

## AN ABSTRACT OF THE THESIS OF

Jennifer L. Cunningham for the degree of Honors Baccalaureate of Science in Geology  
presented on May 29, 2009. Title: The potential influence of database configuration on the  
derivation of trace element partitioning expressions for clinopyroxene.

Abstract approved: \_\_\_\_\_

Roger Nielsen

Decades of experimental work has illustrated the high degree to which the partitioning of most elements is dependent on phase composition, temperature and pressure. In order to quantitatively describe clinopyroxene partitioning it is required to derive expressions using theoretical constraints calibrated with experimental data.

The experimental database available for such an analysis has grown considerably in the past decade, both in number of experiments and the range of compositional and experimental conditions. Our research focused on the compilation of this newly available experimental clinopyroxene data as part of the ongoing update of the Geochemical Earth Reference Model (GERM) partition coefficient database. Previous versions of GERM provided a summary of partitioning information from the literature. In this current update, data on phase composition and experimental conditions are being added.

Our analysis suggests there are great differences in numbers of experiments between different elements, as well as in the distribution of pyroxene composition, melt composition, and experimental temperature and pressure for each element, all of which may have a significant effect on calibration. Understanding the characteristics of the database we are working with when deriving numerical expressions will help us avoid mistakes in application and provide helpful guidelines for future experimental designs.

Key Words: clinopyroxene, trace element partitioning, database configuration, Geochemical Earth Reference Model

Corresponding e-mail address: cunningj@onid.orst.edu

The potential influence of database configuration  
on the derivation of trace element partitioning expressions  
for clinopyroxene

by

Jennifer L. Cunningham

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presented on May 29, 2009.

APPROVED:

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Mentor, representing Geology

---

Committee Member, representing Geology

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Committee Member, representing Oceanography

---

Chair, Department of Geosciences

---

Dean, University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, University Honors College. My signature below authorizes release of my project to any reader upon request.

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Jennifer L. Cunningham, Author

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## TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
BACKGROUND.....	3
History of Clinopyroxene Experiments.....	3
Reasons for new compilation.....	6
Element Partitioning.....	7
ANALYSIS.....	10
Procedures.....	10
Elements Chosen for Analysis.....	12
Assumptions.....	13
RESULTS.....	16
Composition.....	16
Temperature.....	19
Pressure.....	21
Water Content.....	23
Error.....	24
CONCLUSIONS.....	27
BIBLIOGRAPHY.....	29
APPENDICIES.....	31
Appendix A Equations and Definitions.....	31
Appendix B Acronyms.....	32
Appendix C Publications Included in Compilation.....	33

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Papers containing data on partitioning by year.....	5
2. Rock Types.....	11
3.1. Scandium Experiments.....	17
3.2. Titanium Experiments.....	17
3.3. Lanthanum Experiments.....	17
3.4. Samarium Experiments.....	17
3.5. Yttrium Experiments.....	17
3.6. Zirconium Experiments.....	17
4.1. Scandium-Al <sup>IV</sup> Paired Partitioning.....	19
4.2. Yttrium-Al <sup>IV</sup> Paired Partitioning.....	19
4.3. Scandium-Al <sup>VI</sup> Paired Partitioning.....	19
4.4. Yttrium-Al <sup>VI</sup> Paired Partitioning.....	19
5.1. $D_{Sc}$ by Temperature (°C).....	20
5.2. $D_{Sm}$ by Temperature (°C).....	20
6.1. $D_{Sc}$ by Pressure.....	22
6.2. $D_{Sc}$ by Publication.....	22
7.1. $D_{Ti}$ by water content.....	24
7.2. $D_{Zr}$ by water content.....	24

## LIST OF APPENDICES

<u>Appendix</u>	<u>Page</u>
A. Equations and Definitions.....	31
B. Acronyms.....	32
C. Publications Included in Compilation.....	33

*This thesis is dedicated to:*

*The Nerdlings, for their willingness to step up when I was too busy,*

*James Patterson, for his friendship and support,*

*Henri Mason for always making me smile,*

*David Reese, for always being there,*

*My Brother, for driving me forward,*

*Orion Peavy, for proof-reading and caring,*

*My Sister, for going first and lighting the way,*

*But most of all, to My Parents, who raised me right.*

The potential influence of database configuration  
on the derivation of trace element partitioning expressions for clinopyroxene

## INTRODUCTION

Clinopyroxene, a mineral of formula  $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ , plays a large role in controlling the trace element budget in the crust and upper mantle due to its moderate level of compatibility with respect to many trace elements (e.g. Rare Earth Elements (REE), High Field Strength Elements (HFSE) ) and its role in melting and crystallization processes. Decades of experimental work has illustrated the high degree to which the partitioning of most elements is dependent on phase composition, temperature and pressure. In order to quantitatively describe clinopyroxene partitioning, it is required to derive expressions using numerical constraints that are calculated from and calibrated with experimental data (Forsythe et al 1994; Hack et al 1994; Wood and Triguila 2001).

The experimental database available for such an analysis has grown considerably in the past decade, both in number of experiments and the range of compositions and experimental conditions. Our research is focused on the compilation and evaluation of this newly available experimental clinopyroxene data. This compilation was conducted as part of the ongoing update of the Geochemical Earth Reference Model (GERM) partition coefficient ( $D$ ) database (<http://earthref.org/databases/KDD>). Previous versions of the partitioning database provided a summary of partitioning information from the literature; however, they contained no data on phase compositions. In this current update, data on phase compositional and experimental conditions are being added on an investigation by investigation basis. Our initial area of concentration has been on

clinopyroxene, due to the relatively large size of the available data and the significance of the dataset as a whole.

As an example of the utility of the database, we have compiled the available clinopyroxene trace element experimental data on natural, modified natural, and synthetic materials, focusing on the data for REEs and HFSEs. Our analysis suggests there are great differences in numbers of experiments between different elements and between different groups of elements. In addition, the distribution of pyroxene composition, melt composition, and experimental temperature and pressure varies greatly both between and within each group. These differences will all have a significant effect on any method of calibration/regression describing trace element partitioning constraints.

This compilation is both a contribution to experimental investigators and a method of providing better understanding of the constraints on the numerical models for element partitioning in clinopyroxenes. Understanding the characteristics of the database we are working with when deriving numerical expressions will help us avoid mistakes in application, as well as provide helpful guidelines for future experimental designs.

