

THE COMPUTATION OF CHEMICAL EQUILIBRIUM AND THE DISTRIBUTION
OF FE, MN AND MG AMONG SITES AND PHASES IN OLIVINES AND
GARNETS

by

CHRISTIAN DE CAPITANI

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Department of Geological Sciences

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date: September, 1987

Abstract

A general algorithm for the computation of chemical equilibria in complex systems containing non-ideal solutions has been developed. The method is a G-minimization based on repeated linear and nonlinear programming steps. A computer program (THERIAK) based on this algorithm has been written and was used to solve a great variety of problems, ranging from a simple blast furnace calculation to liquid-liquid unmixing in a four component silicate melt. The computing times are in the magnitude of 1/2 to 2 seconds for each calculation. The method can also be used to test the consequences of thermodynamic models and data in systems of interest to many fields, including chemistry, geochemistry and metallurgy.

Integrated powder diffraction intensities can be used to measure Mn-Mg and Fe-Mg site occupancies in olivines because of the difference in scattering factors between Mg and Mn or Fe. Theoretically calculated intensity ratios are subject to uncertainties from positional parameters (less than 3.5 % for peaks with a relative intensity greater than 25 %) and unknown charge distribution (up to 30 %). Several peak ratios are less subject to this last uncertainty and may be used to measure the site occupancies in olivines. 27 synthetic Fe-Mn-Mg olivines (800 °C, vacuum, with graphite) were investigated with Mössbauer spectroscopy and XRD intensity evaluation, producing occupancies accurate to approximately 0.03 per site. A thermodynamic speciation

model represents the data very well.

Preliminary Fe-Mn-Mg exchange experiments involving olivine and garnet place some limits on element distributions between these two minerals.

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INTRODUCTION

The partitioning of elements between coexisting phases and between different structural sites of a single phase is of central importance for geothermometry and geobarometry. In a system with more than two exchangeable elements, as in most natural assemblages, the equilibrium involving different phases can become a very complex problem for experimental and theoretical work. The aim of the present thesis was to investigate problems related to heterogeneous equilibria in multicomponent and multiphase systems. Naturally, only a few of these problems can be pursued in more detail. The sample system chosen consists of the ternary Fe-Mn-Mg olivines and garnets. The reactions between Fe-Mg olivines and garnets have been proposed as a geothermometer by Kawasaki and Matsui (1977) and O'Neill and Wood (1979). These authors also point out that in order to investigate the thermodynamic properties of the garnet solid solutions, experimental work with olivine as coexisting phase may prove more useful than with the more complex pyroxene solid solutions. A ternary system was chosen to emphasize the typical complications encountered in higher than binary order systems. Although Ca may be a more important element than Mn, it was not considered because its mixing properties are expected to be more complicated (Dempsey (1980)) and because of my subjective sympathy for Mn minerals. At a very early stage of the investigation it became obvious that no final model for olivine - garnet equilibria would be

possible. Because the experimental part of the problem demands extensive analytical work and the department microprobe was not available for two years, only few, preliminary exchange experiments were planned and carried out. Their results are presented in Appendix H.

One of the most important fundamental problems when dealing with complex multiphase systems is the computation of the equilibrium assemblage at given conditions. Although the literature on the subject is huge and still growing, a completely general method for non-ideal systems has to my knowledge not been published. One specific approach, the "linear programming method" (White et al. (1958)), seemed very promising and is developed to a general algorithm in the first part of the present thesis. This part was also submitted for publication (de Capitani and Brown (1987)). The second problem investigated in more detail is the distribution of Fe, Mn and Mg in ternary olivines. The non-linear behaviour of the lattice parameters for the Fe-Mn and Mn-Mg olivines (Annersten et al. (1984)) suggest that these solutions are non-ideal. For a thermodynamic mixing model it is important to chose a realistic entropy of mixing term based on our knowledge of order-disorder of that phase. The site distribution of the ternary olivines could be measured with a combination of Mössbauer spectroscopy and XRD intensity evaluation. The principles of the latter method were also presented at a AGU meeting. (de Capitani and Greenwood (1985)).

1. THE COMPUTATION OF CHEMICAL EQUILIBRIUM IN COMPLEX SYSTEMS CONTAINING NON-IDEAL SOLUTIONS

1.1 THE FORMULATION OF A GENERAL ALGORITHM

1.1.1 INTRODUCTION

One of the important problems in theoretical petrology is the determination of the equilibrium phase assemblage for any specified set of conditions. Computations of equilibria permit comparison with natural or experimental assemblages and thus test the validity of theoretical models and thermodynamic data. The computed results can be used to design future experiments or to calculate assemblages at conditions beyond the range of current experimental techniques.

In many respects the computational approach to equilibrium resembles the experimental approach, because both operate on the principle of progressively reducing the free energy until a minimum is reached. We cannot guarantee, however, that the absolute minimum has been reached in either case. The experiment may terminate with metastable phases due to difficulty in nucleating the stable phases. Similarly, a computation may converge to a local minimum or lack the presence of a stable phase due to its omission from the data base. It is clear that very careful interpretation is required for both computed and experimentally determined equilibria.

The aim of the present investigation is to present a technique for minimizing the Gibbs free energy which is an extension of an algorithm published by Brown and Skinner (1974). The new method shows some similarities with the "linear programming method" originally proposed by White, Johnson and Dantzig (1958).

In the discussion below, I attempt to give enough detail to allow the interested reader to program or improve the algorithm himself. A program (called THERIAK), written in FORTRAN 77 is described and listed in appendix A and B.

1.1.2 THEORETICAL FUNDAMENTALS

We will restrict our discussion here to some of the assumptions and implications that are important for the computation of chemical equilibria. For a more detailed treatment of the axioms and laws of thermodynamics the reader is referred to any one of a number of good textbooks (e.g. Prigogine and Defay (1954), Denbigh (1971) or Becker (1978)). The systems we consider are all chemically closed; that is, the bulk composition is fixed. We assume that there are only two possible types of energy, namely heat and energy related to pressure-volume work. This assumption fixes the number of independent variables for any function of state to two, which is also the maximum degree of freedom in the phase rule sense. The most general formulation of the chemical equilibrium problem follows from the second law of thermodynamics, and provides that the

equilibrium state is the state in which the total entropy of the closed system and its surroundings has reached the maximum value. If we take the independent variables to be pressure and temperature, this state is also characterized by a minimum in the Gibbs free energy of the closed system. Thus a chemical experiment can be simulated by solving a mathematical optimization problem which, for independent P and T , corresponds to the minimization of the Gibbs free energy, G ($G=U-TS+PV$). Although different choices of independent variables are possible, I have restricted the present investigation to the calculation of equilibrium assemblages for constant P and T .

In the past twenty years many algorithms have been developed for solving the chemical equilibrium problem. Comprehensive reviews can be found in papers by Smith and Missen (1982) or Smith (1980a,1980b). Earlier work was summarized by Zeleznik and Gordon (1968), Van Zeggeren and Storey (1970) and Holub and Vonka (1976). Most popular algorithms are based on Brinkley (1947), Huff et al. (1951) (NASA-algorithm), White et al. (1958) (RAND-algorithm), Naphtali (1959,1961), Villars (1958), Cruise (1964) and Smith and Missen (1968). All these algorithms assume that the chemical equilibrium problem has a unique solution.

1.1.2.1 Non-unique solutions to the equilibrium problem

A solution to the chemical equilibrium problem is non-unique if more than one assemblage fulfills the conditions of equilibrium. Strictly speaking these

conditions are only fulfilled for the global minimum G assemblage and for most cases this assemblage is the unique solution to the chemical equilibrium problem. However, most mathematical formulations of the equilibrium conditions may allow an algorithm to converge to a solution which is not the true equilibrium assemblage. For a computation these mathematically non-unique solutions are very important and we will therefore use the term "unique solution" only for equilibrium problems that have a single solution in the mathematical sense. For these problems the only assemblage to which an algorithm can converge to is the equilibrium assemblage. The types of non-unique solutions that may exist depend on the computational method.

In fig. 1 three situations with non-unique equilibria are shown. An indifferent state (also called degenerate non-uniqueness) results if several phase assemblages are stable and have the same Gibbs free energy. (Fig. 1a). Although this is a case with multiple global minima it is generally not considered a serious problem, because this situation is usually only encountered on univariant curves in the P - T -plane. Local minima (Fig. 1b) can be very difficult to avoid and finding them can be of interest, because they may correspond to metastable states found in experimental and natural assemblages. However, it is important and unfortunately difficult to recognize the difference between a local and the global solution in a G -minimization. The third example is a constrained minimum

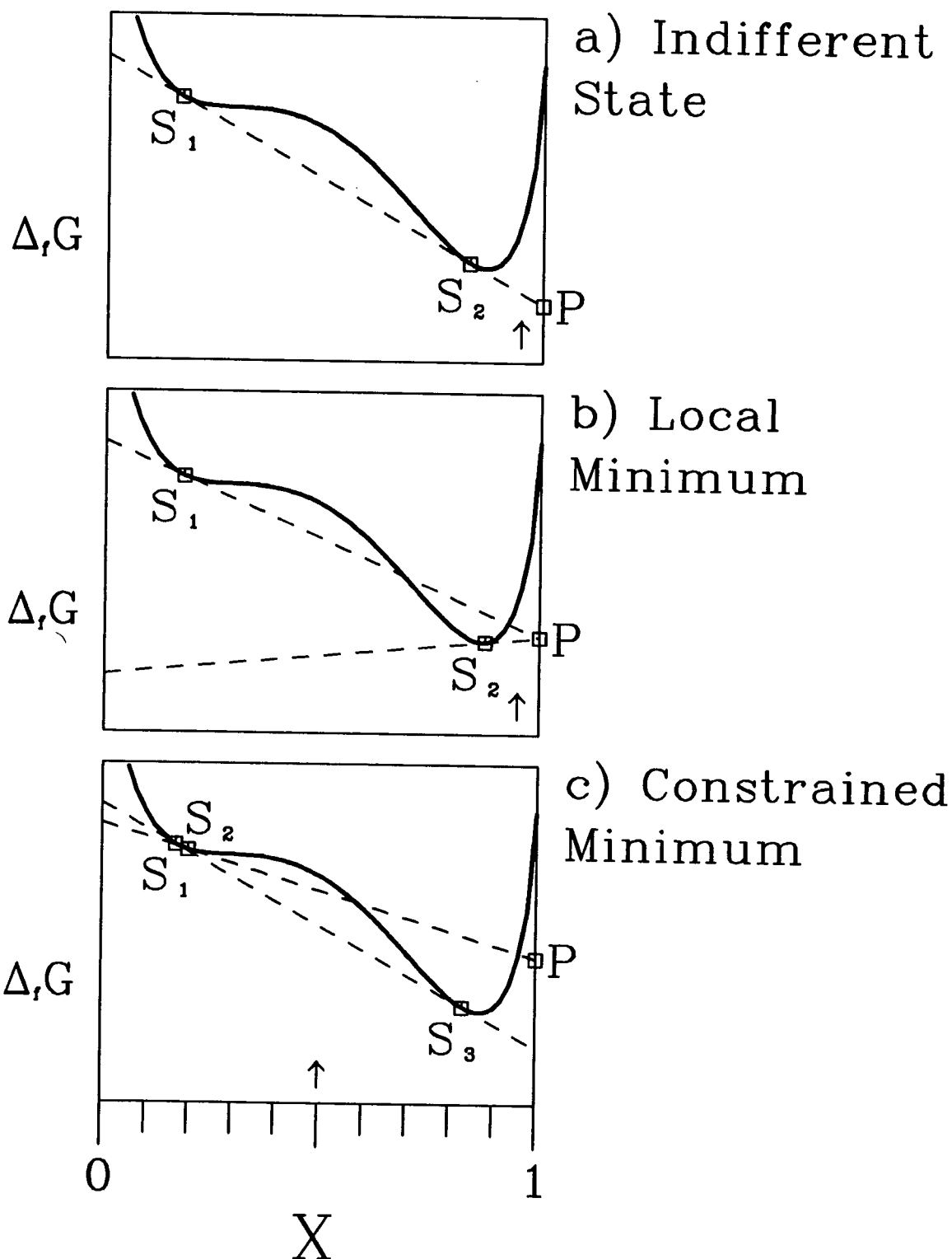
Fig. 1: (page 8)

Examples of non-unique equilibria.

The bulk composition is given by the arrow.

- a): The phase assemblages S_1 -P and S_2 -P have the same Gibbs free energy, so that both satisfy the equilibrium criteria of minimum $\Delta_f G$ for a given composition.
- b): The mathematical formulation of the equilibrium conditions may be satisfied by two different assemblages. The assemblage S_1 -P represents a local minimum. S_2 -P is the global minimum.
- c): S_2 -P is a possible "stable" assemblage if we do not explicitly allow for the possibility of two coexisting phases from the same solution. The true equilibrium assemblage is S_1 - S_3 .

Fig. 1: Examples of non-unique equilibria



(Fig 1c), meaning not only that the ranges of certain variables are restricted, but also the number of variables we consider. If an algorithm is constrained to assume that no more than one solution phase S_1 can be part of the stable assemblage, then the global minimum for this problem is the assemblage S_2 -P. The true equilibrium S_1 - S_3 can only be found if we allow two co-existing phases from the same solution. Whereas systems with only ideal solutions have unique equilibria (Shapiro and Shapley (1965)), this is generally not the case if nonideal solutions are involved. This fact and some implications for computational algorithms were pointed out by Caram and Scriven (1976), Othmer (1976), Heidemann (1978) and Gautam and Seider (1979).

Many algorithms used today in connection with nonideal solutions were originally developed for use with ideal systems and assume unique solutions. (e.g. Fickett (1963), Eriksson (1971,1974), and Harvie and Weare (1980)). If deviation from ideality is large and the possibility of phase separation is not considered explicitly, e.g. by phase-splitting (Gautam and Seider (1979)), such algorithms may converge to an improperly constrained minimum.

The published algorithms that were specially designed for nonideal solutions are usually restricted to one phase separation or assume that a maximum of two phases from the same solution can co-exist (e.g. Kaufmann and Bernstein (1970), Sanderson and Chien (1973), George et al. (1976) and Prausnitz et al. (1980)).

As will be discussed below, the reason why most algorithms are not completely general for nonideal systems lies in the formulation of the equilibrium condition.

1.1.2.2 Formulation of the chemical equilibrium condition

For any system of fixed composition the general equilibrium condition is:

$$\text{minimize } G = \sum_{k=1}^N n_k \cdot g_k$$

subject to the constraints that all $n_k \geq 0$
and that the mass balance equations are satisfied.

where n_k is the number of moles and g_k is the molar Gibbs free energy of the phase k .

At the start of any computation, the total number of coexisting phases (N) is not known, and because the solution phases have a range of possible compositions, their Gibbs free energies at stability also are not known. This seemingly chaotic situation usually leads to an alternate formulation of the equilibrium condition, where g_k is replaced by the chemical potential μ_j of *species* j . The total number of species is known and each can be assigned to one phase. Unfortunately this formulation assumes a unique solution to the equilibrium problem, because each species can be present in only one amount n_j . A generalization including possible phase separations becomes extremely difficult.

A possible way to use the general equilibrium condition with no further assumptions was proposed by White, Johnson and Dantzig (1958). They called it the "linear programming method". The procedure as originally described assumes that the Gibbs energy functions of the solutions are convex, but the basic idea of varying the number of phases considered during computation can easily be used for nonideal systems in which the G functions locally may be concave.

Although several authors have used phases and not species in their computations, (e.g. Brown and Skinner (1974), Connolly and Kerrick (1984,1986)) no completely general algorithm seems to have been published. The formulation proposed here is surprisingly simple and much more effective than initially anticipated.

