystal for 2000X segregation height using zero surface condition and evaporation surface condition.

Figure 19. $^{12}\text{C}/^{13}\text{C}$ ratio due to surface contamination assuming desorption rate of ^{12}C to ^{13}C goes as the square root of the masses $(12/13)^{1/2}$.

Figure 20. Diagram of gas handling system.

Figure 21a. The integrated absorbances of individual rotational lines from the ν_3 bands of ^{13}C (dashed lines) and ^{12}C (solid lines).

Figure 21b. An expanded plot of the overlapped region of the ν_3 bands of CO_2 .

LOG ABSORBANCE VS WAVENUMBER

Figure 22. Weak absorption band (hot band) $\text{P}^*(40)$ between $\text{P}(60)$ and $\text{R}(10)$

Figure 23. Schematic diagram of the diode laser spectrometer.

Figure 24. Diode laser injection current waveform.

Figure 25. Flow diagram of the data analysis and reduction required to obtain the isotopic ratio from spectra.

Figure 26. Spectra of Germanium etalon inserted into laser beam path with measurement cells evacuated.

Figure 27. Raw spectra covering the region of the $^{13}\text{C}^{16}\text{O}_2$ R(10) and $^{12}\text{C}^{16}\text{O}_2$ P(60) spectral lines for an evacuated cell, saturated cell and spectrum of CO_2 lines at 770 mTorr.

Figure 28. Calibration-corrected spectra overlapped with Voigt profile fit to the data. Below is the residual error times 10 between the two plots.

Figure 29. Test of system precision using standard gas at 500 mTorr in sample and reference cells calculated with calibration spectra before and after the string of measurements.

Figure 30. Same as Figure 29 using a 5 point smooth.

Figure 31. Pressure dependence of the $^{12}\text{C}/^{13}\text{C}$ ratio as a function of sample cell pressure with the reference cell kept at 500 mTorr. Both cells used standard gas.

Figure 32. $^{12}\text{C}/^{13}\text{C}$ ratio dependence as a function of percent non-condensable gas (N_2).

Figure 33. Flowchart of basic data collection procedure for an experimental run.

CUMULATIVE PRESSURE VS SQUARE ROOT TIME

Figure 34. Cumulative pressure of evolved CO_2 from MgO sample at 390°C for series 1 and series 2 experiments. Series 1 is segregated sample; Series 2 is freshly crushed sample. Series 1 used 6g MgO powder and series 2 used 40g MgO powder.

ISOTOPIC RATIO VS SQUARE ROOT OF TIME

Figure 35. $^{12}\text{C}/^{13}\text{C}$ ratio for two reproduced runs of series 1 and series 2 experiments at 390°C . Series 1 is segregated sample and series 2 is freshly crushed sample. Each data point is average of 5 independent $^{12}\text{C}/^{13}\text{C}$ ratios derived from 5 spectral measurements.

Figure 36. 3 point smooth of plots in Figure 35.

Figure 37a. 390°C series 1 data overlaid with zero surface condition modeling result (heavy line) giving the best fit.

Figure 37b. 390°C series 1 data overlaid with evaporation surface condition modeling result (heavy line) giving the best fit.

Isotopic Ratio vs Time

Figure 37c. 390°C series 1 data overlaid with zero surface condition modeling result (heavy line) with diffusion coefficient 10 times slower than modeling result (Figure 37a) giving the best fit.

Figure 37d. 390°C series 1 data overlaid with evaporation surface condition modeling result (heavy line) with diffusion coefficient 10 times slower than modeling result (Figure 37d) giving the best fit.

Figure 38. $^{12}\text{C}/^{13}\text{C}$ ratio for series 1 experiments at 350°C, 380°C and 440°C using a 3 point smooth. The 380°C and 440°C curves have 5 and 10 mils offsets added to separate curves for ease of viewing.

Figure 39. Cumulative pressure of evolved CO₂ from MgO sample in series 1 experiments at 350°C, 380°C and 440°C.

Chapter 7

REFERENCES

1. M. Schidlowski, J. M. Hayes and I. R. Kaplan, "Isotopic Inferences in Ancient Biochemistries: Carbon, Sulfur, Hydrogen, and Nitrogen" in *Earth's Earliest Biosphere, Its Origins and Evolution*, J. W. Schopf, ed., Princeton: Princeton University Press (1983).
2. D. J. DesMarais and J. G. Moore, "Carbon and its Isotopes in Mid-oceanic Basaltic Glasses", *Earth and Planetary Science Letters*, 69: 43-57 (1984).
3. L. Melander and W. H. Saunders, "Reaction Rates of Isotopic Molecules", New York: John Wiley & Sons (1980).
4. M. H. O'Leary, "Carbon Isotope Fractionation in Plants", *Phytochemistry* 20: 553-567 (1980).
5. B. P. Tissot and D. H. Welte, "Petroleum Formation and Occurrence", Berlin: Springer-Verlag (1981).
6. A. Kröner, G. N. Hanson and A. M. Goodwin, "Archaean Geochemistry: The Origin and Evolution of the Archaean Continental Crust", Berlin: Springer-Verlag (1984).
7. W. Berner, B. Stauffer and H. Oeschger, "Past Atmospheric Composition and Climate, Gas Parameters Measured on Ice Cores", *Nature* 276: 53-55 (1978).
8. Lunar Planetary Institute. "Scientific Results of the NASA Sponsored Study Project on Mars: Evolution of Volcanism, Tectonics and Volatile", Houston: Technical Report Number 90-06 (1990).