## **BACKGROUND**

### **History of Clinopyroxene Experiments**

Experiments on clinopyroxene have been taking place for decades (e.g. McCallum and Charette, 1978). These experiments provide data on the composition-, temperature-, and pressure-related dependence of the partitioning of trace elements between minerals and melts during the formation of the mineral. Trace elements are elements that are present in amounts less than one tenth of a percent of the weight of a mineral or melt (Blatt, p51). Trace elements in minerals provide a reservoir of information to researchers, such as information about the formation environment and clues to where the melt originated. Trace elements that have radioactive isotopic components (strontium, samarium, uranium, etc.) add a time dimension to the recoverable data by allowing researchers to date the age of the minerals (Blundy and Wood 2003).

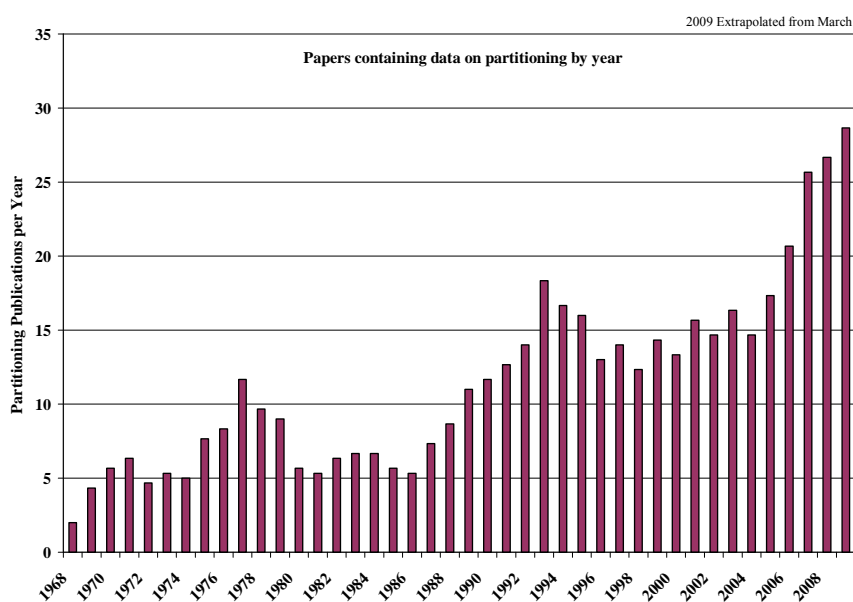
The experimental and analytical technology has improved significantly since these experiments began. These technical advances provide a means of gathering more precise data in far greater amounts, allowing for more experiments to be run (Francis and Minarik 2008, Blundy and Wood 2003). While this plethora of data is readily available as part of the published literature, changes in analytical and experimental procedures over the past 30 years have resulted in a wide range of publication formats, published analytical error, and degree of completeness. This creates a number of significant challenges for any investigator who wishes to understand the entire body of literature or to compile an accessible data resource.

Our primary goal in working with trace elements is to obtain a higher level of knowledge on element partitioning in order to interpret and model the data (both experimental and on natural systems) that has recently been accumulating in large quantities (Blundy and Wood 2003). Instead of the greater accuracy constraining the elemental partition coefficients to single, or near single, numerical values, the partition coefficients have proven to be far more temperature, pressure, and compositionally dependent than originally hoped. The value offered by trace elements, that they would provide an easy ratio to define elemental partitioning with little or no need to look at other parameters, “has slowly tarnished and now a wide range of values are quoted for the partition coefficients of many trace elements” (Francis and Minarik 2008). Unfortunately, this element partitioning data has still been used to create partitioning expressions (Wood and Trigila 2001). In doing so, much of the temperature and pressure dependence of these elements have been ignored. While phase composition may exert a strong influence on partitioning (Wood and Trigila 2001), the pressures and temperatures of formation may exert an influence just as strong. For a researcher to accurately model the partitioning of any elements, without a large-scale compilation of the available data, a previous experiment had to be found that used only pressures, temperatures, and water contents similar to those in the model.

The development of new technologies has allowed us to expand both the range of pressures and temperatures we can cover, and have substantially enhanced the level of analytical precision, particularly over the past two decades. One of the central controversies in the field of trace element geochemistry is the behavior of elements as a function of composition. This can be expressed as a function of the degree to which we

understand the activity coefficients for trace elements. Geoscientists need to be able to describe the behavior of trace elements in complex multi-component systems. However, in order to constrain the behavior of those elements quantitatively it is easiest to run experiments that have as few unknown variables as possible.

One may describe the progress of the field of experimental trace element geochemistry as an interactive solution to a complex multidimensional problem. Experimental studies conducted over a period of over 30 years have resulted in a wide range of presentation formats, approaches to the problem, analytical techniques and errors produced by dozens of different research groups. By performing partitioning experiments beyond the natural range of pressures, temperatures, and compositions, the theoretical models may be calibrated to cover almost any possible situation (Blundy and Wood 2003). This work represents an analysis of the results of the first attempt to produce an accessible database of the available experimental studies.



**Figure 1: Publications per year from 1968 to 2009 that contain data on trace element partition coefficients. (rolling three year average)**

## **Reasons for new compilation**

As shown in Figure 1, the past decade or so has brought a large number of the most accurate compositional experiments into existence. To gain a better understanding of the relationships between partitioning behavior and the pressure, temperature, and compositional components, the information gained so far must be compiled. The larger the database, the less likely error is to affect any encompassing information gleaned from it. The evidence of this is discussed in detail in the “Error” section later in the paper. Due to the higher quality and greater number of experiments, the regression equations defining element partitioning that could be developed from this compilation will provide a basis for updating current models.

To understand geochemical processes, including, but not limited to, the crystallization of magmas and planetary differentiation, a thorough knowledge of the ways elements partition between minerals and melts in different environments is required (Blundy and Wood, 1994; Blundy and Wood, 1997). The expressions that could be determined using a complete and accurate base of experimental data could be used to create functional geochemical models of the Earth and other terrestrial planets (Blundy and Wood, 2003).

For the community to affirm the work of a scientist, the dataset the scientist used needs to be available to everyone. If the data is unavailable, the community loses the ability to determine for themselves the accuracy of the scientists’ conclusions. In a community where each paper is peer reviewed, this availability is essential. In the past this wasn’t a problem; the data used for a paper would be expressed in a table within the paper itself. More recently, the reservoir of experimental data for clinopyroxene, and

many other minerals, has grown so large that it is no longer practical to present all the data used for calculations within each paper. Therefore, most current investigations cite the existing work, and add new experiments to it – often reported in a distinct format. This has resulted in a wide range of reporting styles, nomenclatures and terminology. This is a problem that the GERM project is attempting to rectify. As our new stage of the online database, GERM is in the process of compiling all of the existing published data, reconfiguring the information into a common format and developing a metadata structure that will allow us to provide access to the research community. We are building this database to provide a mechanism for scientists to publish data-briefs, and to facilitate a way to display data that has been produced, but not included in scientific reports, to the community at large.