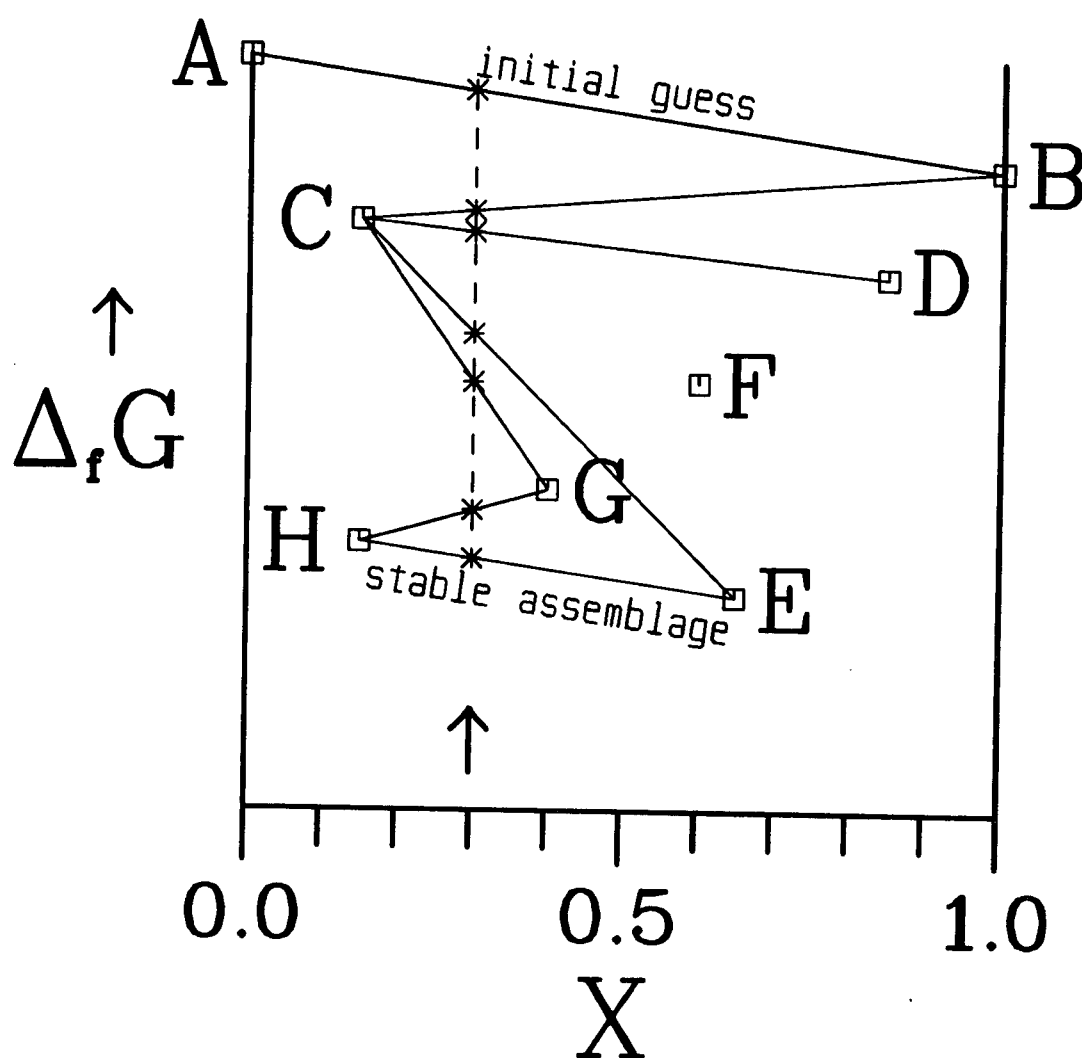
1.1.3 PHASES WITH FIXED COMPOSITIONS

Because G as a function is only calculable relative to a reference state, the following discussion refers to the Gibbs free energy function as $\Delta_f G$, the ΔG of formation from a reference state. Let us first consider a system of fixed T, P and bulk composition for which each phase has an invariable composition and a calculable $\Delta_f G$. In this case, the problem of finding the minimum $\Delta_f G$ assemblage can be solved by any linear programming method. How such a method may work is outlined below and illustrated in Fig. 2. With two independent variables the maximum number of stable phases is equal to the number of components (C) in the

Fig. 2: (page 13)

Example of computing the assemblage having minimum $\Delta_f G$ for a selection of phases with fixed compositions. The bulk composition is given by the arrow. Starting with an initial guess (here A-B), one phase at a time is replaced by another to achieve a lower total $\Delta_f G$. In this example A is replaced by C, then B by D, and so on until the stable assemblage, of lowest $\Delta_f G$, is found. The sequence of calculations will depend on the order of considering new phases.

Fig. 2: Example of computing the equilibrium assemblage for phases with fixed compositions



system. We will start initially with any assemblage of exactly C linearly independent phases. For a specified bulk composition some of these phases may have zero amounts. All other phases considered are related to this initial assemblage by one reaction each. Fig. 2 shows an example of a simple binary system where we have chosen the initial assemblage to be $A+B$. As we go through the list of phases considered (in this case in alphabetical order) we notice that the reaction $C = A+B$ has a $\Delta_r G > 0$. This means that C is more stable than $A+B$ and for the chosen bulk composition, $C+B$ becomes the new stable assemblage. For the next phase in the list (D), a similar procedure ($\Delta_r G$ of $D=C+B$ is > 0) leads to the lower $\Delta_f G$ assemblage $C+D$ and so on, until the stable assemblage $H+E$ is located. Each time a phase is found that lies below the $\Delta_f G$ tie-line of the currently considered assemblage, this phase replaces one phase from that assemblage. Which phase is replaced depends on the bulk composition. We must go through the list of considered phases several times, until we find the true stable assemblage where all other phases lie above (or on) the $\Delta_f G$ tie-line. For multicomponent systems the components and $\Delta_f G$ define a hyperspace and the $\Delta_f G$ tie-lines become $\Delta_f G$ hyperplanes, but the procedure remains the same. If $\Delta_r G$ between two or more assemblages happens to be exactly zero then this is called an "indifferent state" (see Prigogine and Defay (1954)). An equilibrium calculation will find only one assemblage, but because the phases of the other

assemblages have the same chemical potentials, this situation is easily recognized.

1.1.4 ADDING SOLUTION PHASES TO THE SYSTEM

If we now add solution phases to the system the mathematical treatment becomes more complex. As a first approximation we consider all the phases of fixed composition plus all endmembers of the solutions and calculate for this simplified system the minimum $\Delta_f G$ assemblage by linear programming as described above. The essence of the new algorithm is that we now simplify further calculations by transforming the reference state of the complete system so that the phases of the "currently stable assemblage" all have $\Delta_f G = 0$, but that the $\Delta_r G$ of all possible reactions in the system remain unchanged. If originally $\Delta_f G$ meant "formation from the elements" and the stable assemblage consists of the phases A, B and C, then after this transformation the values of $\Delta_f G$ have the meaning "formation from A, B and C", but all stability relations remain the same. This change of base operation is easily accomplished by linear algebra. For each solution we now search for the composition with the smallest $\Delta_f G$. (This is a nonlinear programming problem and is discussed in more detail below.) The compositions so determined are now treated as if they were phases of fixed composition and a new minimum $\Delta_f G$ assemblage is computed by linear programming. Again we transform the system, find for each

solution the minimum $\Delta_f G$ composition and calculate the stable assemblage by linear programming. These three steps are repeated until some convergence criteria is satisfied. Fig. 3 shows an example with two nonideal binary solutions. In Fig. 3a only the four endmembers A_1 , A_2 , B_1 and B_2 are considered and the stable assemblage is calculated to be pure B_1 + pure B_2 . The step from Fig. 3a to Fig. 3b involves the change of base operation such that the $\Delta_f G$ tie-line B_1 - B_2 becomes horizontal and $\Delta_f G_{B_1} = \Delta_f G_{B_2} = 0$. ($\Delta_f G_{A_1} - \Delta_f G_{B_1}$) and ($\Delta_f G_{A_2} - \Delta_f G_{B_2}$) remain unchanged. Now we search for the minima of both solutions, add these points as phases to those already considered and compute the minimum $\Delta_f G$ assemblage again with linear programming, finding the assemblage B_3 - A_3 . The step to Fig. 3c is by the same procedure with the $\Delta_f G$ tie-line of the currently most stable assemblage B_3 - A_3 being transformed to a new zero level, whereupon a new stable assemblage is computed. The convergence is relatively fast (averaging about 6 iterations) in binary solutions but, of course, slows down with a larger number of endmembers. This procedure always computes an assemblage with C (=number of components) phases, although some of these phases may be present in a zero or, owing to round off errors, near-zero amount. If two or more stable phases from the same solution have almost identical compositions, (e.g. all mole fractions within 10^{-5}) these have to be interpreted as corresponding to one phase only. The algorithm makes no assumptions about the

Fig. 3: (page 18)

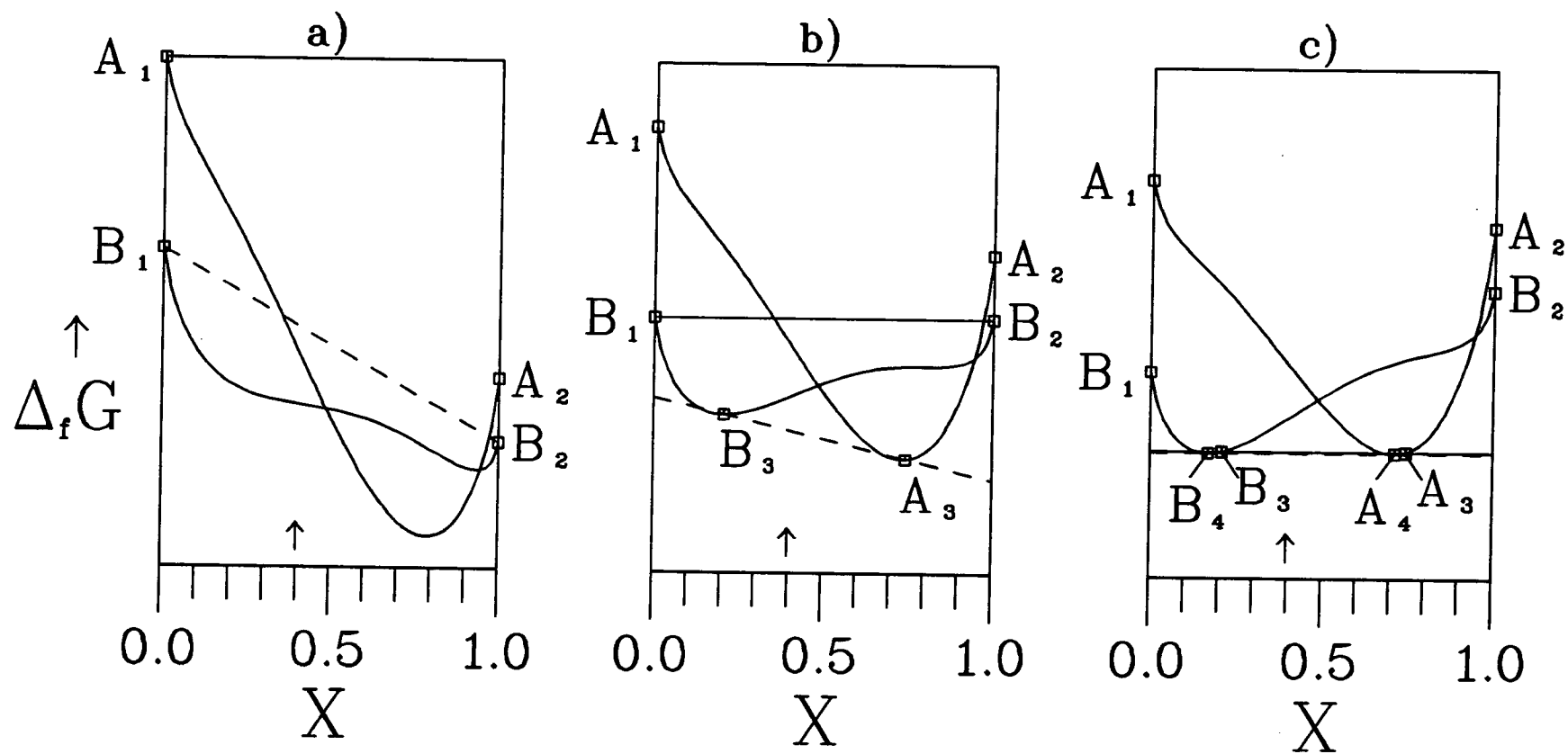
Illustration of the algorithm including solution phases.

The system has two components with two non-ideal solutions A and B. The endmembers of the two solutions have identical compositions. The temperature is 1 K and $\Delta_f G$ for A1, A2, B1 and B2 are -3, -8, -6 and -9 (J/mol) respectively. The excess functions are $21 \cdot x_{A1}^2 \cdot x_{A2}$ for solution A and $15 \cdot x_{B1}^2 \cdot x_{B2} + 23 \cdot x_{B1} \cdot x_{B2}^2$ for solution B. The bulk composition is 0.6 moles of the first component and 0.4 moles of the second.

The stable phases are:

A1_{0.28658} A2_{0.71342} and B1_{0.83061} B2_{0.16939}

Fig. 3: Illustration of the algorithm including solution phases



number of phases in a stable assemblage and some unexpected results stemming from this approach are discussed in the examples later.

The success of the algorithm naturally depends on how fast and how accurately we can compute the minimum $\Delta_f G$ composition of a solution.

1.1.5 SUMMARY OF THE ALGORITHM

The following is a general summary of the algorithm. Each step is discussed in more detail in the next chapter. We assume that we are given a temperature T , a pressure P and a bulk composition. The list of considered phases contains initially the names, the compositions and $\Delta_f G$ for all possible phases of fixed composition. Further, $\Delta_f G$ of each solution is a known function of the composition.

We start with a feasible assemblage of C (=number of components) linearly independent phases, each having $\Delta_f G = 0$. Feasible means that all amounts are non-negative and that the mass balance equations are satisfied. The first iteration is used to generate a better initial assemblage and therefore step 1 is skipped.

1. Search each solution phase for the composition with the smallest $\Delta_f G$. (nonlinear programming problem).

Add these compositions as "new phases" to the list of considered phases.

2. Find from all considered phases the assemblage with minimum $\Delta_f G$. (linear programming problem)

The phases computed in step 1 which turn out to have zero amount after this step can be discarded from further consideration.

3. The assemblage with minimum $\Delta_f G$ (from step 2) is considered to be the new reference state. $\Delta_f G$ of all phases are computed relative to this assemblage. This change of base operation leaves us in a situation identical to that before step 1.

Continue again with step 1.

After the linear programming (step 2), the most stable assemblage defines a $\Delta_f G$ reference hyperplane, and no considered phase can have a $\Delta_f G$ below it. In the next iteration we can only calculate a more stable assemblage if new solution phases with a $\Delta_f G$ below that reference hyperplane are considered. The search for phases with $\Delta_f G$ below the the reference hyperplane is greatly facilitated by the change of base operation (step 3), because now all phases with $\Delta_f G$ below have $\Delta_f G < 0$ and all phases above have $\Delta_f G > 0$. If a solution phase has any points with $\Delta_f G < 0$ after step 3, then the global minimum (step 1) is guaranteed to have a $\Delta_f G$ less than zero and therefore the following step 2 will compute a more stable assemblage. The algorithm continues to calculate new assemblages as long as any phases

with a $\Delta_f G$ below the current reference hyperplane exist. The iterations are terminated when the sum of all non-positive $\Delta_f G$ before step 3 exceeds a threshold value. (e.g. -10^{-8}).

1.2 DETAILS OF THE COMPUTATION OF CHEMICAL EQUILIBRIUM

1.2.1 THE INITIAL ASSEMBLAGE

We have stated above that initially we start with a feasible assemblage for which all phases have $\Delta_f G = 0$. Because the bulk composition is often given in terms of components, (elements, oxides) it is convenient to define imaginary "phases" having the same composition as these components and a $\Delta_f G$ of zero. These "phases" are linearly independent and are used as initial assemblage. To avoid problems with real phases which may have positive $\Delta_f G$, the "phases" of the initial assemblage are assigned an absurdly high $\Delta_f G$ (e.g. 10^{20}) just before the first linear programming step. After this, their values are restored to zero, but in later loops they are not considered again.

1.2.2 THE NONLINEAR PROGRAMMING (STEP 1 OF ALGORITHM)

The central part of the algorithm is the procedure that searches the minimum $\Delta_f G$ composition for every solution. The details of how this nonlinear programming routine is set-up depend on the formulation of the solution models. It is required that each solution be defined over its entire compositional and structural range. I have chosen to use the

concept of endmembers. That is, each solution is considered to be made up of any number of species, where each of these species is a structurally valid endmember. The only constraint for a solution is that the mole fractions of the species be non-negative. Most solution models used in geochemistry follow this concept.

Let us take as an example a binary orthopyroxene $(\text{Fe,Mg})_2\text{Si}_2\text{O}_6$. The obvious endmembers are $\text{Fe}_2\text{Si}_2\text{O}_6$ and $\text{Mg}_2\text{Si}_2\text{O}_6$. If the model should include information on site occupancies for the two sites M_1 and M_2 , then the endmembers are: $\text{FeFeSi}_2\text{O}_6$, $\text{FeMgSi}_2\text{O}_6$, $\text{MgFeSi}_2\text{O}_6$ and $\text{MgMgSi}_2\text{O}_6$. Every possible and structurally different configuration of the smallest unit considered becomes an endmember itself. Such speciation models for complex solutions are frequently used for gaseous systems and were also proposed for solids by Brown and Skinner (1974), Brown and Greenwood (in preparation), and was used by Engi (1983) in modelling the ternary spinel solid solution. A completely different approach would be to define the solution as a mixture of $\text{Fe}_{M_1}\text{SiO}_3$, $\text{Fe}_{M_2}\text{SiO}_3$, $\text{Mg}_{M_1}\text{SiO}_3$ and $\text{Mg}_{M_2}\text{SiO}_3$, with the constraint that the amount of M_1 -species is equal to the amount of M_2 -species. In that case the structural homogeneity is controlled by an additional explicit constraint, and would require a different nonlinear programming routine than the one proposed.