9. R. Yaldaeï , "Isotopic Ratio Measurements Using Ultra-High Resolution Infrared Tunable Diode Laser Spectroscopy", Masters Thesis, Physics Dept., San Jose State University (1988).
10. P. J. Saldanha, "Temperature and Pressure Effects on Spectral Line Broadening of CO₂ Using Ultra-High Resolution Infrared Tunable Diode Laser Spectroscopy", Masters Thesis, Physics Dept., San Jose State University (1990).
11. J. F. Becker, T. B. Sauke and M. Loewenstein, "Stable Isotope Analysis Using Tunable Diode Laser Spectroscopy", Applied Optics 1991 (In Press).
12. H. Kathrein, H. Gonska and F. Freund, "Subsurface Segregation and Diffusion of Carbon in Magnesium Oxide", Appl. Phys. 30A: 33-41 (1983).
13. F. Freund, "Solute Carbon and Carbon Segregation in Magnesium Oxide Single Crystals - a Secondary Ion Mass Spectroscopy Study", Phys. Chem. Minerals 13: 262-276 (1985).
14. F. Freund, H. Kathrein, H. Wengeler, R. Knobel and G. Demortier, "Atomic Carbon in Magnesium Oxide, I: Carbon Analysis by the ¹²C(d,p)¹³C Method", Mat. Res. Bull. 15:1011-1018 (1980).
15. H. Wengeler, R. Knobel, H. Kathrein and F. Freund, "Atomic Carbon in Magnesium Oxide Single Crystals - Depth Profiling, Temperature and Time-Dependent Behavior", J. Phys. Chem. Solids 43: 59-71 (1982).
16. R. Knobel and F. Freund, "Atomic Carbon in Magnesium Oxide Part IV: Carbon Dioxide Evolution Under Argon and Oxygen", Mat. Res. Bull. 15: 1247-1253 (1980).
17. F. Freund, R. Knobel, G. Oberheuser, G. C. Maiti and R. G. Schaefer, "Atomic Carbon in Magnesium Oxide Part V: Hydrocarbon Evolution", Mat. Res. Bull. 15:1385-1391 (1980).

18. F. Freund and H. Wengeler, "The Infrared Spectrum of OH-Compensated Defect Sites in C-Doped MgO and CaO Single Crystals", *J. Phys. Chem. Solids* 40: 129-145 (1982).
19. C. T. Butler, B. J. Sturm and R. B. Quincy, "Arc-Fusion Growth and Characterization of High-Purity MgO Crystals", *J. Crystal Growth* 8: 197-204 (1971).
20. J. Rungis and A. J. Mortlock, "The Diffusion of Calcium in Magnesium Oxide", *Philos. Mag.* 14: 821-827 (1966).
21. D. McLean, "Grain Boundaries in Metals", Oxford: Oxford University Press (1957).
22. C. Lea and M. P. Seah, "Kinetics of Surface Segregation", *Philos. Mag.* 35: 213-228 (1977).
23. R. E. McCune and P. Wynblatt, "Calcium Segregation to a Magnesium Oxide (100) Surface", *J. Am. Ceram. Soc.* 66: 111-117 (1983).
24. E. A. Colbourn, W. C. Mackrodt and P. W. Tasker, "The Segregation of Calcium Ions at the Surface of Magnesium Oxide: Theory and Calculations", *J. Mat. Sci.* 18: 1917-1924 (1983).
25. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids", Oxford: Oxford University Press (1959).
26. H. S. Carslaw, "Introduction to the Mathematical Theory of the Conduction of Heat in Solids", London: Macmillan (1921).
27. D. L. Wall, R. S. Eng and A. W. Mantz, "Development of a Tunable Diode Laser Isotope Ratio Measurement System", Pittsburg Conference (1981).
28. D. E. Jennings, "Absolute Line Strengths in ν_4 , $^{12}\text{CH}_4$: A Dual-beam Diode Laser Spectrometer with Sweep Integration", *Appl. Opt.* 19: 2695-2700 (1980).

29. J. Wormhoudt, "Infrared Methods for Gaseous Measurements: Theory and Practice", New York: Marcel Dekker, Inc. (1985).
30. W. H. Press, B. P. Flannery, S. A. Teakolsky and W. T. Vetterling, "Numerical Recipes in C: The Art of Scientific Computing", New York: Cambridge University Press (1988).
31. L. S. Rothman, R. R. Gamache, A. Goldman, L. R. Brown, R. A. Toth, H. M. Pickett, R. L. Poynter, J. M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C. P. Rinsland and A. H. Smith, "The HITRAN Database: 1986 Edition", Appl. Opt. 26: 4058-4097 (1987).
32. R. Knobel, "H - C - N - O Gaseous Compounds Released from the Surface of MgO and Selected Silicate Minerals", Ph. D. Thesis, University Koln (1983).