## Element Partitioning

The partition coefficient of an element  $i$  ( $D_i$ ) is defined as the ratio of the concentration of element  $i$  in the mineral to the concentration of element  $i$  in the liquid, or  $D_i = (i^{\text{mineral}})/(i^{\text{melt}})$ . This provides a measurable constant for use in future compositional calculations. However, the partition coefficient for a single element may vary based on pressure, temperature, the presence of water, and the compositions of the mineral and the melt<sup>§</sup>. Unfortunately, we have yet to constrain exactly how these variables affect the element partitioning (Blundy and Wood 1994, Blundy and Wood, 2003). Until the time

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<sup>§</sup> Other factors, such as oxygen fugacity ( $fO_2$ ), may also affect element partitioning; however, those factors have not been added into the compilation at this point. They will be considered in future versions.

that the dependencies for partitioning can be quantified, the partition coefficient must be treated as an approximation. A much more accurate measure of element partitioning is found through thermodynamics. The activity of the element is a more exact measurement of what is occurring geochemically. The activity of an element  $i$  is equal to the concentration of  $i$  scaled by the activity coefficient, or  $a = \gamma c$  where  $a$  is the activity,  $\gamma$  is the activity coefficient, and  $c$  is the concentration. If elements behaved ideally (activity coefficient = 1), the concentration would equal the activity and allow us to accurately approximate the partitioning behavior independent of the concentration of other components in the system; however, ideal mixing in natural systems is a rarity, and the presence of multiple elements interferes with the ideal reactions of all the other elements, complicating their partitioning behavior.

The activity coefficient takes into account this interference, so the activity of the mineral should be true to how the elements actually interact. Unfortunately, except for cases in which there are a very small number of constituents, we do not know what the activity coefficient is. For mineral-melt interactions in a life-like setting, the number of constituents is far too great, and they interact in far too complicated a manner, to attempt to calculate the activities. Thus, we are again forced to fall back upon the estimate provided by a calculated partition coefficient, an obtainable quantity.

Besides the temperature and pressure variables for element partitioning, any element entering a crystal structure must also conform to Goldschmidt's Rules for Partitioning. Goldschmidt's rules state two basic requirements. For an element which is not part of the basic structure of the mineral to enter that structure, the element must both be within 15% of the volume of the element that it is replacing, and must maintain the charge neutrality

of the crystal structure. If these specifications are not met, the element would deform the crystal structure beyond its level of stability. In such cases, the element is considered an incompatible element (an element that prefers not to be part of the mineral crystalline structure). As a general rule, if the partition coefficient of an element for a certain mineral is equal to or greater than one, it is considered a compatible element. This means that the element prefers to reside in the mineral rather than in the melt. If the partition coefficient greatly exceeds one, then the element is considered highly compatible. Incompatible and highly incompatible elements help to determine the elemental partitioning between different mineral phases.

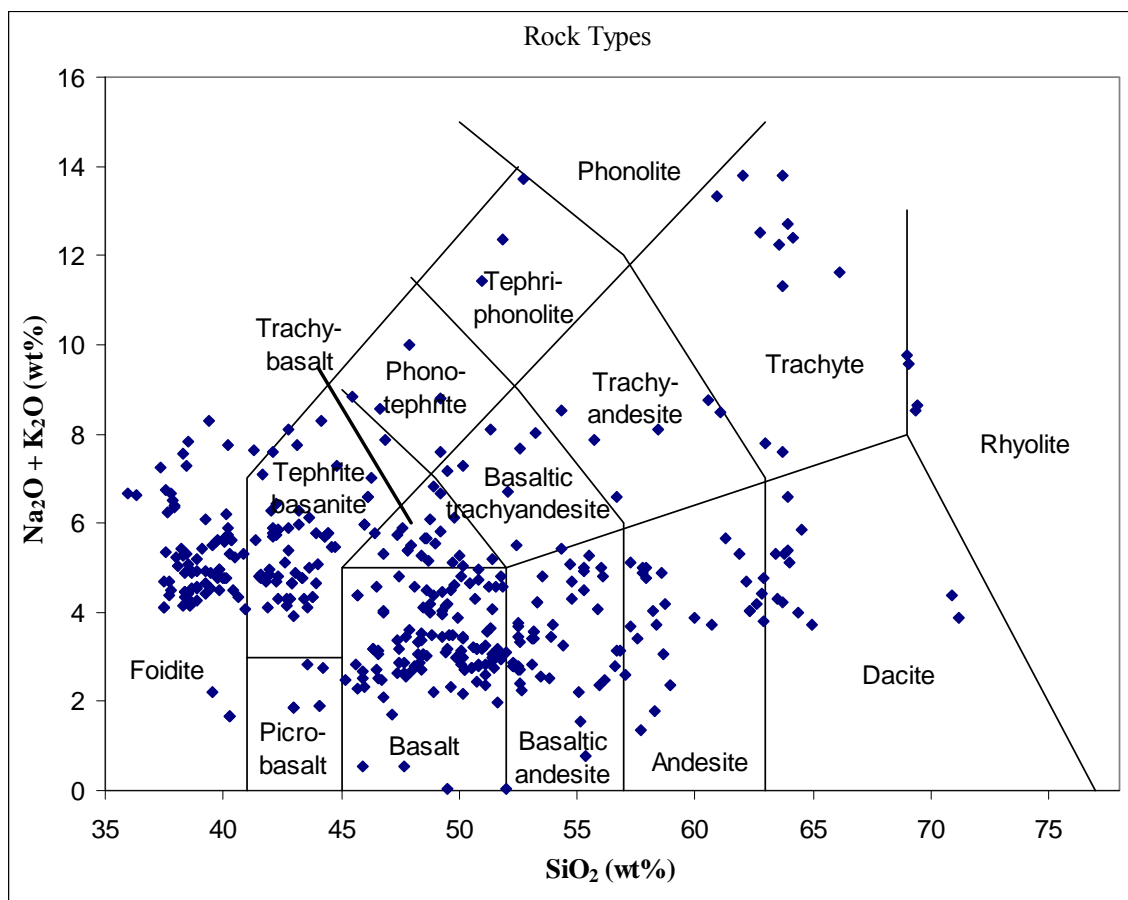
## ANALYSIS

### Procedures

This compilation was mainly created as an example of the utility of the GERM Database. Publications included in this compilation that were not found in GERM are currently in the process of being added to the database. The compositional data reported from analyses of the clinopyroxene and glass formed in experimental runs were downloaded from GERM and compiled into one large table. Only data from experimental runs have been included in this compilation, in order to provide the most coherent report of current information. In addition, only those publications in which the phase compositions and run conditions were reported were included in the dataset. Numerically generated data were not compiled because any constants used to generate this data must have been based on a smaller quantity of experimental data than that available through this database. Phenocryst-matrix, or non-experimental, data were not included because the temperatures and pressures of formation are unknown.