The problem is to find the minimum $\Delta_f G$ composition of a given solution.

ne : Number of endmembers (species) in the solution.

$\bar{x}$: 1 x ne row vector: x_j = concentration of endmember j in solution phase. Where several phases from the same solution are discussed their concentration vectors will be $\bar{x}_n$, $\bar{x}_m$ etc.

$\bar{\mu}^0$: 1 x ne row vector: μ_j^0 = chemical potential of pure endmember j.

$\bar{\mu}$: 1 x ne row vector: μ_j = chemical potential of endmember j in solution phase.

$$\mu_j = \mu_j^0 + a \cdot R \cdot T \cdot \ln(a_j)$$

(where a = site occupancy integer)

If several phases from the same solution are discussed their chemical potential vectors will be $\bar{\mu}_n$, $\bar{\mu}_m$ etc.

$\Delta_f G$ of a solution phase with the concentration vector $\bar{x}$ is:

$$\Delta_f G(\bar{x}) = \sum_{j=1}^{ne} x_j \cdot \mu_j = \bar{x} \cdot \bar{\mu}^T \quad (\text{Gibbs-Duhem equation})$$

where $\bar{\mu}^T$ = transpose of $\bar{\mu}$

1.2.2.1 Ideal solutions

$$\mu_j = \mu_j^0 + a \cdot R \cdot T \cdot \ln(x_j)$$

The $\Delta_f G$ -function of an ideal solution is everywhere convex and there is a unique minimum where $\mu_1 = \mu_2 = \dots = \mu_{ne}$

The concentration vector $\bar{x}$ for this minimum can be calculated in one step. First the endmember J with the smallest μ_j^0 is found. Then all x_j 's are calculated as

$$x_j = e^{-(\mu_j^0 - \mu_j^0)/(a \cdot R \cdot T)} \quad j=1,2,\dots,ne$$

The exponent is always ≤ 0 , but if it is smaller than -150 x_j is set to $\approx 10^{-66}$. ($=e^{-150}$, this is about 10 magnitudes bigger than the smallest number our computer can handle). The sum of all x_j will be between 1 and ne . Thus we can safely divide all x_j by this sum and get the concentration vector $\bar{x}$ for minimum $\Delta_f G$.

1.2.2.2 Nonideal solutions

There are of course many ways to find the minimum of a nonideal solution. Good introductions into the topic are e.g. Dantzig (1963), McCormick (1980) and Dixon (1980). For our strategy the following key points were considered:

- It is rather ineffective to use a highly sophisticated (and computer intensive) method, because the reference hyperplane is moved after each iteration. This rules out any method that uses directly or indirectly second-derivative information (i.e. Newton's method). On the other hand, to guarantee locating the minimum $\Delta_f G$ assemblage the algorithm requires the exact and global minimum. Our compromise is that we use a strategy that can refine a minimum to any desired precision, if required, but may for standard use converge to a more approximate value.

- Although we are primarily searching for the global minimum, the local minima prove useful as well,

especially if two (or more) phases of the same solution are found to coexist.

All local minima found are added to the list of considered phases in the hope that at least one of them is close to the global minimum. (Adding more phases than just those defining the local minima may accelerate the algorithm in some cases).

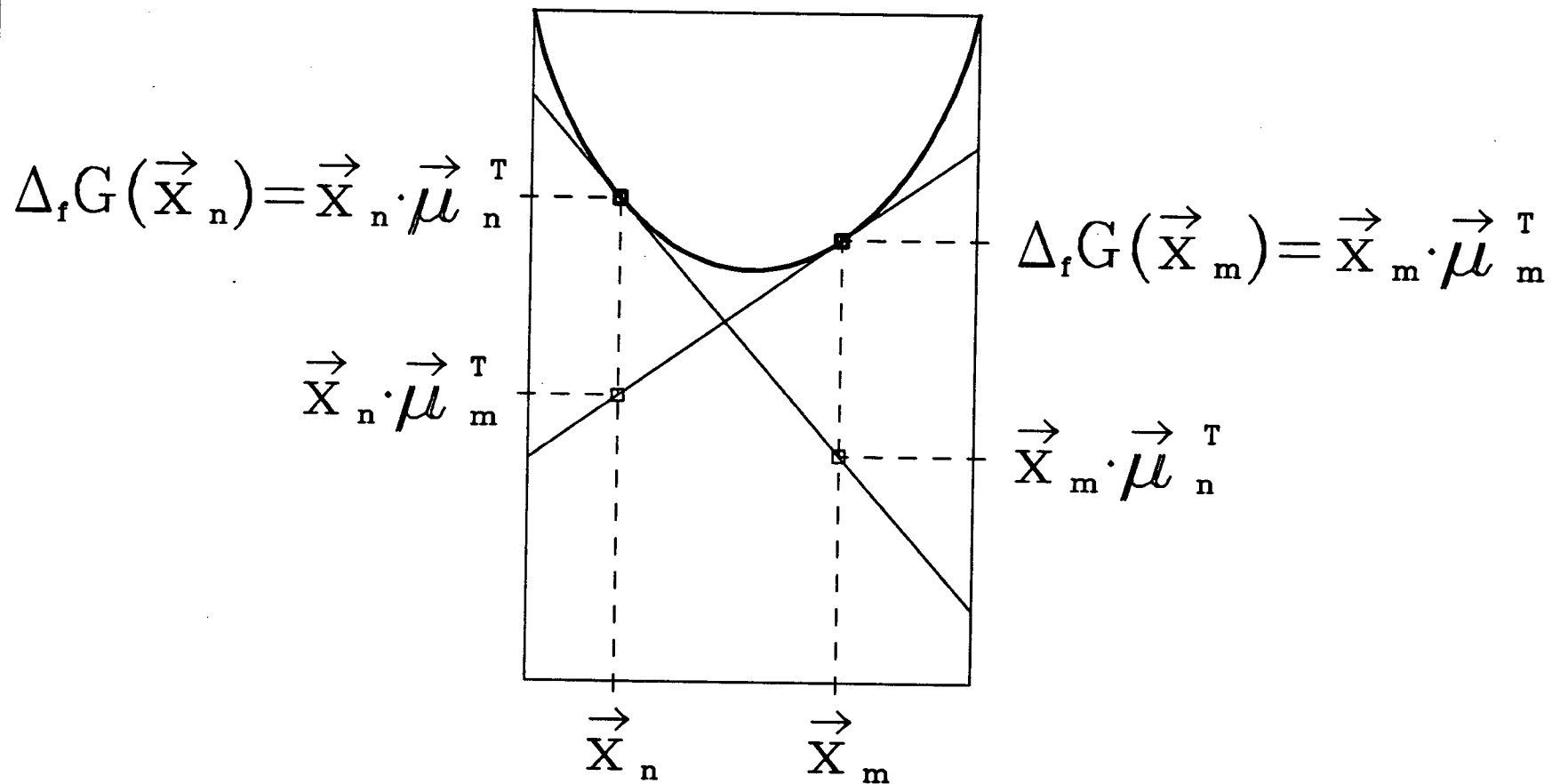
The strategy that we have adopted is a gradient method. Starting from an initial guess, one step consists of searching a new solution phase with smaller $\Delta_f G$ along a descent direction $\vec{v}$. The steps are repeated until a minimum is reached or some other stopping criteria is satisfied. The phase found in the last step is added to the list of considered phases. For each step first a descent direction $\vec{v}$ and an approximate stepsize Δ is calculated, then the actual stepsize is determined in a so-called stepsize procedure. Because $\Delta_f G$ of non-ideal solutions may have local minima, several initial guesses are used, to increase the probability of finding the global minimum. During the minimization we will make use of some special properties of the $\Delta_f G$ function:

- a) $\Delta_f G(\vec{x}_n) = \vec{x}_n \cdot \vec{\mu}_n^T$: This allows us to calculate easily a function value on the tangent hyperplane to $\vec{x}_n$ at any position $\vec{x}_m$. This will be: $\vec{x}_m \cdot \vec{\mu}_n^T$. (see Fig. 4). if $\vec{x}_m \cdot \vec{\mu}_n^T < \Delta_f G(\vec{x}_n)$ then the vector $\vec{v} = (\vec{x}_m - \vec{x}_n)$ starting at $\vec{x}_n$ and pointing towards $\vec{x}_m$ is a descent direction.

Fig. 4: (page 27)

Illustration of how the relation $\Delta_f G(\bar{x}) = \bar{x} \cdot \bar{\mu}^T$ is used to detect descent directions and possible locations of one-dimensional minima. (See text for details).

Fig. 4: Illustration of the use of the Gibbs–Duhem equation



Further: if $(\bar{x}_m - \bar{x}_n)$ is a descent direction or $\Delta_f G(\bar{x}_m) < \Delta_f G(\bar{x}_n)$ and $\bar{x}_n \cdot \bar{\mu}_m^T < \Delta_f G(\bar{x}_m)$ then we know that there is a minimum along a line between $\bar{x}_m$ and $\bar{x}_n$. (The absence of a minimum cannot be proved).

- b) If $\bar{x}$ has a component $x_j = 0$ then $\mu_j = -\infty$. (in practice μ_j may be set to a large negative number. e.g. -10^{20}) and any vector $\bar{v}$ starting from $\bar{x}$ with positive v_j is a descent direction. Thus any descent direction $\bar{w}$, starting from anywhere in the solution, with negative w_j will contain a minimum within the feasible region. (all $x_i \geq 0$). This is a necessary condition to use a simple stepsize procedure, and in fact allows us to treat each $\Delta_f G$ minimization as an *unconstrained* optimization problem.

The initial guesses:

If one or more solution phases are part of the "currently stable assemblage", these will be used as initial guesses. In addition, if one endmember is stable or the number of stable phases from that solution is zero or changed after the previous iteration, we scan the solution for a reasonable starting point. It has usually proved sufficient to choose a grid width of 1, that is to select the endmember with the lowest $\Delta_f G$, but very ill-behaved solutions may require a finer grid or more initial guesses. (e.g. all

endmembers).

The calculation of $\bar{v}$ and Δ :

The refinement of each initial guess is done in steps each defined by a direction $\bar{v}$ and a stepsize Δ . In the following $\bar{x}_n$ is the concentration vector after the n^{th} step.

$\bar{v}$ is always defined in a way that the sum of all the v_i equals zero and the length of $\bar{v}$ is one. This is not absolutely necessary but gives a uniform meaning to the stepsize Δ .

For the first two steps $\bar{v}$ is always the direction of the steepest descent:

$$v_j = (\tilde{\mu} - \mu_j) \quad , \quad \text{where } \tilde{\mu} = \left[\sum_{j=1}^{ne} \mu_j \right] / ne$$

($\bar{v}$ is then normalized so that $|\bar{v}| = 1$)

and Δ is either an initial value Δ_{init} (e.g. 0.02) if the starting point is a new initial guess, or a value computed in a previous minimization for the same solution phase if the starting point is a previous minimum.

To prevent zigzagging, for further steps, $\bar{v}$ and Δ depend on the position of a supposed minimum in the direction of

$$(\bar{x}_n - \bar{x}_{n-2}):$$

$$\text{if } \bar{x}_{n-2} \cdot \bar{\mu}_n^T < \bar{x}_n \cdot \bar{\mu}_n^T \quad (\text{note: } \bar{x}_n \cdot \bar{\mu}_n^T = \Delta_f G(\bar{x}_n))$$

then $\bar{v} = \text{steepest descent}$

$$\Delta = |\bar{x}_n - \bar{x}_{n-2}| / 2$$

$$\text{else } \bar{v} = (\bar{x}_n - \bar{x}_{n-2}) \quad (\text{Normalized: } |\bar{v}| = 1)$$

$$\Delta = |\bar{x}_n - \bar{x}_{n-2}|$$

The refinement is terminated when either the maximum number of steps allowed is reached or Δ becomes smaller than the smallest stepsize $\Delta_{\min}$ considered. The number of steps should be kept minimal (e.g. =3). The only situation that requires more steps is if the minimum is close to a hyperplane defined by other possibly stable phases.

The stepsize procedure:

Now that we have established $\bar{v}$ and Δ , we search for a point close to the minimum along the descent direction. Each time a new composition vector $\bar{x}_{n+1}$ is calculated, it has to be defined so that the sum of the $x_i = 1$ and all $x_i \geq 0$. This is achieved by setting all $x_i < \Delta_{\min}$ to zero and normalizing $\bar{x}_{n+1}$ to a sum of 1.

The new composition vector $\bar{x}_{n+1}$ is calculated as follows:

$$\bar{x}_{n+1}(m) = \bar{x}_n + m \cdot \Delta \cdot \bar{v} \quad (m=0,1,2,\dots)$$

where m is increased until

$$\Delta_f G(\bar{x}_{n+1}(m)) < \Delta_f G(\bar{x}_{n+1}(m+1))$$

or $m > \text{allowed maximum (e.g. 100)}$

If m after this step is zero then

$$\bar{x}_{n+1}(m) = \bar{x}_n + \bar{v} \cdot \Delta / (2 \cdot m) \quad (m=1,2,\dots)$$

where m is increased until $\Delta_f G(\bar{x}_{n+1}(m)) < \Delta_f G(\bar{x}_n)$

or $m > \text{allowed maximum}$

or $\Delta / (2 \cdot m) < \Delta_{\min}$ (in the last two cases $\bar{x}_{n+1} = \bar{x}_n$).

If Δ is in the magnitude of the optimal stepsize, m will be a small number. After the first few iterations the described procedure to calculate Δ yields $m \approx 3$. (with some notable exeptions where $m \approx 50$.)

Like all gradient methods the convergence can become very slow. This may occur if the algorithm is "caught in a narrow trough". Therefore, if Δ becomes smaller than $\Delta_{\min}$ we should test whether we are close to a minimum or whether the above situation is encountered. Fortunately, solutions show these narrow troughs usually along tie-lines of species with low $\Delta_f G$. We can thus escape by defining additional steps in the direction towards each endmember (e.g. with $\Delta = \Delta_{\text{init}}$)

If the computed minimum becomes a stable phase, in the next iteration it will be used as an initial guess with a stepsize

$$\Delta = |\bar{x}_n - \bar{x}_0| \text{ or } \Delta_{\min} \text{ whichever is greater.}$$

1.2.3 THE LINEAR PROGRAMMING (STEP 2 OF ALGORITHM)

nc: Number of components in the system

np: Number of currently considered phases

$\bar{n}$: 1 x np row vector: n_k = number of moles of phase k

$\bar{g}$: 1 x np row vector: $g_k = \Delta_f G$ of one mol of phase k

$\bar{b}$: nc x 1 column vector:

b_i = amount of component i in system

$||X||$: nc x np matrix of phase compositions.

x_{ik} = amount of component i in phase k

A feasible assemblage is characterized by: $||X|| \cdot \bar{n}^T = \bar{b}$ and all $n_k \geq 0$

The problem to find the equilibrium assemblage from a set of fixed composition phases can be formulated as:

$$\text{minimize } G = \bar{n} \cdot \bar{g}^T$$

subject to the constraints: $||X|| \cdot \bar{n}^T = \bar{b}$ and all $n_k \geq 0$

This can be solved with a special case of the simplex method (see e.g. Dantzig (1963)). The following procedure assumes that at the beginning of step 2 of the algorithm the first nc columns in $||X||$, $\bar{n}$ and $\bar{g}$ define a feasible assemblage of linearly independent phases and that the rank of $||X||$ is nc . These conditions are satisfied by the initial assemblage as defined earlier and remain so throughout all iterations. First the matrix $||X||$ is reduced, so that the first nc columns are the identity-matrix. (To avoid accumulations of rounding errors, the X_{ik} are first expressed in terms of the system-components and then reduced). Each column $j=1,2,\dots,nc$ represents a "currently stable phase". Each column $k=nc+1,nc+2,\dots,np$ can be interpreted as a reaction relating the phase k to the "currently stable phases".:

$$\text{phase}_k = \sum_{i=1}^{nc} X_{ik} \text{phase}_i$$

$$\text{with a } \Delta_r G(k) = \left[\sum_{i=1}^{nc} (g_i \cdot X_{ik}) \right] - g_k$$

Each reaction is tested for $\Delta_r G(k) > 0$. If one is found then

that phase k is more stable than a linear combination of the "currently stable" phases. At this point a 5-step procedure is started:

-A- Locate the "currently stable phase" to be replaced by the newly-found phase k : The smallest positive n_i/X_{ik} ($i=1,2,\dots,nc$) is called F_x and the corresponding i is called i_x . Phase i_x will be displaced by phase k .

-B- Force agreement with the constraints $||X|| \cdot \bar{n}^T = \bar{B}$ and $n_i \geq 0$ by defining new phase-amount vectors

$$n'_i = n_i - F_x \cdot X_{ik} \quad (i=1,2,\dots,nc),$$

$$n'_k = F_x.$$

(Note that the number of moles of phase i_x becomes zero.)

-C- Switch columns k and i_x in the matrix $||X||$, $\bar{g}$, $\bar{n}$ and other book-keeping arrays.

This achieves replacement of phase i_x by phase k .

-D- Reduce $||X||$ with the pivoting element now occupying position i_x, i_x .

This normalizes the reactions to refer to the phases now occupying the first nc columns of $||X||$.

-E- Search for the next phase with $\Delta_r G(k) > 0$.

If none is found, terminate the linear programming, otherwise return to step -A-.

1.2.4 THE CHANGE OF BASE OPERATION (STEP 3 OF ALGORITHM)

Theoretically it would be possible to hide this step in the nonlinear programming routine (minimizing *relative* to the "currently stable assemblage"). The advantage of performing the change of base operation after each linear programming step is that the algorithm becomes more transparent and thus easier to program. It transforms the general chemical equilibrium problem into a series of individual function minimizations.

For each phase g_k is replaced by:

$$g_k' = g_k - \sum_{i=1}^{nc} x_{ik} \cdot g_i$$

For $k \leq nc$ the above equation yields $g_k' = 0$.

1.3 APPLICATIONS OF THE COMPUTATION OF CHEMICAL EQUILIBRIUM

1.3.1 INTRODUCTION

The algorithm presented in this chapter is especially designed for equilibrium calculations in complex systems involving phase separation in more than one phase. It would be rather inefficient to use it for an ideal one-phase system. The examples are chosen primarily to demonstrate the variety of problems that can be solved with the described method. Although some of the data or models may be of questionable utility, the calculated results show that the algorithm allows a quick insight into complex stability

relations. (Or at least into the models we have of them.) For most of the following applications the models are taken directly from the literature or are given in a table, so that a critical re-examination of the results is possible.

1.3.2 EXAMPLE 1: BLAST FURNACE PROBLEM

This example is taken from Smith and Missen (1982, pp. 208-211) who use it to demonstrate the capacities and limitations of different computation methods. The problem was originally formulated and solved with slightly less CH_4 in the bulk composition by Madeley and Toguri (1973). All data and the result are listed in table 1. As we would expect from a blast furnace the stable phases are iron, a gas phase and impurities (CaO). This problem has a unique solution and in addition nitrogen is an inert species in the gas phase. Our method cannot take advantage of any of these special cases but still converges at very acceptable speed and the calculated concentrations are identical to those published by Smith and Missen (1982).

1.3.3 EXAMPLE 2: SILICATE MELTS

The system considered is $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$. All data for the solid phases and the ternary non-ideal melt model are taken from Berman and Brown (1984). Let us first concentrate on the melt alone. The thermodynamic model of the melt phase involves a 4th degree Margules-type excess function with 12 interaction parameters. Fig. 5 shows the

Table 1.: Equilibrium calculations for the blast furnace
example. (1050 K, 1 atm)

Species	$\Delta_f G[\text{J/mol}]$	Bulk	Stable	m.f.
<u>Solid phases</u>				
C(Graphite)	0	85.5901		
Fe(Iron)	0	3.5270	42.8270	
CaO(Lime)	-529190	0.6063	0.7562	
Fe ₃ O ₄ (Magnetite)	-762660	13.1000		
CaCO ₃ (Calcite)	-942450	0.1499		
FeO(Wustite)	-193930			
<u>ideal gas</u>			282.2639	
O ₂	0	20.4600		$6.1303 \cdot 10^{-22}$
H ₂	0			$2.2766 \cdot 10^{-2}$
N ₂	0	187.1000		$6.6286 \cdot 10^{-1}$
CH ₂ O	-86110			$8.3543 \cdot 10^{-9}$
CHO	-62550			$3.7258 \cdot 10^{-9}$
OH	22590			$2.8093 \cdot 10^{-13}$
CO ₂	-395970			$2.3608 \cdot 10^{-2}$
H ₂ O	-189870	1.7750		$1.5723 \cdot 10^{-3}$
CH ₄	24850	2.5540		$2.3201 \cdot 10^{-5}$
CO	-204640			$2.8918 \cdot 10^{-1}$

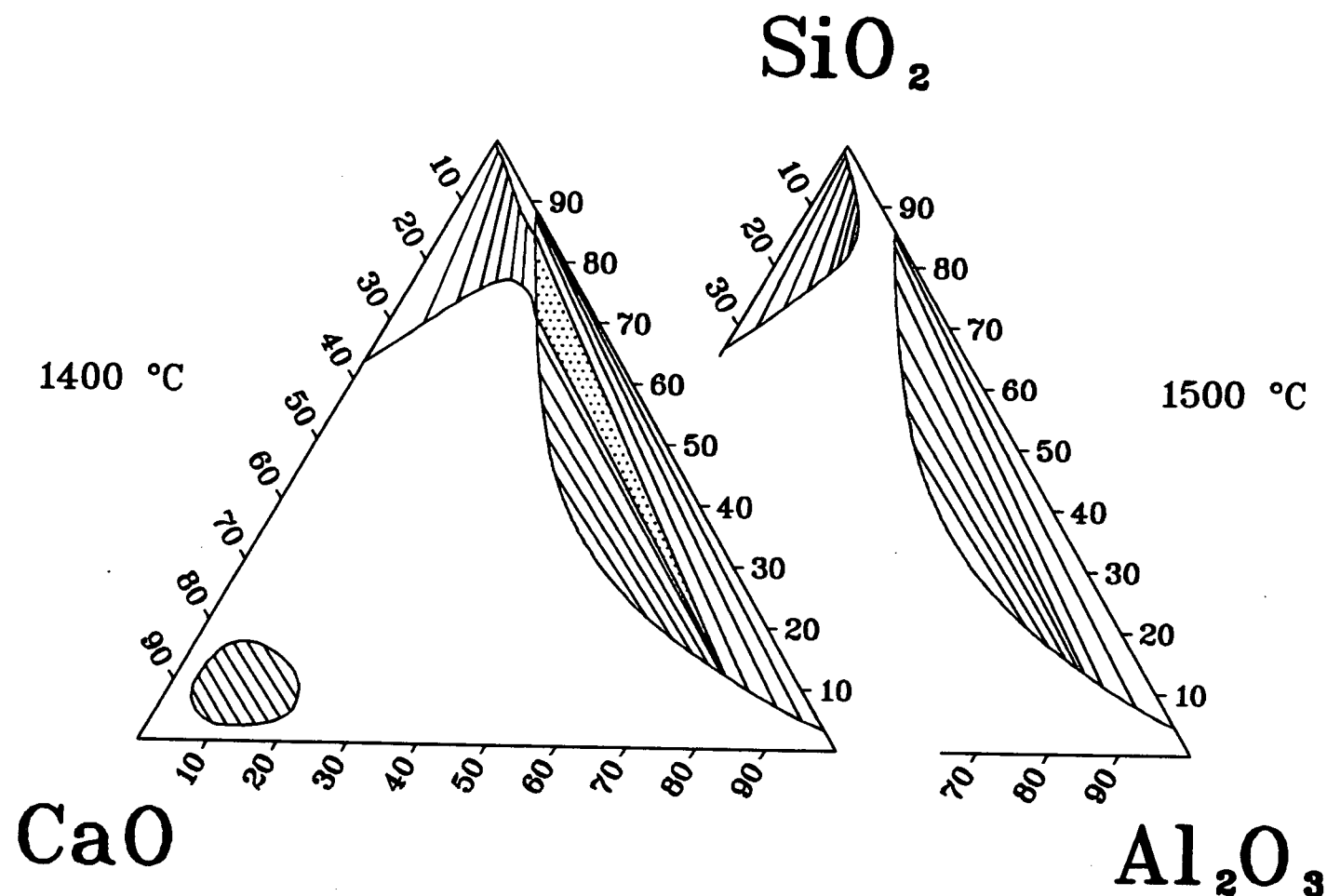
Bulk: initial mixture of phases in moles.

m.f.: mole fraction in stable gas phase.

Fig. 5: (page 38)

Miscibility gaps in the $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ melts according to the data from Berman and Brown (1984). The concentrations are in mol %. The straight lines are calculated tie-lines between coexisting phases. The dotted area is a field where three different ternary melts are in coexistence at 1400 °C. Their compositions are in terms of $(\text{CaO}/\text{Al}_2\text{O}_3/\text{SiO}_2)$:
(0.02135/0.13489/0.84376), (0.09798/0.77994/0.12208) and
(0.08535/0.20656/0.70809).

Fig. 5: Miscibility gaps in the
 $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ melts



results of equilibrium computations for varying compositions at 1400° and 1500° C. For the two diagrams some 70 calculations were performed.

There has been some discussion about the temperature extensions of that model (Barron (1985), Berman and Brown (1985b), Connolly and Kerrick (1986)) to which we can now add a new spice: below ca. 1478 °C there is a field with three coexisting melts. This arises from the interference of two two-phase fields. Although it is metastable relative to possible solid phases and has no further implications for this system we should once more be reminded that multicomponent solutions may exsolve to more than only two phases. Similar results have been reported for the same system by Connolly and Kerrick (1986) at temperatures higher than those for which the model was calibrated.

Fig. 6. is the phase diagram for this system at 1400 °C including the solid phases. Mullite is not considered because of inadequate thermodynamic data. If mullite were included the field with two coexisting melts in the SiO₂-rich corner might prove to be metastable.

For the quaternary system MgO - CaO - Al₂O₃ - SiO₂ the mixing properties of the melt were investigated by Berman (1983). The model is similar to the ternary system but now has 31 Margules parameters. They have a validity range defined by the location of the liquidus surface and experimentally determined two-liquid fields and are listed in table 2 together with a calculated tie-line in table 3.

Fig. 6: (page 41)

c

Phase diagram for the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ at 1400 °C. All thermodynamic data are from Berman and Brown (1984). The liquidus field includes a two-phase region in the SiO_2 -rich corner. The stippled areas are the stable melt fields. The tie-lines between the melt and the solid phases are omitted.

Fig. 6: Phase diagram for the system
 $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ at 1400°C

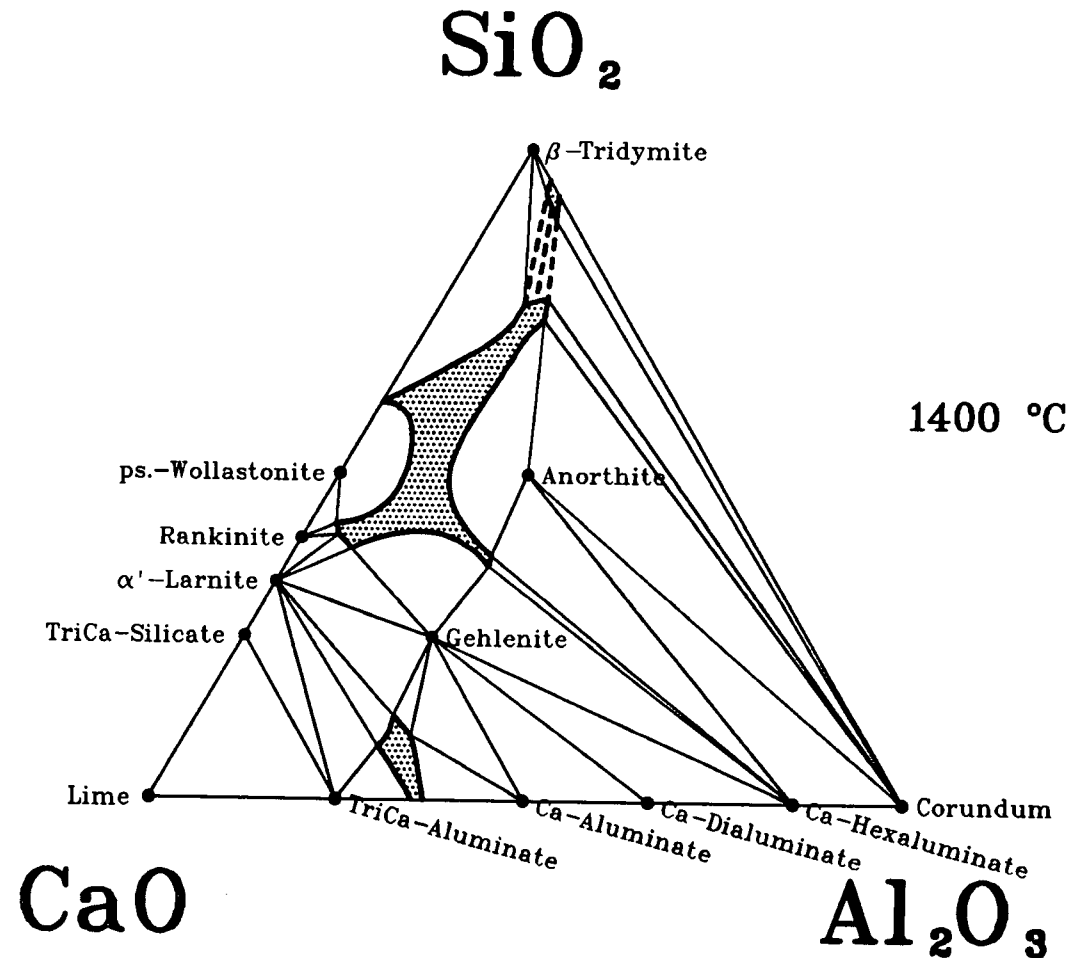


Table 2.: Interaction parameters for the quaternary system
MgO - CaO - Al₂O₃ - SiO₂, according to Berman (1983).

The index is as defined by Berman and Brown (1984).

$W = W_H - T \cdot W_S$	index	W_H	W_S
Binary	SSSA	-161039.81	-60.41
SiO ₂ - Al ₂ O ₃	SSAA	1803871.61	844.79
	SAAA	258911.07	110.47
Binary	SSSC	-25525.64	34.19
SiO ₂ - CaO	SSCC	-341962.81	56.62
	SCCC	-960867.88	-247.11
Binary	SSSM	94145.91	52.77
SiO ₂ - MgO	SSMM	-270581.70	-59.98
	SMMM	-610906.87	-195.01
Binary	AAAC	-197743.47	-1.11
Al ₂ O ₃ - CaO	AACC	-734020.10	-251.94
	ACCC	-617537.61	-76.83
Binary	AAAM	-641890.87	-224.47
Al ₂ O ₃ - MgO	AAMM	727706.30	290.88
	AMMM	-691193.17	-227.94

Table 2. (continued)

$W = W_H - T \cdot W_S$	index	W_H	W_S
Binary	CCCM	318144.87	154.79
CaO - MgO	CCMM	590616.72	322.37
	CMMM	114076.93	58.66
Ternary	SSAC	-2685775.05	-917.87
SiO ₂ - Al ₂ O ₃ - CaO	SAAC	-2833471.13	-976.80
	SACC	580678.70	526.17
Ternary	SSCM	-1143506.91	-279.90
SiO ₂ - CaO - MgO	SCCM	-2464803.70	-669.00
	SCMM	-2026666.90	-555.03
Ternary	AACM	343546.79	160.77
Al ₂ O ₃ - CaO - MgO	ACCM	-2440837.52	-526.78
	ACMM	-3334297.25	-1148.10
Ternary	SSAM	-1828080.99	-693.44
SiO ₂ - Al ₂ O ₃ - MgO	SAAM	-3201173.35	-1382.29
	SAMM	-1828080.99	-693.44
Quaternary	SACM	2179011.74	1328.50
SiO ₂ - Al ₂ O ₃ - CaO - MgO			

Table 3.: Calculated coexisting quaternary liquids at 1400 °C, 1 bar. The bulk composition is 30% SiO₂, 40% Al₂O₃, 10% CaO and 20% MgO. All concentrations are in mol%.