Compositional data presented in any format other than oxide weight percent were converted into this form. From this were calculated normalized mol fractions, partition coefficients between the clinopyroxene and glass, and clinopyroxene end-member components. The formulas were calculated using a modified version of an excel workbook created by John Brady and Dexter Perkins ([http://serc.carleton.edu/research\\_education/equilibria/mineralformulaerecalculation.html](http://serc.carleton.edu/research_education/equilibria/mineralformulaerecalculation.html)). Rock

types were assigned based upon the fit of the glass data on the standard classification scheme for igneous rocks (Le Bas, 1985) (Figure 2).<sup>§</sup>



**Figure 2: Distribution of liquid compositions represented in the clinopyroxene/melt partitioning dataset analyzed for this study. Based on classification scheme by LeBas (1986).**

Other information recorded for each experiment included the temperature, pressure, length of the run, the type of machine that performed the analysis, and whether the initial material was natural, modified natural, or synthetic. The natural experiments involved melting and re-crystallizing a natural rock sample. Modified natural experiments involved melting and re-crystallizing a natural rock sample that has been doped (mixed

<sup>§</sup> The rock type “Carbonatite” shown in later graphs is not shown here, but plots in the region less than 25% SiO<sub>2</sub> and less than four weight percent combined Na<sub>2</sub>O + K<sub>2</sub>O. The gap between carbonatites and the rest of the rock types is due those compositions not occurring naturally on Earth.

with extra amounts of specific elements) to influence the results. Synthetic experiments include completely synthetic mixes of elements or mixes of two or more natural samples. In the case of modified natural experiments, the doping materials are also recorded.

### **Elements Chosen for Analysis**

As it would be highly impractical to relate the exact behavior of every element included in this compilation, the analysis of the quality of the data compiled will focus on six elements: scandium (Sc), titanium (Ti), lanthanum (La), samarium (Sm), yttrium (Y), and zirconium (Zr). These elements were chosen based on their ability to represent different groups of elements, namely the Major Elements, HFSEs, and the Light and Heavy REEs (LREE and HREE).

Titanium was included in this focus group to provide an example of the partitioning behavior of the major elements. The major elements are expected to vary in partitioning far less than the trace elements because they appear in such large abundances. This means that the concentration of Ti is historically a less telltale indicator of the conditions of the formation environment than trace elements.

The REEs, or the Lanthanides, are a group of elements that show a consistent decrease in ionic radius across the periodic table of elements, which produces a consistent change in chemical properties. As these elements are also only available in trace amounts, they become an almost ideal way to constrain partition coefficients over a range of elements. The REEs are separated into two main subgroups: LREEs and HREEs. Three elements were chosen from the REEs as an attempt to cover the full range of the

spectrum. La represents the LREE end of the spectrum. Sm comes from around the middle of the scale. Y, while not technically classified as a REE, has properties that place it in the HREE region. Y was used instead of a more technically classified HREE because there is significantly more data for Y than for the others. Sc was chosen because it has similar properties to the Rare Earth Elements, but has a higher compatibility with clinopyroxene than with other minerals.

Zr is a representative of the HFSE group, which also includes Hafnium (Hf), Niobium (Nb), and Tantalum (Ta). These elements are insoluble in water; therefore, they should have a high preference for partitioning into a solid state, especially from hydrous (water bearing) melts.

### **Assumptions**

There are some general assumptions that we operated under in the making of this compilation. Not all the papers we have borrowed data from supplied all the information about the experimental conditions they used. Specifically, we are assuming that for all experiments used in our analysis, the glass was in equilibrium with the clinopyroxene and other minerals at the time the rock was cooled and analyzed. This assumption is necessary because the glass compositions are being used as stand-ins for the whole rock compositions, and only at equilibrium are the whole rock compositions and glass compositions equivalent, even though the glass is what is left behind after the minerals crystallize from the whole melt. We must assume that the minerals are at equilibrium because otherwise the data would be, for our practical purposes, useless. This will introduce error, but it is our hope that the

database is large enough to allow us to ignore the error introduced by the few experiments for which our assumption is false. As most experiments are designed to end at equilibrium, it is also highly unlikely that an experimental dataset made it through the required peer reviews and into publication with this large error; this decreases the likelihood that error will enter our analysis through these means.

We are also assuming that all the data have been copied over correctly from the original papers, and that the data were not mistyped in those papers initially. This error has been reduced by double and triple checking the values and by checking the reasonability of answers produced from calculations. We have even contacted the authors of specific papers to double-check any original numbers that fall far outside of the range of the rest of the database, in an attempt to locate typographical errors. In some cases, the authors replied and admitted that the numbers were mistyped in the published papers. Those values were corrected for this database.

At this point in our analysis we are also operating under the assumption that all compositions were measured correctly, and that there were no biases between different measurement techniques. This may be a large assumption because each individual machine would have to be calibrated exactly alike to keep error from entering the data, but at this point, it is necessary. This assumption will be removed in later versions of our analysis when we will look into the effects of different analytical techniques on the reported phase compositions.

Another assumption is that the scientific basis behind all calculations that were used in the analysis of the data were sound. While there does not seem to be much of

a chance of this, we must always remember that we have been wrong in the past.

After all, "it is disconcerting to reflect on the number of students we have flunked in chemistry for not knowing what we later found to be untrue" (Weber 159).