	12.023 %	87.977 %
	<u>liquid 1</u>	<u>liquid 2</u>
SiO ₂	32.625	29.641
Al ₂ O ₃	38.721	40.175
CaO	22.914	8.235
MgO	5.740	21.949

Although the algorithm was developed having mainly binary and ternary systems in mind, it also works well for calculating quaternary solvi. The computing time seems to increase roughly in proportion to the square of the number of endmembers. If the method were used to study phase separation models in higher order multicomponent melts, it would be useful to accelerate the convergence for this special case. In principle, this can be achieved by using a previously calculated equilibrium to generate the initial guess and by adding more than just the minimum $\Delta_f G$ composition phases at each iteration (e.g. some points in the vicinity of these minima and around the bulk

composition.)

1.3.4 EXAMPLE 3: MICA - FELDSPAR EQUILIBRIA

1.3.4.1 Thermodynamic models

Let us assume we were interested in doing an experimental study on the reactions between white mica (paragonite - muscovite) and feldspar. This system is relatively well-known and we can predict most of the results.

The data-base used was compiled by Berman et al. (1985) and is consistent with most experiments performed in this system. Albite and K-feldspar have low-feldspar standard state properties. A disordering function is used, so that at high temperatures their $\Delta_f G$'s are those of the high-feldspars. The $\alpha - \beta$ transition in quartz is modelled according to Berman and Brown (1985a). $\Delta_f G$ of CO_2 is calculated using a modified Redlich-Kwong equation of state (Kerrick and Jacobs (1981)) and $\Delta_f G$ of H_2O according to Haar et al. (1984). The apparent $\Delta_f G$ for all considered phases are listed in Table 4. The most important reactions for which the data have to be consistent are paragonite + quartz = albite + aluminosilicate + water (Chatterjee (1972)). and muscovite + quartz = K-feldspar + aluminosilicate + water. (Chatterjee and Johannes (1974)).

The mixing model for muscovite - paragonite is taken from Chatterjee and Froese (1975) which they derived from their own molar volume measurements and the solvus data of Eugster

et al. (1972) for white micas. The notation for the Margules parameters is the same as introduced by Berman and Brown (1984).

$$\begin{aligned}\Delta_f G(\text{Mica}) = & x_{\text{Pa}} \cdot \Delta_f G(\text{Pa}) + x_{\text{Mu}} \cdot \Delta_f G(\text{Mu}) \\ & + R \cdot T \cdot x_{\text{Pa}} \cdot \ln(x_{\text{Pa}}) + R \cdot T \cdot x_{\text{Mu}} \cdot \ln(x_{\text{Mu}}) \\ & + W_{122} \cdot x_{\text{Pa}} \cdot x_{\text{Mu}}^2 + W_{112} \cdot x_{\text{Pa}}^2 \cdot x_{\text{Mu}} \text{ [J/mol]}.\end{aligned}$$

$$\text{Where : } W_{122} = 12230.2504 + 0.7104432 \cdot T + 0.665256 \cdot P$$

$$W_{112} = 19456.0184 + 1.6543536 \cdot T - 0.456056 \cdot P$$

For the feldspars the model of Ghiorso (1984) was chosen, which on rearrangement, yields:

$$\begin{aligned}\Delta_f G(\text{fsp}) = & x_{\text{Ab}} \cdot \Delta_f G(\text{Ab}) + x_{\text{Or}} \cdot \Delta_f G(\text{Or}) + x_{\text{An}} \cdot \Delta_f G(\text{An}) \\ & + R \cdot T \cdot x_{\text{Ab}} \cdot \ln(x_{\text{Ab}}(1-x_{\text{An}}^2)) + R \cdot T \cdot x_{\text{Or}} \cdot \ln(x_{\text{Or}}(1-x_{\text{An}}^2)) \\ & + R \cdot T \cdot x_{\text{An}} \cdot \ln(x_{\text{An}}(1+x_{\text{An}})^2/4) + W_{112} \cdot x_{\text{Ab}}^2 \cdot x_{\text{Or}} \\ & + W_{122} \cdot x_{\text{Ab}} \cdot x_{\text{Or}}^2 \\ & + W_{113} \cdot x_{\text{Ab}}^2 \cdot x_{\text{An}} + W_{133} \cdot x_{\text{Ab}} \cdot x_{\text{An}}^2 + W_{223} \cdot x_{\text{Or}}^2 \cdot x_{\text{An}} \\ & + W_{233} \cdot x_{\text{Or}} \cdot x_{\text{An}}^2 \\ & + W_{123} \cdot x_{\text{Ab}} \cdot x_{\text{Or}} \cdot x_{\text{An}} \text{ [J/mol]}\end{aligned}$$

Where :

$$W_{112} = 17062.352 + 0.3606608 \cdot P$$

$$W_{122} = 30978.336 - 21.5476 \cdot T + 0.3606608 \cdot P$$

(Thompson and Hovis (1979))

$$W_{113} = 8471.3448$$

$$W_{133} = 28225.6824 \quad (\text{Newton et al. (1980)})$$

$$W_{223} = 27983.0104 + 20.21022624 \cdot T$$

$$W_{233} = 67469.0920 - 11.062496 \cdot T$$

$$W_{123} = 76225.45088 - 8.43465112 \cdot T \quad (\text{Ghiorso (1984)})$$

The mixing properties for H_2O and CO_2 are according to Kerrick and Jacobs (1981). The first column in table 5 shows the calculated assemblages at various temperatures and 4 Kbars for a bulk composition equal to 1/2 paragonite, 1/2 muscovite plus water.

1.3.4.2 Excess phases

Chatterjee and Froese (1975) have calculated the equilibrium assemblages in the same system, assuming that in addition to H_2O , quartz is also always present. Whether quartz is stable in the chosen P-T-range depends on the bulk composition. We can always force quartz into the stable assemblage by adding enough SiO_2 to the system.

Alternatively we can calculate the equilibrium assemblages with excess quartz by assuming the chemical potential of SiO_2 in the stable assemblage to be equal to $\Delta_f G$ of quartz. In that case we have to allow that quartz may be present in a negative amount. Because the linear programming routine is based on the constraint that all amounts are positive, I propose a slightly different approach: we define a phase called -quartz with the composition $-\text{SiO}_2$ and a $\Delta_f G$ which is the negative of that of quartz. The phases quartz and -quartz have the same chemical potentials and if quartz alone is stable (relative to tridymite, cristobalite, Si +

O₂ etc.) then one of the two will always be part of the stable assemblage: quartz, if enough SiO₂ is present and -quartz if not. The number of moles of stable -quartz is the amount of SiO₂ we would have to add to the system to saturate it with quartz.

In column 2 of table 5 the results with excess quartz are listed. As long as two white micas are stable their compositions are the same as in column 1. For 600 °C Chatterjee and Froese (1975) calculated $x_{Or} = 0.0416$ and $x_{Mu} = 0.8738$. The small difference in our computational results is expected from the slightly different endmember properties used.

1.3.4.3 Addition of calcite

Adding calcite to the system changes the situation drastically. The feldspars have an additional endmember, the fluid becomes a mixture of H₂O and CO₂ and more phases have to be considered. These changes are responsible for quite different equilibrium compositions (column 3, table 5). The three coexisting feldspars at 550 ° are a consequence of Ghiorso's (1984) model which was fitted to data between 600 ° and 900 °C with the intention to extrapolate to *higher* temperatures. The configurational entropy assumes disordered albite/K-feldspar and fully ordered anorthite (according to Newton et al. (1980)). Our extrapolation to *lower* temperatures is intended only to demonstrate the ability of the algorithm to handle such complex stability relations.

1.3.4.4 Addition of a buffer

In many experimental techniques buffers are used to control the activities of one or more species in the fluid phase. Similar (and probably more complex) buffers play an important role in geological processes. If the controlling reactions are simple, the concept of buffering can easily be simulated in a $\Delta_f G$ -minimization. We will hypothetically assume that the reaction $\text{brucite} = \text{periclase} + \text{H}_2\text{O}$ is buffering the activity of H_2O . This reaction was chosen because the activity of H_2O will vary considerably over the considered temperature range. We define a new phase which we call BP-buffer. Its composition is H_2O and $\Delta_f G(\text{BP-buffer}) = \Delta_f G(\text{brucite}) - \Delta_f G(\text{periclase})$. We now have to add enough H_2O to the system, so that the BP-buffer becomes stable. If too much is added this does not change the assemblage, because all the excess H_2O will go into the buffer phase. For the calculation of column 4, table 5 I did not add H_2O but have used the same technique as for the excess quartz and have defined a negative buffer phase. The biggest influence of the buffer on the stable assemblage is at 400 and 450 °C, where the H_2O -activity is small.

Table 4.: $\Delta_f G$ [J/mol] for all considered phases in example 3. P = 4 Kbars

	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C	700 °C
ALBITE	-4075566.88	-4096864.29	-4119235.37	-4142625.94	-4166984.24	-4192261.32	-4218411.29
ANDALUSITE	-2654752.33	-2665986.52	-2677855.52	-2690326.99	-2703371.50	-2716962.17	-2731074.42
ANORTHITE	-4365243.60	-4386277.47	-4408347.79	-4431402.77	-4455395.50	-4480283.36	-4506027.43
BOEHMITE	-1026914.47	-1032301.70	-1037984.64	-1043950.40	-1050187.11	-1056683.82	-1063430.40
CALCITE	-1270609.53	-1279423.62	-1288639.10	-1298236.69	-1308198.85	-1318509.58	-1329154.25
CORUNDUM	-1714917.47	-1721749.27	-1728988.88	-1736615.54	-1744610.38	-1752956.19	-1761637.21
CRISTOBALITE	-935769.21	-940463.02	-945383.80	-950519.82	-955860.42	-961395.88	-967117.33
DIASPORE	-1026442.54	-1031171.02	-1036195.21	-1041502.22	-1047080.18	-1052918.14	-1059005.97
GEHLENITE	-4120291.55	-4141299.37	-4163277.56	-4186175.27	-4209946.62	-4234550.00	-4259947.55
GIBBSITE	-1347493.52	-1356203.25	-1365454.08	-1375224.21	-1385493.37	-1396242.70	-1407454.63
GROSSULAR	-6820716.11	-6850766.32	-6882433.84	-6915633.14	-6950286.68	-6986324.01	-7023680.91
JADEITE	-3122061.28	-3137126.10	-3152980.36	-3169584.01	-3186900.74	-3204897.48	-3223544.00
KAOLINITE	-4265285.94	-4288420.54	-4312781.45	-4338308.43	-4364946.79	-4392646.66	-4421362.44
KYANITE	-2655718.71	-2666485.69	-2677890.85	-2689902.21	-2702490.61	-2715629.44	-2729294.30
LAUMONTITE	-7581274.72	-7627497.71	-7676025.56	-7726741.68	-7779540.35	-7834325.31	-7891008.64
LAWSONITE	-5035238.32	-5061677.06	-5089582.82	-5118891.96	-5149546.07	-5181491.30	-5214677.94
LIME	-661949.37	-665876.09	-669982.32	-674257.68	-678692.92	-683279.72	-688010.56
MARGARITE	-6428119.55	-6458716.13	-6490976.10	-6524818.08	-6560168.00	-6596958.26	-6635126.99
MEIONITE	-14346560.88	-14420543.81	-14498043.78	-14578886.74	-14662915.02	-14749985.14	-14839966.08
MUSCOVITE	-6185113.43	-6216798.67	-6250141.51	-6285060.13	-6321479.82	-6359332.25	-6398554.76

Table 4. (continued)

	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C	700 °C
PARAGONITE	-6141210.88	-6172241.75	-6204913.85	-6239143.93	-6274855.89	-6311980.05	-6350452.50
POTASSIUM FELDSPAR	-4114965.26	-4136665.82	-4159424.00	-4183184.04	-4207894.55	-4233508.34	-4259982.05
PREHNITE	-6401100.31	-6432810.31	-6466161.13	-6501073.20	-6537474.24	-6575298.31	-6614485.08
PYROPHYLLITE	-5808596.81	-5836291.37	-5865503.69	-5896161.71	-5928199.70	-5961557.49	-5996179.88
QUARTZ	-938516.34	-942969.67	-947658.46	-952574.78	-957712.45	-963066.98	-968653.89
SILLIMANITE	-2654516.62	-2665892.71	-2677898.25	-2690502.49	-2703677.47	-2717397.67	-2731639.75
STELLERITE	-11378078.94	-11449229.40	-11523978.12	-11602143.94	-11683562.49	-11768084.10	-11855572.00
TRIDYMIT	-936240.56	-940873.57	-945736.62	-950817.94	-956106.76	-961593.20	-967268.19
CA-AL PYROXENE	-3400457.16	-3416215.49	-3432792.79	-3450146.98	-3468239.87	-3487036.71	-3506505.75
WAIRAKITE	-6915351.05	-6953799.26	-6994141.16	-7036280.80	-7080131.10	-7125612.71	-7172653.15
WOLLASTONITE	-1687570.02	-1696055.53	-1704948.08	-1714226.16	-1723870.29	-1733862.84	-1744187.72
PSEUDOWOLLASTONITE	-1685346.75	-1693992.11	-1703041.89	-1712474.65	-1722270.96	-1732413.18	-1742885.21
YUGAWAIRALITE	-9453495.64	-9508560.64	-9566381.59	-9626819.52	-9689748.21	-9755052.74	-9822628.04
ZOISITE	-7105190.98	-7138292.66	-7173133.63	-7209628.74	-7247700.69	-7287279.04	-7328299.35
CLINOZOISITE	-7102840.97	-7135417.64	-7169733.61	-7205703.72	-7243250.66	-7282304.00	-7322799.30
CARBON DIOXIDE	-489581.23	-498243.82	-507116.90	-516186.73	-525441.37	-534870.33	-544464.30
STEAM	-337079.75	-343366.37	-349892.75	-356643.87	-363605.91	-370765.97	-378111.94
BP-Buffer							
(=BRUCITE-PERICLASE)	-351616.51	-355636.63	-359867.93	-364299.76	-368922.36	-373726.80	-378704.91

Table 5.: Calculated mica - feldspar equilibria.

Bulk comp.:	0.5 Parag + 0.5 Musc + 1 H ₂ O	0.5 Parag + 0.5 Musc + 1 H ₂ O + excess Qz	0.5 Parag + 0.5 Musc + 1 H ₂ O + 2 Qz + 2 Cc	0.5 Parag + 0.5 Musc + 1 H ₂ O + 2 Qz + 2 Cc (+ BP-Buffer)
400 °C	Pa(0.0907)Mu(0.9093)	Pa(0.0907)Mu(0.9093)	Pa(0.0907)Mu(0.9093)	Pa(0.0370)Mu(0.9630)
4 Kbar	Pa(0.9537)Mu(0.0463)	Pa(0.9537)Mu(0.0463)	Pa(0.9537)Mu(0.0463)	
			Ab(0.7911)Or(0.0071)An(0.2018)	Ab(0.8877)Or(0.0261)An(0.0862)
	Steam	Steam	H ₂ O(0.9928)CO ₂ (0.0072)	H ₂ O(0.0279)CO ₂ (0.9721)
		Quartz	Quartz, Calcite, Zoisite	Quartz, Calcite, Zoisite
450 °C	Pa(0.1158)Mu(0.8842)	Pa(0.1158)Mu(0.8842)	Pa(0.1158)Mu(0.8842)	Pa(0.0326)Mu(0.9674)
4 Kbar	Pa(0.9387)Mu(0.0613)	Pa(0.9387)Mu(0.0613)	Pa(0.9387)Mu(0.0613)	
			Ab(0.5782)Or(0.0040)An(0.4178)	Ab(0.7549)Or(0.0271)An(0.2180)
			Ab(0.1187)Or(0.0003)An(0.8810)	
	Steam	Steam	H ₂ O(0.9369)CO ₂ (0.0631)	H ₂ O(0.0600)CO ₂ (0.9400)
		Quartz	Quartz, Calcite	Quartz, Calcite, Kyanite
500 °C	Pa(0.1448)Mu(0.8552)	Pa(0.1448)Mu(0.8552)	Pa(0.0308)Mu(0.9692)	Ab(0.0568)Or(0.9372)An(0.0060)
4 Kbar	Pa(0.9208)Mu(0.0792)	Pa(0.9208)Mu(0.0792)	Ab(0.5157)Or(0.0159)An(0.4684)	Ab(0.5175)Or(0.0215)An(0.4610)
			Ab(0.1535)Or(0.0023)An(0.8442)	Ab(0.1508)Or(0.0030)An(0.8462)
	Steam	Steam	H ₂ O(0.7502)CO ₂ (0.2498)	H ₂ O(0.1152)CO ₂ (0.8848)
		Quartz	Quartz, Calcite	Quartz, Calcite

Table 5. (continued)

Bulk comp.:	0.5 Parag + 0.5 Musc + 1 H ₂ O	0.5 Parag + 0.5 Musc + 1 H ₂ O + excess Qz	0.5 Parag + 0.5 Musc + 1 H ₂ O + 2 Qz + 2 Cc	0.5 Parag + 0.5 Musc + 1 H ₂ O + 2 Qz + 2 Cc (+ BP-Buffer)
550 °C	Pa(0.1783)Mu(0.8217)	Pa(0.1783)Mu(0.8217)	Ab(0.0730)Or(0.9185)An(0.0085)	Ab(0.0730)Or(0.9185)An(0.0085)
4 Kbar	Pa(0.8993)Mu(0.1007)	Pa(0.8993)Mu(0.1007)	Ab(0.4412)Or(0.0223)An(0.5365)	Ab(0.4412)Or(0.0223)An(0.5365)
			Ab(0.2040)Or(0.0065)An(0.7895)	Ab(0.2040)Or(0.0065)An(0.7895)
	Steam	Steam	H ₂ O(0.6667)CO ₂ (0.3333)	H ₂ O(0.2049)CO ₂ (0.7951)
		Quartz	Quartz, Calcite	Quartz, Calcite
600 °C	Pa(0.2169)Mu(0.7831)	Pa(0.1404)Mu(0.8596)	Ab(0.0892)Or(0.8993)An(0.0115)	Ab(0.0892)Or(0.8993)An(0.0115)
4 Kbar	Pa(0.8734)Mu(0.1266)	Ab(0.9432)Or(0.0568)	Ab(0.3078)Or(0.0168)An(0.6754)	Ab(0.3078)Or(0.0168)An(0.6754)
	Steam	Steam	H ₂ O(0.6667)CO ₂ (0.3333)	H ₂ O(0.3460)CO ₂ (0.6540)
	Corundum	Quartz, Sillimanite	Quartz, Calcite	Quartz, Calcite
650 °C	Pa(0.0963)Mu(0.9037)	Ab(0.8105)Or(0.1895)	Ab(0.1044)Or(0.8804)An(0.0152)	Ab(0.1044)Or(0.8804)An(0.0152)
4 Kbar	Ab(0.8666)Or(0.1334)	Ab(0.3952)Or(0.6048)	Ab(0.3025)Or(0.0229)An(0.6746)	Ab(0.3025)Or(0.0229)An(0.6746)
	Steam	Steam	H ₂ O(0.6667)CO ₂ (0.3333)	H ₂ O(0.5691)CO ₂ (0.4309)
	Corundum	Quartz, Sillimanite	Quartz, Calcite	Quartz, Calcite
700 °C	Ab(0.5000)Or(0.5000)	Ab(0.5000)Or(0.5000)	Ab(0.1183)Or(0.8622)An(0.0195)	Ab(0.1183)Or(0.8622)An(0.0195)
4 Kbar			Ab(0.2972)Or(0.0304)An(0.6724)	Ab(0.2972)Or(0.0304)An(0.6724)
	Steam	Steam	H ₂ O(0.6667)CO ₂ (0.3333)	H ₂ O(0.9178)CO ₂ (0.0822)
	Corundum	Quartz, Sillimanite	Quartz, Calcite	Wollastonite

1.3.5 DISCUSSION

The method presented for computing phase equilibria can be used to solve a great variety of problems and to test the consequences of thermodynamic models and data in a reasonable amount of computer time. The timings presented in table 6 show that even for very complex problems the computing times are in the order of one to two seconds. For extensive calculations in a specific system it might be more efficient to use a more specialized algorithm, and to use the general algorithm only if difficulties are encountered or to check some of the assemblages. For example, the position of the liquidus in Fig. 6 can be calculated much faster with an algorithm used by Berman and Brown (1984), but their procedure will not recognize the two-liquid field in the SiO_2 -rich corner. Exploring the P-T-plane for several systems with varying bulk compositions it was found that the algorithm always converged, but as with all other methods, we cannot completely exclude the possibility that some of our results are local minima. In future applications I will include further solution models (e.g. electrolytes) and a different choice of independent variables.

Table 6: Computing times for the examples on a 48 megabyte
Amdahl 5850 computer

1. Blast furnace example (table 1)..... 0.43 sec

2. Silicate melts (figs. 5 & 6, table 2)

two binary liquids..... ca. 0.10 sec

One ternary liquid..... 0.40 - 0.60 sec

two ternary liquids..... 0.30 - 0.40 sec

three ternary liquids..... ca. 0.50 sec

one ternary liquid

+ one solid phase..... 0.25 - 0.35 sec

one ternary liquid

+ two solid phases..... ca. 0.20 sec

three solid phases..... ca. 0.10 sec

two quaternary liquids..... 1.40 sec

3. mica - feldspar example (table 4)

column 1..... 0.20 - 0.30 sec

column 2..... 0.20 - 0.30 sec

column 3..... 0.50 - 1.20 sec

column 4..... 0.30 - 1.10 sec

2. ORDER-DISORDER IN TERNARY FE-MN-MG OLIVINES

2.1 INTRODUCTION

Thermodynamic models of solutions always include a configurational entropy term which is based on our knowledge of ordering. A very important type of ordering is the "site preference" of certain atoms in certain structures. Because the olivines have two octahedral cation sites of different size and symmetry, it can be expected that there will be a noticeable ordering. According to the crystal chemical considerations of Ganguli (1977), the larger atoms will prefer the larger M2 site. This may be demonstrated with different techniques (e.g. Shinno, 1981) for Kirschsteinite (CaFeSiO_4), Fe-Mn olivines (Annersten et al., 1984) Fe-Ni and Fe-Ni-Mg olivines (Annersten et al., 1982, Nord et al., 1982). The Fe-Mg distribution is almost disordered, (Brown and Prewitt (1973), Wenk and Raymund (1973), Basso et al. (1979)) but the different degrees of ordering given by different authors suggest that a dependency on some intensive variables must exist. (e.g. oxygen fugacity as proposed by Will and Nover (1979)). The aim of the investigation presented in this chapter is to determine the cation occupancies in synthetic ternary Fe-Mn-Mg olivines. This knowledge will be used to propose an entropy of mixing model for these olivines.

2.2 THE SYNTHESIS OF OLIVINES

Over the last half century, many olivines and olivine type structures have been synthesized. They are usually crystallized from a melt or glass at 1100 to 1400 °C. The method described below takes into account that the synthesis temperature was intended to be very close to the temperature of the planned exchange experiments. The starting materials were :

Fe₂O₃: Fisher Certified Reagent. LOT 725030.

Fired at 600 °C for 13 hours. Powder stored 110 °C. A microprobe analysis of synthetic fayalite revealed later that this substance was contaminated with ca. 0.6 % Mn. All compositions were then recalculated with this correction.

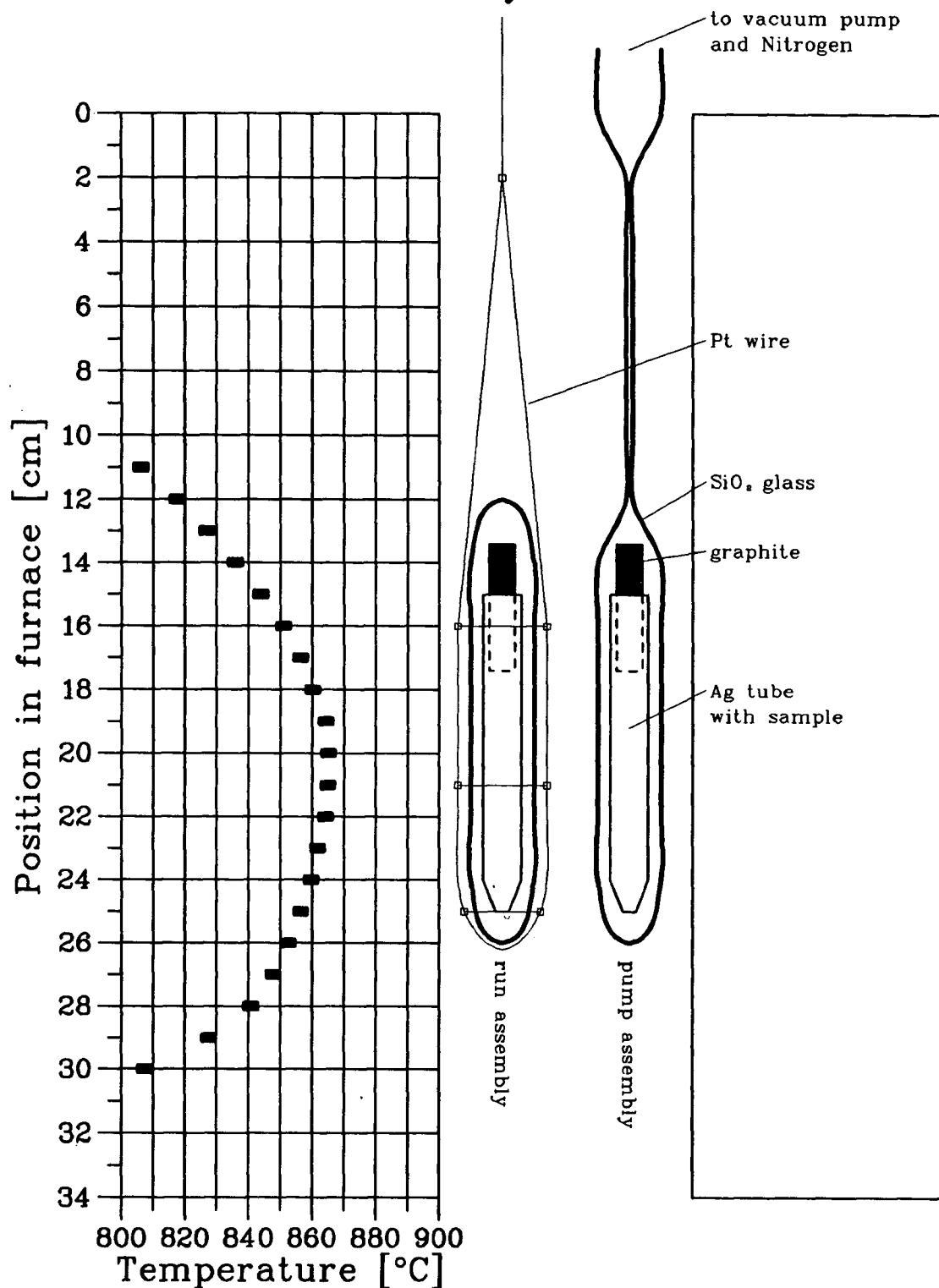
MnCO₃: Fisher Certified Reagent. LOT 734606.

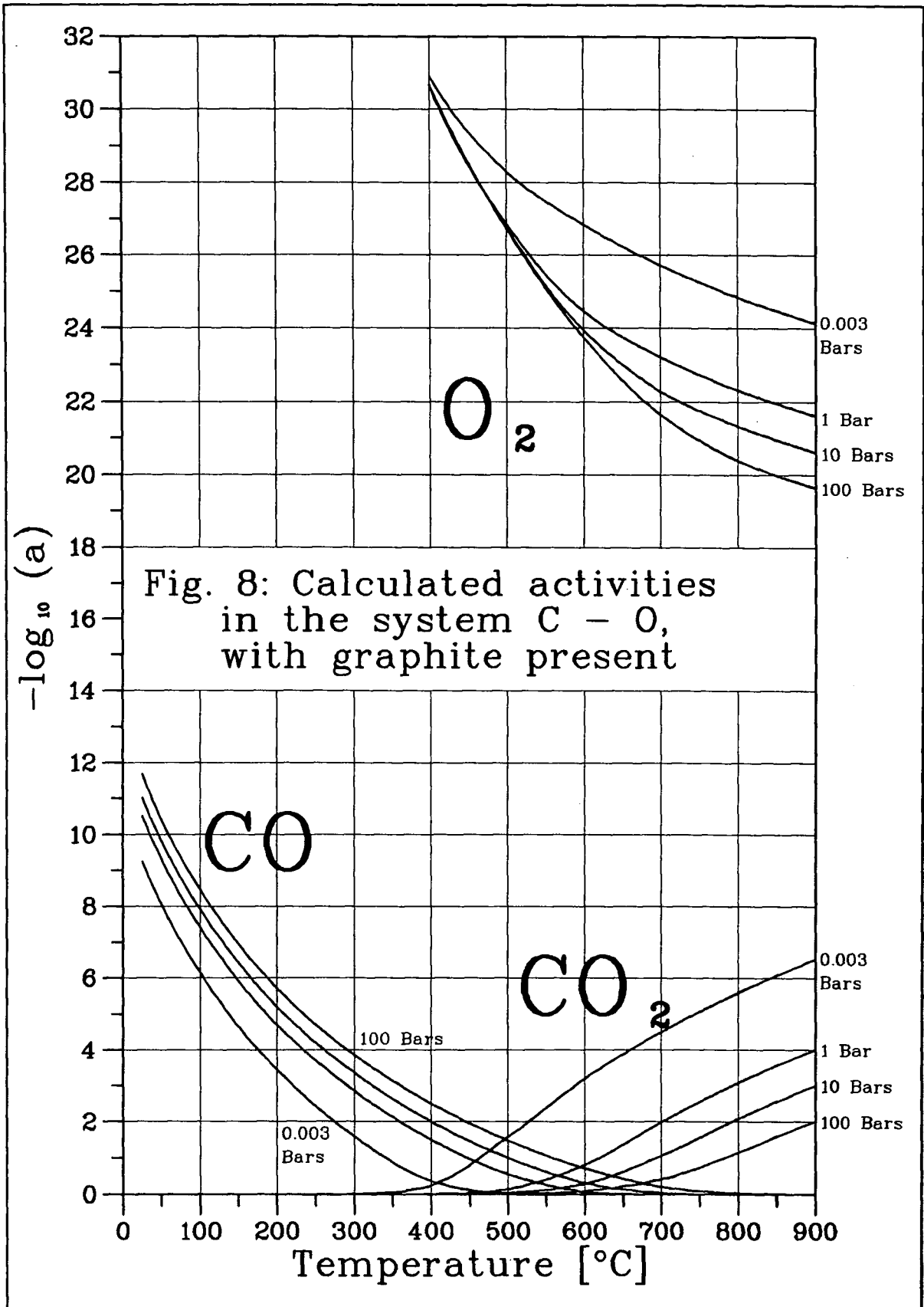
Lot analysis of 48.4 % assay as Mn used. Powder stored in desiccator. MgO: Fisher Certified Reagent. LOT 741694

Powder stored at 110 °C. SiO₂: From SiO₂·xH₂O, Mallinckrodt Analytical Reagent. LOT KMNG. The silicic acid was converted to Cristobalite by slowly heating to 800 °C in a platinum crucible, and leaving the sample at this temperature for 24 hours. Powder stored at 110 °C.

For each desired olivine composition an oxide/carbonate mixture is prepared, then enough graphite is added so that the bulk composition contains at least one mole graphite for each mole of Fe₂O₃ and MnCO₃. The mixture is then placed into a Ag-tube, (ca. 3 cm long, 1.0 cm diam. and closed at the bottom) inside a SiO₂ glass tube (1.2 cm inner diam.)

Fig. 7: Experimental set-up
for the Olivine synthesis





and connected to the vacuum pump, after being flushed three to four times with nitrogen. Then it is heated to 850 °C for ca. 3 hours. This preliminary heating is necessary to let all MnCO_3 decarbonate. In the smaller diameter tubes used for the synthesis, there would be too much loss of material. Most of the Fe_2O_3 will also have reacted to Fe_3O_4 and FeO . Then the sample is cooled and transferred to a smaller Ag-tube (0.6 cm diam., ca. 8 cm long). A small graphite cylinder is inserted on top and the whole tube is placed in a SiO_2 tube (0.7 cm inner diam.). (See. Fig. 7) It is exposed to 850 °C for 3 to 4 hours while connected to the vacuum pump. At about that time a graphite deposit develops in the SiO_2 -tube at a position corresponding to a temperature of 600-700 °C. We may speculate that this reflects the reaction:



The tube is then sealed and left at 850 °C for one to three weeks. Fig. 7 shows the run conditions and the temperature distribution in the furnace. Because up to three samples could be accommodated in the furnace, which were not all inserted or removed at the same time, the temperature varied up to ± 20 °C for short times during the synthesis. The pressure could not be controlled and varied around one bar, the lower limit being the limit of the vacuum pump (0.003 Bars) and the upper limit the strength of the silica glass (around 100 Bars). The calculated activities for O_2 , CO and CO_2 are shown in Fig. 8. The presence of graphite in the

experiments guarantees a O_2 -activity less than 10^{-20} .