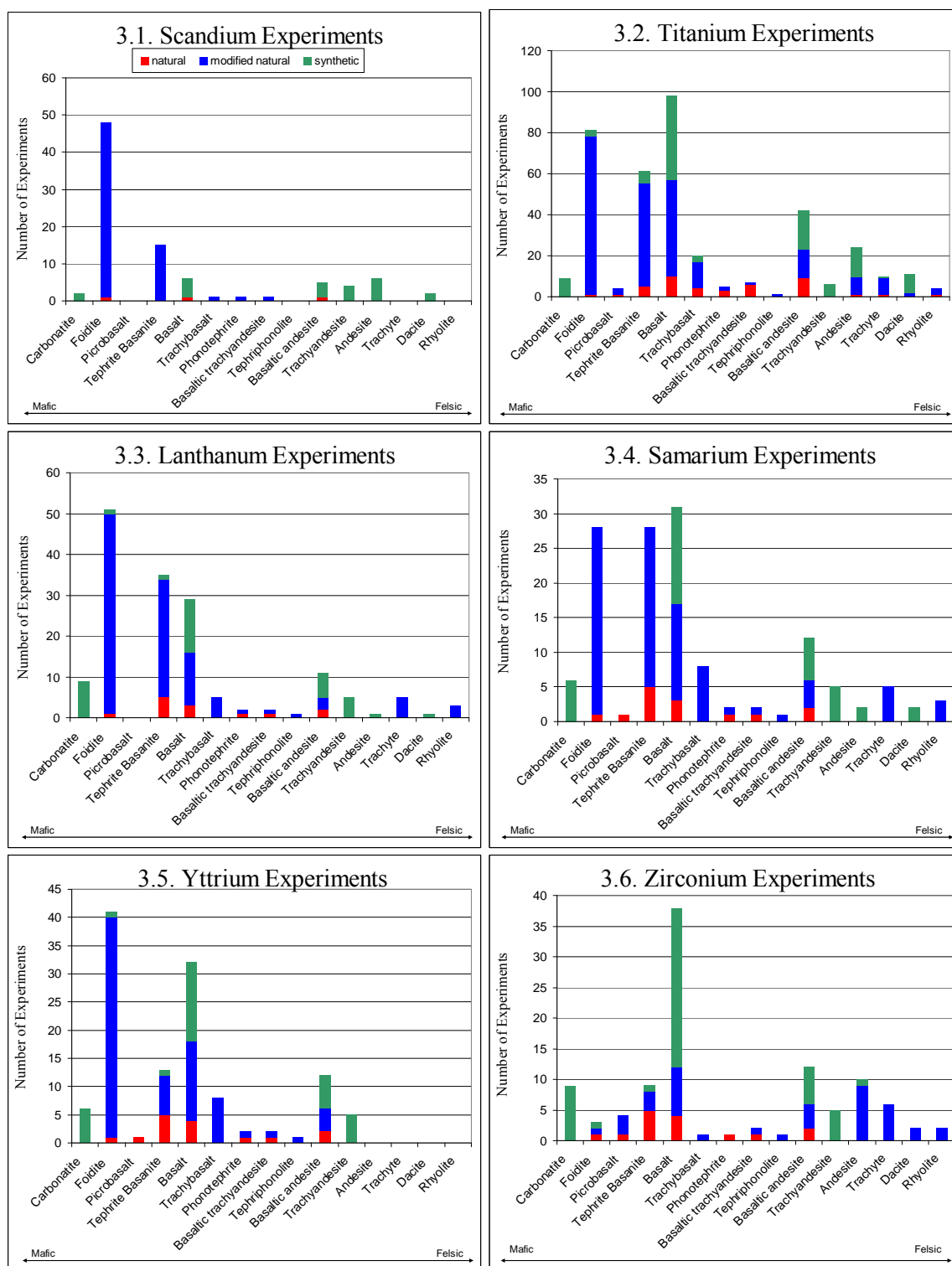
## RESULTS

### Composition

Looking at the graph of rock types of the experimental data (Figure 2), the experiments are quite heavily weighted toward the lower silica compositions. While understandable, due to the stability range of clinopyroxene, the result is that we have few data representing higher silica rock types, where clinopyroxene is still an important crystallizing phase. The distinctly different distribution of liquid compositions for different elements can be illustrated (Figure 3) by subdividing the compositions by rock type. The data are further divided by whether each experiment, was natural, modified natural, or synthetic.

The number of natural experiments compared to modified natural or synthetic experiments is very small. With reference to the Sc experiments, there are only three total natural experiments in this entire database versus the 23 synthetic and 65 modified natural experiments. While modified and synthetic experiments are useful in widening the range of our partitioning knowledge, the low level of natural experiments suggests a lack of the basic information within the natural range. Before we can widen our base of understanding, we must first understand the base.

While the numbers of experiments are heavily weighted toward the low silica end of the spectrum, this scale is tipped different amounts when different elements are taken into account. The experiments which measured Ti concentrations have about the same balance as the whole-rock spectrum; this is to be expected because Ti, being a major

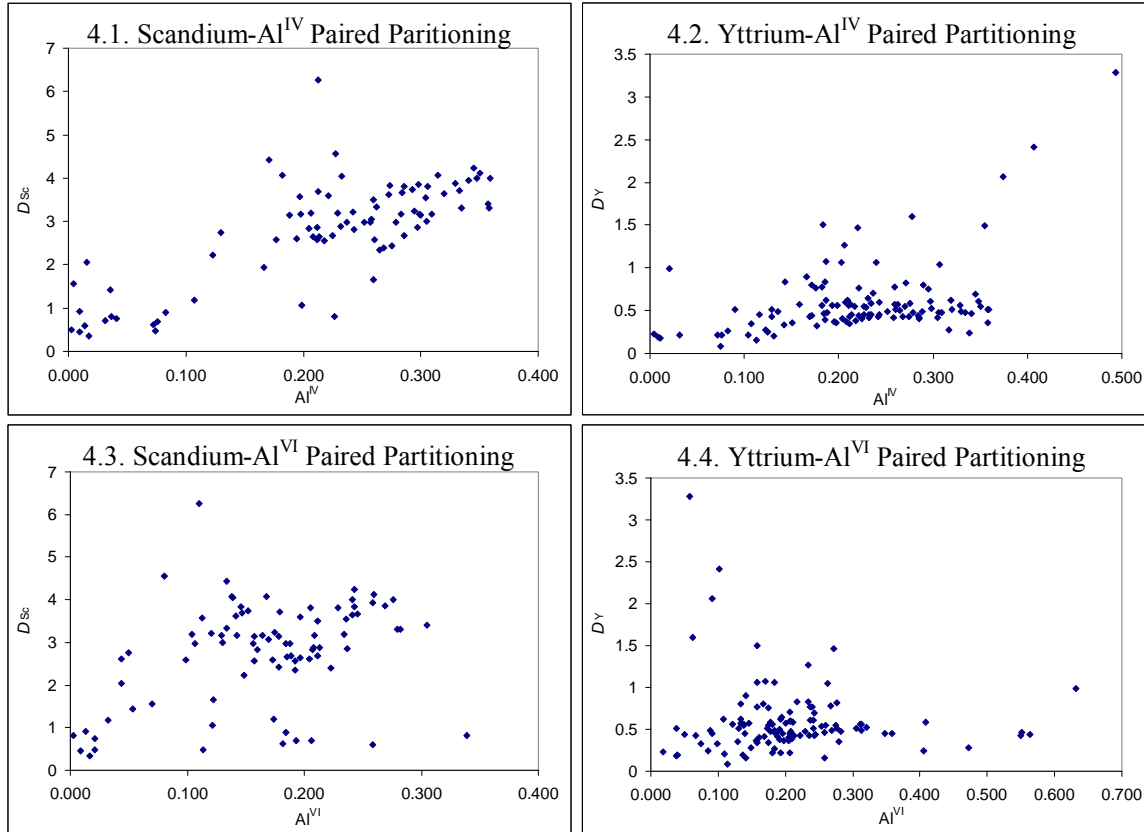


**Figure 3: Histograms of the distribution of liquids for clinopyroxene/melt partitioning data for specific elements.**

element, was measured in nearly every experiment. Trace elements, like Sc, show much stronger weighting toward low-silica concentrations.