The products were examined with a magnet, optically and by X-ray diffraction. A good product is non-magnetic, monomineralic according to optical and X-ray diffraction and has diffraction peak widths at half maximum around $0.3^\circ 2\theta$. All products not conforming with the above criteria were rejected and the synthesis repeated either with the same sample or with a new mixture. It turned out that for the synthesis conditions chosen, olivines with a composition of more than 75% forsterite could not be synthesized even after four weeks without being contaminated with MgO, cristobalite and Fe- and Mn-oxides. Pure forsterite was synthesized at $1100^\circ C$ in two weeks.

2.3 SOME METHODS FOR SITE OCCUPANCY DETERMINATION CITED IN THE LITERATURE

There is no simple, easily available method that could be used to measure all site occupancies of all elements. However several methods are very accurate for certain types of atoms and a combination of methods may be used to extract the desired information. Various methods used for olivines are briefly reviewed below. The literature cited is mainly restricted to applications in the ternary Fe-Mn-Mg olivine system.

2.3.1 MÖSSBAUER SPECTROSCOPY

Within ten years of the discovery of the Mössbauer effect, the first olivines were being investigated with this method. (Eibschütz and Ganiel (1967)). The Fe population on the two sites M1 and M2 can be distinguished if the sample is heated to ca. 300 °C. No other element has been successfully measured in olivines by Mössbauer spectroscopy, and therefore the method applies only to Fe bearing solutions. Systematic investigations involving synthetic olivines were made by Annersten (1982), Nord et al. (1982), Shinno (1981) and Annersten et al. (1984). In addition the technique is often used as an additional source of information to characterize natural or synthetic phases. (Bush et al. (1970), Virgo and Hafner (1972), and others).

2.3.2 SINGLE CRYSTAL STRUCTURE REFINEMENTS

The crystal structure refinement using X-ray diffraction is still the most important method to obtain structure data. If a particular lattice position is occupied by more than one atom, and these differ only slightly in the scattering factors, (e.g. Fe and Mn) then an accurate site occupancy for each atom cannot be obtained by diffraction alone. Further, a minimum grain size of a single crystal ($\approx 100\mu\text{m}$) is required for the method. The crystal structure of olivine (forsterite) was first determined by Bragg and Brown (1926). Later refinements were reported by Belov et al. (1951), Hanke and Zeman (1963), Birle et al. (1968) and

others. (See also list given in appendix F). Site occupancies of olivines from single crystal structure refinements were reported by Wenk and Raymond (1973), Brown and Prewitt (1973), Basso et al. (1979), Francis and Ribbe (1980) and Brown (1980).

2.3.3 THE RIETVELD METHOD

A very promising method is the XRD profile refinement as proposed by Rietveld (1967,1969). The method consists of measuring a large number of intensities (approximately 1000) along a profile and fit the lattice parameters, positional parameters, occupancies etc. to these intensities. Initially the method was used for neutron diffraction patterns with gaussian peak shapes. The major problem of applying the method to XRD data is that the peak shapes have to be known in order to fit the data. Although a Voigt or pseudo-Voigt function was found to be very acceptable, (Hill (1984), David (1986)) some problems are unresolved. Sakala and Cooper (1979) could show that the structural parameters obtained by a Rietveld profile refinement were not the same as those obtained from an integrated intensity refinement of the same data and that the standard deviations of the parameters are incorrect. They argue that a systematic error is introduced due to correlations between residuals across a Bragg peak. Additional difficulties were pointed out by Thompson and Wood (1983), who propose that much more information must be considered for an accurate profile

refinement. (e.g. finite specimen length, eccentricity errors, broadening due to strain or particle size and spectral distribution of the incident X-rays). All these problems led several authors (Cooper et al. (1981), Will et al. (1983)) to concentrate more on pattern decomposition methods, where the useful information such as integrated intensity, the peak maximum position and the peak width of individual reflections are obtained first and then the structure parameters are refined analogous to a single crystal structure refinement. The newest trend among crystallographers was initiated by Prawley (1981) and later Toroya (1986). Their methods are whole-powder-pattern fittings without reference to a structural model. In this approach, the intensities and the positions of all reflections can vary individually.

We may summarize that for X-ray diffraction, the Rietveld method is far from being an established routine investigation and is at present mainly restricted to refinements of solved, simple structures. As further developments in diffraction techniques will produce data with a resolution much superior to that presently available, powder diffraction profile refinements may develop more and more importance for the whole range of structure refinements.

Few Rietveld refinements have been published for the relatively complicated olivine structure. (Lager et al. (1981), Hill and Madsen (1984)). Cation distributions in

olivine-type structures were investigated by Nord (1984) and Nord et al. (1985), who had very encouraging results, despite numerous difficulties. (e.g. negative temperature correction factors).

2.3.4 THE A-B PLOT

A more empirical method for the occupancy determination in olivines is mentioned by Lumpkin and Ribbe (1983) and developed in more details by Lumpkin et al. (1983), Miller (1985) and Miller and Ribbe (1985, 1986). They found that a linear regression could accurately be fitted for each unit cell parameter in terms of the effective radii of the cations occupying the M1 and M2 octahedral sites, using the radii of Shannon (1974). The a_0 -cell edge was found to be strongly dependent on the radius of the cations occupying M1, and the b_0 -cell edge on those occupying M2. This led to the construction of a_0 versus b_0 plots for binary olivines that allow prediction of the bulk compositions together with the M1 and M2 site occupancies. The method requires first a certain number of known occupancies, and because it is not a direct measurement, is subject to misinterpretation due to charge distributions or strains in the crystals. The advantage is that it allows an estimation of occupancies from published bulk composition and lattice parameters. So far the method has only been applied to binary systems.

2.3.5 VIBRATIONAL SPECTRA

Huggins (1973) proposed a simplified interpretation of vibrational spectra which allows an estimation of the site occupancies. However his theory may only be used when a pronounced non-linearity has been demonstrated for a given frequency - composition relationship. This could not be done for the Fe-Mg olivines and therefore the method is restricted to the Fe-Mn and Mn-Mg binaries.

2.3.6 CHEXE SPECTROSCOPY

A new analytical transmission electron microscopic technique known as *Channeling Enhanced X-ray Emission* spectroscopy was used by Smyth and Taftø (1982) to determine the site occupancies of Fe, Ni, Mn and Ca in a natural olivine. The strength of the method is a very high accuracy at very low (0.001 %) concentrations.

2.4 CHOICE OF METHODS

For the present investigation with Fe-Mn-Mg olivines, the choice of the methods used for the determination of the site occupancies was naturally influenced by the small grain size of the samples (usually <5 μm) and by the equipment available at UBC. Because the investigated system includes Fe-olivines, the Mössbauer spectroscopy was chosen as an ideal tool for determining the Fe-site distribution. At first the intention was to use a Rietveld profile refinement to resolve the Mn-Mg distribution. Unfortunately some

preliminary investigations showed that the peak shapes in the profiles were not symmetric and that the widths were not a smooth function of 2θ . This may be due to strains in the synthetic crystals. At present a standard Rietveld profile refinement cannot take into account all these additional problems, and the development of a more sophisticated profile refinement exceeds the aim of the present investigation. The calculation of integrated intensities, however, showed that several peak intensities are strongly dependent on the Mn-Mg site distribution and that a simple method, using only few intensities could very well be used to determine the site occupancies. The intensity ratios used must be only slightly dependent on the positional parameters and the effective charge distribution.

2.5 THE DETERMINATION OF FE-SITE DISTRIBUTIONS BY MÖSSBAUER SPECTROSCOPY

2.5.1 INTRODUCTION

The Mössbauer effect is based on the observation that in crystalline substances the nuclear resonance absorption is essentially recoil-free if $T \ll \Theta_D$. (Θ_D = Debye temperature). (Mössbauer (1958a,b)). For a detailed introduction into the principle and the methodology see Vértés et al (1979), Herber (1971), Gibb (1976) and Gonser (1975). We will restrict our overview to ^{57}Fe . (¹ For a ^{57}Fe nucleus, the energy difference between an excited state and the ground state is ≈ 14.4 keV. If a γ -quantum with the energy E_γ is emitted from a free nucleus, the nucleus is accelerated in the opposite direction, because of the conservation of momentum and energy. The velocity of recoil is $E_\gamma/M \cdot c \approx 81.5$ m/s, resulting in a recoil energy of $(E_\gamma^2)/(2 \cdot M \cdot c^2) \approx 1.9 \cdot 10^{-3}$ eV, thereby reducing the energy of the emitted γ -ray. Similarly the energy of a γ -quantum will be decreased by another $\approx 1.9 \cdot 10^{-3}$ eV when it is absorbed by a free nucleus. As the natural line width of ^{57}Fe is only $\approx 4.7 \cdot 10^{-9}$ eV, no resonance absorption can occur under the

¹ summary of constants:

$$c = 2.997925 \cdot 10^8 \text{ [m/s]}$$

$$k = 1.3804 \cdot 10^{-26} \text{ [J} \cdot \text{K}^{-1}\text{]}$$

$$h = 6.6256 \cdot 10^{-34} \text{ [J} \cdot \text{s]}$$

$$\hbar = h/2\pi = 1.0545 \cdot 10^{-34} \text{ [J} \cdot \text{s]}$$

$$N = 6.02252 \cdot 10^{26} \text{ [molecules/kg-mol]}$$

$$M = \text{Mass of } ^{57}\text{Fe} = 57/N \text{ [kg]}$$

$$1\text{eV} = \text{Energy of wave with } \tilde{\nu} = 8068 \text{ cm}^{-1}$$

$$\text{where } \tilde{\nu} = 1/\lambda = \nu/c$$

$$= h \cdot \nu = h \cdot \tilde{\nu} \cdot c = 1.602551 \cdot 10^{-19} \text{ [J]}$$

above assumed conditions.

As a consequence of thermal motion, the atoms of the absorber and the source approach and move away from each other, and the frequency (energy) of the γ -quanta change as a result of the nuclear Doppler-effect. Let v_x be the velocity of the emitting nucleus in the direction of the emission, E_0 the excitation energy of the nucleus and E_γ the energy of the γ -ray. Then, because of conservation of energy:

$$E_0 + (M \cdot v_x^2)/2 = E_\gamma + (M \cdot (v_x + v)^2)/2$$

and $E_0 - E_\gamma = \Delta E = (M \cdot v^2)/2 + M \cdot v \cdot v_x$

where the recoil velocity $v = E_\gamma / (M \cdot c)$

thus: $\Delta E = E_\gamma^2 / (2 \cdot M \cdot c^2) - E_\gamma \cdot v_x / c$.

Depending on v_x , ΔE may become zero and if such a γ -ray then hits an absorbing nucleus which is moving such that ΔE also equals zero then resonance absorption may occur. However the probability is very low, because for ^{57}Fe , v_x would have to be ≈ 163 m/s to compensate for the total energy difference of $3.8 \cdot 10^{-3}$ eV. The velocity due to thermal vibration can be approximated by the velocity v_t with the maximum probability in the isotropic Maxwell velocity distribution:

$$v_x = v_t = \left[\frac{2 \cdot k \cdot T}{M} \right]^{1/2}$$

For ^{57}Fe at room temperature this is ≈ 9.3 m/s.

In a crystalline lattice the recoil energy is not

absorbed by the emitting nucleus but can be transmitted as lattice vibration to the whole crystal. In a classical interpretation, the proportion of γ -rays that are recoil free is: (e.g. Vértes et al., 1979, p 19)

$$f = e^{-\langle x^2 \rangle / \lambda^2}$$

where $\langle x \rangle$ is the mean amplitude of the lattice vibration. This proportion approaches unity, if the amplitude of the lattice vibration is small relative to the wave length λ of the γ radiation. The amplitude of the lattice vibration decreases with decreasing temperature and increasing bond interactions. The factor f is called the Debye-Waller factor and its exact calculation is only possible using quantum mechanics. (see e.g. Gonser (1975)).

A Mössbauer spectrum is obtained by moving the source relative to the absorber at a speed up to some cm/s and measuring the absorption as a function of relative speed. The energy of the γ rays will change according to the Doppler relation $E_D = E_\gamma - E_\gamma \cdot v/c$. For $E_\gamma \approx 14.4$ keV and assuming that we can correlate absorption events with speed intervals on the order of 0.05 mm/s we can detect energy differences between different nuclei or between different energy levels of a nucleus on the order of 10^{-9} eV. To facilitate the interpretation of the results, some frequently used terms are explained below:

Line width Γ

The natural linewidth Γ_τ of a γ -ray with the energy E_γ can

be calculated on the basis of the Heisenberg uncertainty principle. ($\Delta t \cdot \Delta E \approx \hbar$, where $\Delta t = \tau$ = lifetime of the excited state.) Assuming that the linewidth at low temperatures for emission and absorption is the natural linewidth, this relation can be used to measure the lifetime of the excited state. (Mössbauer (1958b)). The measurable linewidth at room temperature is usually considerably greater than Γ_τ , due to thermal motion and finite sample thickness. In addition, any vibration in the experimental set-up (vacuum pump, air conditioning etc.) will contribute to line broadening. Therefore, to obtain an optimal spectrum the source, the absorber and the detector must be suspended carefully.

Isomer shift δ

According to the theory of quantum mechanics the electrons, especially from the s-orbitals, have a non-zero density inside the nucleus, and interact with the nuclear charge. This interaction influences the energy levels of the nucleus, and if source and absorber have different chemical environments, their excitation energies will also be different. This energy difference (= isomer shift) is of the order 10^{-8} to 10^{-6} eV and can be compensated using the Doppler effect by moving the source relative to the absorber at a speed of some mm/s. The isomer shift is not generally given in units of energy in the literature, but as a velocity [mm/s] and not as an absolute shift, but relative to a standard. (e.g. iron foil at room temperature).

Inseparable from the isomer shift is the temperature shift: When a γ -photon is emitted, the mass of the nucleus is decreased by $\Delta m = h \cdot \nu / c^2$. At any temperature above 0 K this mass decrease influences the lattice vibration and therefore the phonon energy. This has exactly the same effect as if the recoil energy was not zero.

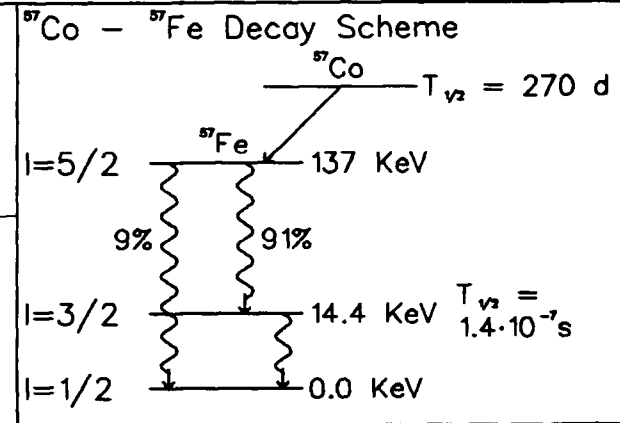
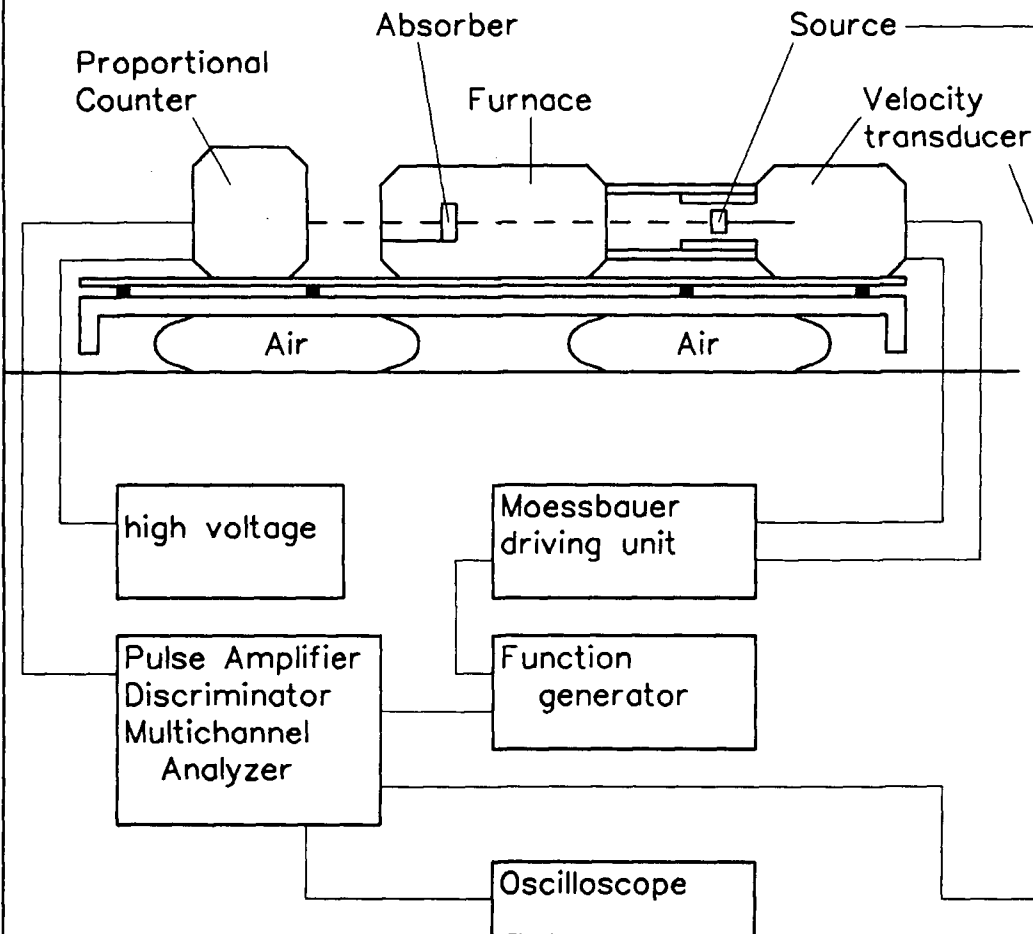
Quadrupole splitting ΔE_Q

If the electrons around a molecule are not spherically symmetric, they give rise to an electric field gradient at the site of the nucleus. The interaction with the quadrupole moment of the nucleus partially removes the degeneracy of the $(2I+1)$ possible states, resulting in a splitting of the energy levels. These differ from the mean energy by approximately 10^{-8} eV and can be measured in a Mössbauer spectrum.