Trace element partitioning is also interdependent on the partitioning of the major elements. For example, Al can enter the crystal structure of clinopyroxene in two different sites, the tetrahedral, or T, site and the smaller octahedral, or M1, site; these two varieties of Al are referred to as  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  respectively. Trace elements may partition differently based on the availability or activity of the aluminum in the system and due to the preference of different trace elements to fit into each of these sites or into the larger M2 site. As has been shown by a number of previous investigators (Hack et al 1994; Wood and Blundy, 2001) and in Figure 4, Y, Ti, and Sc partitioning show correlation to the amount of  $\text{Al}^{\text{IV}}$ . However, this correlation is by no means well defined. In order for the dependence to be quantified, there need to be many more experiments run to constrain what is actually happening with respect to the nature of the substitution mechanism by which each element enters the pyroxene structure.

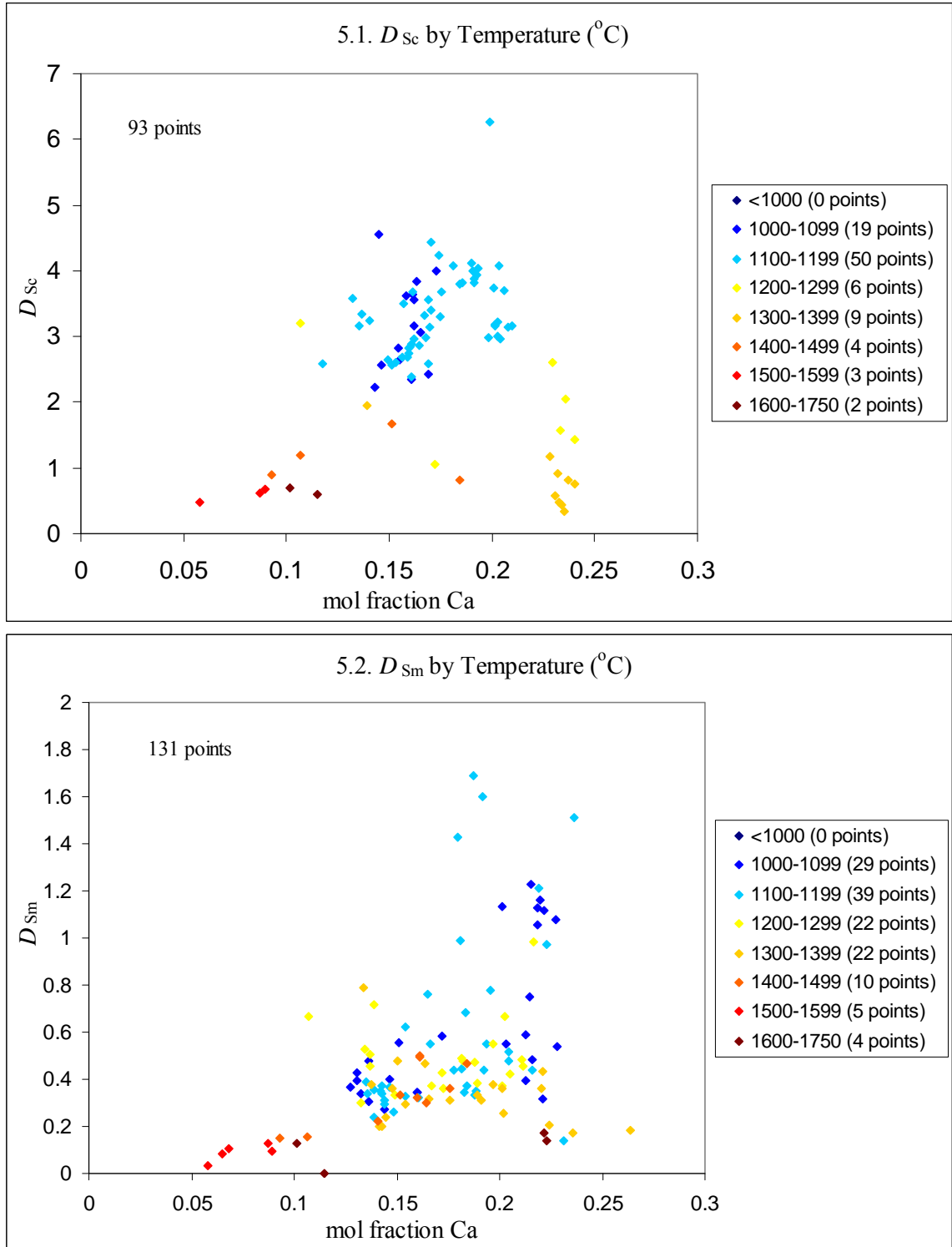
This complexity is evident in the distinctly different trends exhibited by Sc and Y (Figure 4) when correlated with Al. If we are to quantify the specific relationships, we must have a dataset that is consistent between elements. Examination of the data in Figure 4 illustrates that is not the case for these elements – with the data for Y extending to higher values of  $\text{Al}^{\text{IV}}$  and  $\text{Al}^{\text{VI}}$  than Sc. Similar differences are exhibited between individual REEs and between the REEs and HFSEs.



**Figure 4: Correlation of partition coefficient with tetrahedral Al. This relationship has been predicted to be an important indicator of paired substitution for some specific elements.**

## Temperature

The affects of temperature on element partitioning are shown in Figure 5. While the temperature appears to have relatively little effect on the partitioning of Ti, there is a visible correlation between temperature and the partitioning of the trace elements. In the case of both Sc and La, the experiments run at lower temperatures yielded both higher partition coefficients and a higher Ca content in the clinopyroxene than in the higher temperature experiments. However, to make this trend clearer, more data is needed for the upper end of the spectrum. There are only nine data points for experiments

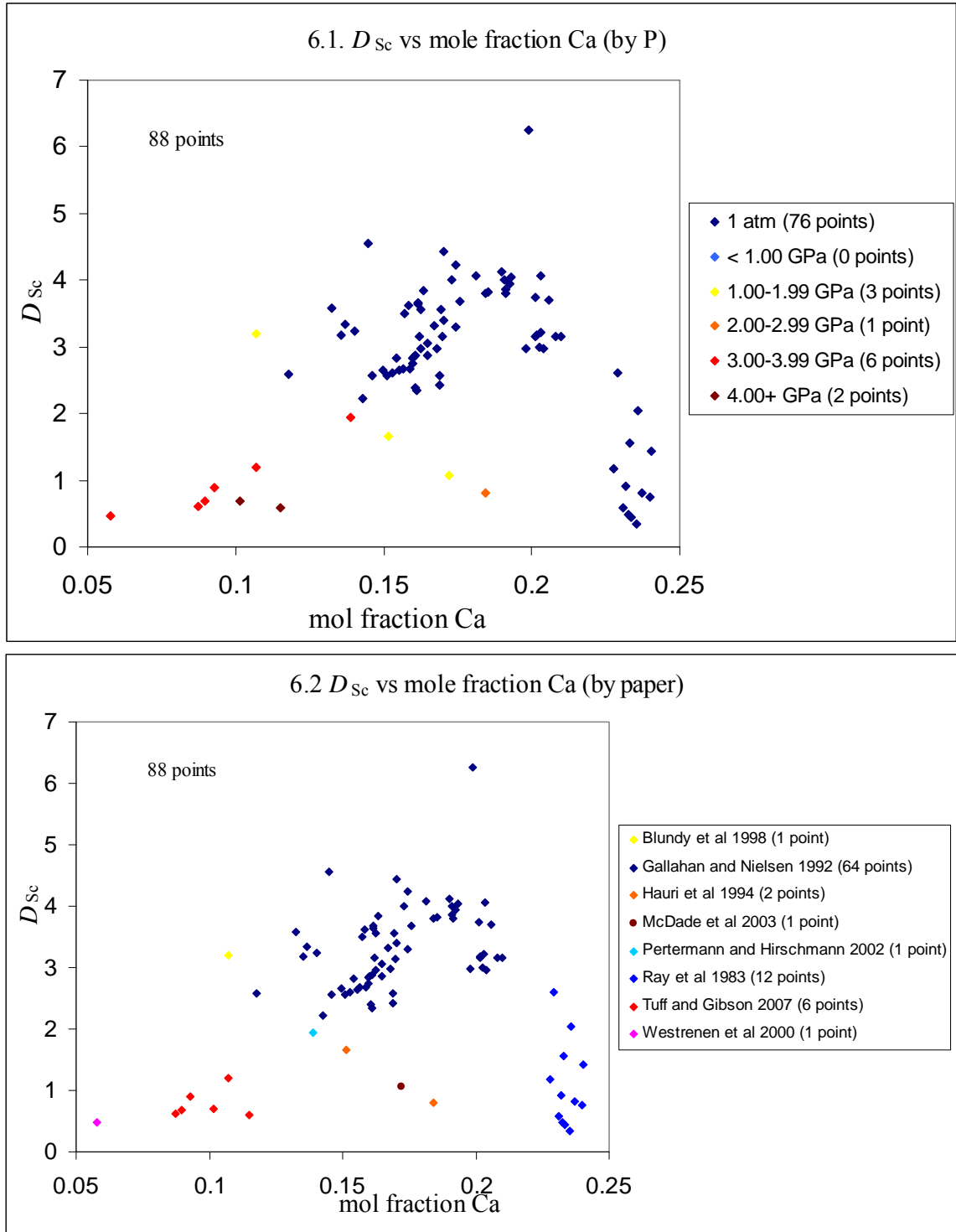


**Figure 5: Partition coefficient for clinopyroxene versus mole fraction Ca in the pyroxene. For each plot, the data is subdivided by temperature to illustrate the range of the size of the dataset for each element.**

performed above 1400°C for Sc, compared to 50 data points in the temperature range of 1100-1199°C alone. For the La data, only fifteen data points exist for temperatures above 1400°C, compared to the 155 points total.

## Pressure

Only one element analyzed exhibited any correlation between pressure and partitioning (Figure 6.1). While there appears to be a negative correlation of  $D_{Sc}$  and pressure, examination of Figure 6.2 reveals that the correlation is also tied to the individual investigation. This suggests the possibility that there are more complex dependencies at play, including the characteristics of the specific systems being investigated. Specifically, the low pressure investigations are heavily weighted towards alkalic (foidite) compositions, whereas the high pressure experiments are dominantly synthetic or low-alkali mantle or MORB analogs. This runs into the introduction of error caused by the availability of too few experiments in specific compositional domains (e.g. the weighing of the dataset). This concept is discussed in the “Error” section later in this paper. At this point, there can be no conclusions made about the effects of pressure on element partitioning. To get clearer results, a greater amount of experiments need to be performed. This is especially true in the high pressure range. There are no more than three data points at or above 4.0 GPa pressure for any one element in the whole database, while there are as many as 200 experiments done at one atmospheric pressure.



**Figure 6: Correlation of partition coefficient with Ca in clinopyroxene, subdivided by experimental pressure, and by publication.**

## Water Content

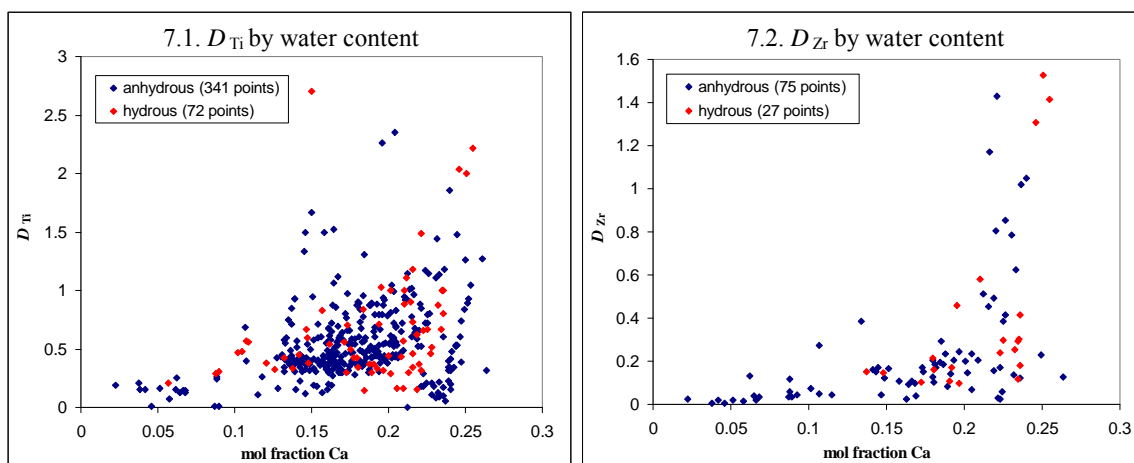
In past experiments, the presence of water has been shown to greatly affect the partitioning of elements between minerals and melt (Wood and Blundy 2002). In the presence of water, the partition coefficients of the major elements increase relative to the partition coefficients of the trace elements. Perhaps it would actually be more accurate to say that the partition coefficients of the trace elements decrease with respect to the major elements, as the presence of water actually seems to have only minor influence over the partitioning of major elements, while it can dramatically decrease the ability of trace elements to enter the mineral phase.<sup>Ⓔ</sup> For many experiments, water was not independently analyzed, but was assumed to be at saturation, or determined by difference. One of the most important recent analytical advances in the past five years is the increased availability of tools to measure water directly in experimental charges. This promises to dramatically enhance the precision of the future experimental data.

For the purposes of the current compilation, only a designation as to which experiments are hydrous or anhydrous has been recorded. The exact levels of water in experiments will be added into the database at a later point. Due to past studies on the effect of water on partitioning, described above, it was assumed that by splitting the hydrous and anhydrous data into different groups and plotting them against each other, the effect of water in the process would be apparent. Somewhat unexpectedly, the

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<sup>Ⓔ</sup> Due to time restrictions, the actual amount of water in each experiment was not recorded in this version of the compilation.

hydrous and anhydrous datasets had little or no distinction from each other in this compilation (Figure 7). An exception is the absence of Zr data below 15 mole percent Ca – a critical compositional realm for predicting the partitioning of low Ca clinopyroxene andesites.



**Figure 7: Correlation of partition coefficient with Ca in the pyroxene - subdivided by presence of water in the experimental system.**

The reason for the lack of distinction could be simply the existence of too many parameters within these graphs to be able to see the subtle changes made by the water content. It may be that the distinction will be more prevalent when the actual amounts of water in each experiment are taken into account. As this is a strong possibility, further analysis of the affects of water on trace element partitioning will be postponed until the next version of the compilation is completed in a few years.

## Error

There are many potential sources of error in experimental geochemistry that occur prior to publication, including analytical error, data handling error, and interpretive error. Additional sources of error may be introduced in the creation of this database due to the

necessity of combining a large number of different datasets, each with its own analytical technique, presentation format, and degree of completeness. To reduce this error, those experiments that did not report both the clinopyroxene compositions and the corresponding glass compositions were dropped from this analysis. Unfortunately, this can result in an increase of the effect of error introduced by individual papers, because error within the database also stems from the data being weighted toward single sets of experiments. For example, while most papers report between one and ten experiments, a few papers, such as Gallahan and Nielsen (1992), provide as many as 110 experiments. For the less analyzed trace elements, like Sc and La, Gallahan and Nielsen (1992) provides 73% and 42% of the data respectively\*. Because of this, not only is the data weighted toward the rock types used in those experiments, but also toward any error that may have been introduced by faulty calibration of the equipment or by a faulty standard. It is far from our intention to imply that error exists in Gallahan and Nielsen's data specifically, just that the situation dictates that the possibility of such an error would have a far more profound effect on the accuracy of the dataset as a whole than would error from a paper that only contributed a few pieces of data. For example, if there was error in the experimentation of a paper that reported two or three data points, those points could be shown graphically to be outliers. However, as in the case of Sc mentioned above, if the data from Gallahan and Nielsen (1992) did contain error, 73% of the data points being out of place will not be apparent. It would not normally occur to a

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\* This is based off of the number of partition coefficients calculated, due to some experiments providing data for different elements in the melt analysis than in the clinopyroxene analysis. Using the partition coefficients provides for a way to count only those experiments that supply information about each element for both phases.

researcher to label 73% of the data as outliers. The best way to limit error of this type is to increase the size of the database to decrease the effects of error introduced by any single set of experiments.

## CONCLUSIONS

To quantitatively describe clinopyroxene partitioning, it is required to derive expressions using theoretical constraints that are calibrated with experimental data (Forsythe et al 1994; Hack et al 1994; Wood and Trigila 2001). Unfortunately, the experimental data available at this point, though in far greater quantities than just a few years ago, does not yet cover a wide enough range to allow for calibration of expressions for all elements under all conditions (Bedard, 2006; Bedard, 2007). More experiments in specific areas are needed to complete the dataset, and this will require a comprehensive analysis of the completeness of the data for each element before this may happen. In general, more high-silica and a wider range of high temperature and pressure, hydrous experiments are needed to fill in the gaps. To improve our understanding of the compositional base, more natural experiments need to be performed. More experiments at temperatures greater than 1400°C and pressures greater than 4.0 GPa are needed to provide a complete range of data with which to work. Above all, there is a need for enhanced analytical precision for all conditions. The major element concentrations are significantly less dependent on small errors of beam placement and calibration – resulting in datasets where the percent analytical error for major elements differs dramatically from that of the trace elements. In addition, due to the mixing properties of many trace element components, their behavior is far more dependent on pressure, temperature, and other components of the formation environment, and so act as much more efficient gauges of the formation environment than the major elements.

Should anyone wish to contend the analyses put forward in this publication, they are welcome to visit the GERM website to conduct their own analysis.

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## APPENDICIES

### APPENDIX A Equations and Definitions

Activity:  $a=\gamma c$  where  $a$  is the activity,  $\gamma$  is the activity coefficient, and  $c$  is the concentration. Activity is the molar concentration after being corrected for the interference by other elements in real solutions. (Faure, p.113)

Activity Coefficient:  $\gamma$ . The activity coefficient corrects the molar concentration of elements for the interference by other elements in real solutions. (Faure, p.113)

GPa: Gigapascal, a measurement of pressure equivalent to 10,000bar or 9869.2 standard atmospheric pressure.

Normalized Mol Fraction: The normalized molar fraction of an element is the molar proportion of the melt or mineral that consists of that element, with the sum of the proportions of either state normalized to one.

Oxide Weight Percent: The Oxide Weight Percent of an element is the concentration of the oxide state of the element in the mineral or melt (Si as  $\text{SiO}_2$ , Al as  $\text{Al}_2\text{O}_3$ , etc.) as a function of its weight.

Partition Coefficient:  $D=C^{\text{mineral}}/C^{\text{liquid}}$ . The partition coefficient is the ratio of the concentration of an element in the mineral to the concentration of the element in the liquid.

## APPENDIX B     Acronyms

$D_i$ : Partition coefficient of element  $i$  between mineral and melt

GERM: Geochemical Earth Reference Model database

GPa: Gigapascal

HFSE: High Field Strength Element

HREE: Heavy Rare Earth Element

La: Lanthanum

LREE: Light Rare Earth Element

MORB: Mid Ocean Ridge Basalt

REE: Rare Earth Element or Lanthanide

Sc: Scandium

Sm: Samarium

Ti: Titanium

Y: Yttrium

Zr: Zirconium

## APPENDIX C Publications Included in Compilation

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