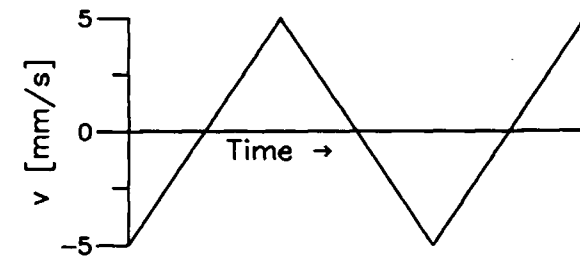
2.5.2 EXPERIMENTAL SET-UP

Figure 9 shows a schematic diagram of the Mössbauer apparatus used in the present investigation. The furnace is described in more detail in Appendix C. The source is ^{57}Co in a rhodium matrix. ^{57}Co decays to the excited state of ^{57}Fe with $T_{1/2}$ of 270 days. The sample was mixed with graphite (which shows little absorption of the γ -rays) to obtain an optimal concentration of approximately 7 mg iron/cm² and placed between two graphite or boron nitride discs in the sample holder. It was found by several authors (Eibschütz

Fig. 9: Schematic Set-up of the Moessbauer Apparatus



Velocity of Source versus Time



and Ganiel (1967), Bush et al. (1970)) that the M_1 and M_2 sites in olivine cannot be resolved in a Mössbauer spectrum recorded at room temperature, but that by heating the absorber to 300-400 °C the spectra corresponding to the two sites were well separated, although the linewidth Γ did increase.

The observed effect at elevated temperatures is a generally increased difference of the quadrupole splitting between M_1 and M_2 . Eibschütz and Ganiel (1967) explain that this is because at low temperatures only the inner electrons contribute significantly to the quadrupole splitting. These inner shells are nearly identical for the M_1 and M_2 sites. The symmetry difference ($\bar{I}$ for M_1 and m for M_2) becomes noticable in a Mössbauer spectrum only above ≈ 100 °C.

The absorber temperature was kept constant at around 300 ± 1 °C. The spectra were accumulated for two to three days, until two absorption peaks at high velocity could be easily resolved by eye. The spectra were recorded with a multichannel analyzer with 512 channels in multi-scanning mode. The mechanical vibrator for the source was driven in a constant acceleration mode with a triangular velocity waveform. (See Fig. 9).

2.5.3 EVALUATION OF THE MÖSSBAUER SPECTROSCOPY MEASUREMENTS

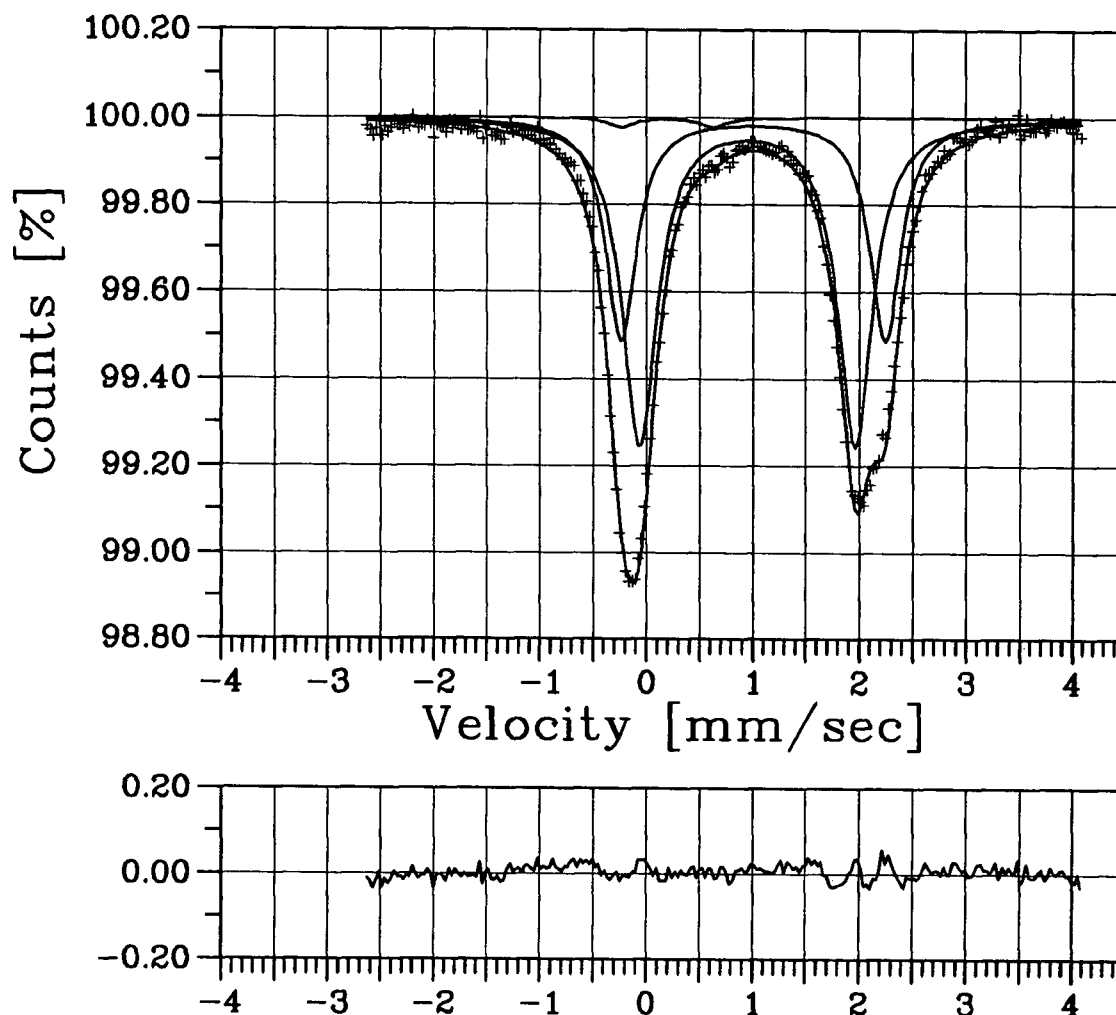
The data collected in the multichannel analyzer were transferred to a computer-readable disk for further analysis. The conversion from channel number to velocity was calibrated with Fe-foil with known line positions. (-5.3089, -3.0771, -0.8404, 0.8403, 3.0772 and 5.3150 [mm/sec]). The spectra were then fitted with a linear combination of Lorentzian curves. The number of counts corresponding to the velocity v can be expressed as:

$$N(v) = N(\infty) + \sum_{i=1}^n \frac{A_i}{1 + \left[\frac{v - v_i^0}{\Gamma_i/2} \right]^2}$$

where $N(\infty)$ is the height of the baseline, and A_i , v_i^0 and Γ_i are the amplitude, position and half width of the i^{th} line respectively. All calculations were performed with a computer program written by R.J. Pollard utilizing subroutines from the CERN library. This is a general purpose fitting program using first a nonlinear simplex approach and then refining the result with a gradient method. All spectra were fitted with three quadrupole doublets. In some cases a successful convergence could only be achieved by constraining the position or the linewidth of the small Fe^{+3} doublet, resulting in an increased uncertainty for these measurements. The assignment of the two main doublets to the M_1 and M_2 sites was made according to Annersten et al. (1982), Shinno (1981) and Finger and Virgo (1971). The

interpretation of Annersten et al. (1984), where the low velocity peaks are crossed over for the Fe-Mn olivines gave a less satisfactory fit for our data. It should be noted however, that this crossover makes no significant change in the area ratios for the M_1 and M_2 sites. The Fe^{+3} doublet is discussed by Shinno (1981). Heating several samples in air, he showed that the Fe^{+2} populations of M_2 decreased with increasing Fe^{+3} content, leaving M_1 unchanged within the error limits. We may therefore assign as a good approximation all Fe^{+3} to M_2 . This assumption is also supported by the measurement of pure fayalite (Table 7), and the consistent K_D values despite the Fe^{3+} variation (Table 16). Fig. 10 and 11 show two examples of Mössbauer spectra. The first (Fig. 10) converged easily, resulting in an uncertainty for the relative occupancies of $\approx 2\%$. The second (Fig. 11), because of the low Fe content and the strong preference of Fe to occupy the M_1 site, is more difficult to interpret. The uncertainty in this case is $\approx 5\%$. The results of the Mössbauer measurements are summarized in Tables 7 and 8.

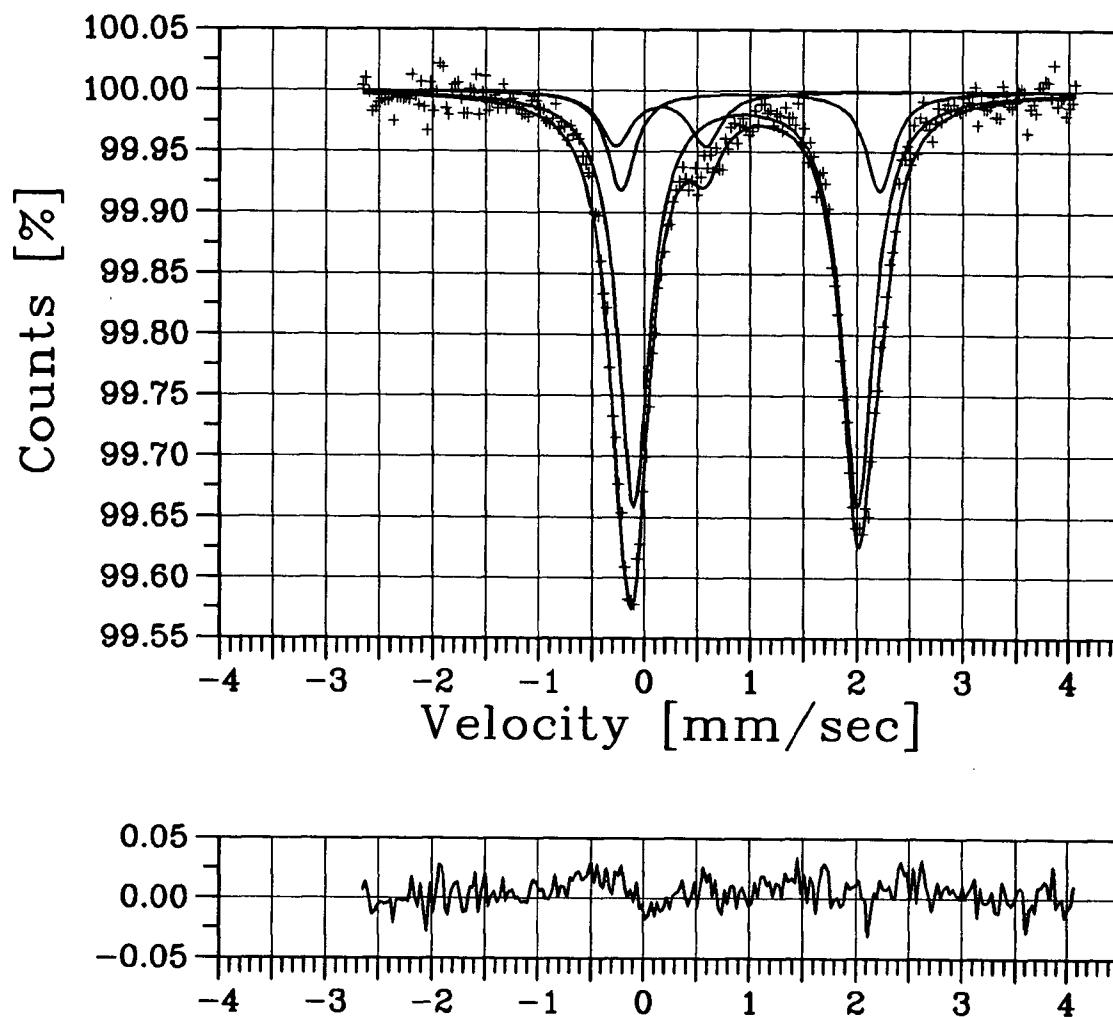
Fig. 10: Moessbauer spectrum for
fay 6 teph 4 fo 2 + C, at 298 °C



$$B_0 = 42247000$$

	ΔE_q	δ	Γ	A_i	%
$\text{Fe}^{2+}(\text{M}_1)$	2.0282	0.94914	0.39000	1.50140	61.30
$\text{Fe}^{2+}(\text{M}_2)$	2.4836	1.00460	0.34887	1.02130	37.30
Fe^{3+}	0.8607	0.19385	0.30793	0.04319	1.39

Fig. 11: Moessbauer spectrum for
fay 2 teph 10 + C, at 301 °C



$$B_0 = 51755000$$

	ΔE_0	δ	Γ	A_1	%
$\text{Fe}^{2+}(\text{M}_1)$	2.1096	0.95486	0.36366	0.67922	74.56
$\text{Fe}^{2+}(\text{M}_2)$	2.4389	0.99917	0.32011	0.16369	15.82
Fe^{3+}	0.8475	0.15366	0.36017	0.08846	9.62

Table 7.: Isomer shift (δ), Quadrupole splitting (ΔE_Q) and the full width at half height (Γ) for the synthetic Fe-Mn-Mg olivines. All units are in mm/sec.

NR.	$\delta \text{Fe}^{2+}_{M1}$	$\Delta E_Q \text{Fe}^{2+}_{M1}$	$\Gamma \text{Fe}^{2+}_{M1}$	$\delta \text{Fe}^{2+}_{M2}$	$\Delta E_Q \text{Fe}^{2+}_{M2}$	$\Gamma \text{Fe}^{2+}_{M2}$	δFe^{3+}	$\Delta E_Q \text{Fe}^{3+}$	ΓFe^{3+}
1:120000	0.9402	2.0096	0.3125	1.0006	2.4753	0.2946	0.0953	0.8001	0.2905
4:080400	0.9508	1.9880	0.3702	1.0010	2.4682	0.3333	0.1988	0.7697	0.2503
5:050700	0.9360	2.0201	0.3441	0.9935	2.4138	0.2944	0.1395	0.7501	0.2702
6:040800	0.9508	2.0477	0.3759	0.9946	2.4309	0.3184	0.2000	0.8605	0.2503
7:030900	0.9600	2.0866	0.4047	0.9921	2.4524	0.3318	0.1087	0.7507	0.2519
8:021000	0.9549	2.1096	0.3637	0.9992	2.4389	0.3201	0.1537	0.8475	0.3602
11:100002	0.9407	2.0189	0.3148	0.9942	2.4732	0.2855	0.2067	0.8041	0.2011
12:080202	0.9442	1.9971	0.3498	1.0051	2.4648	0.3180	0.1001	0.7502	0.3717
13:060402	0.9491	2.0282	0.3900	1.0046	2.4836	0.3489	0.1939	0.8607	0.3079
14:040602	0.9465	2.0304	0.3800	0.9994	2.4626	0.3297	0.1004	0.7502	0.4989
15:020802	0.9302	2.0827	0.3567	0.9828	2.4283	0.2908	0.1430	0.7525	0.3060
17:080004	0.9446	2.0761	0.3499	0.9977	2.4890	0.3212	0.1197	0.8644	0.4082
18:060204	0.9294	2.0246	0.3499	1.0017	2.4563	0.3177	0.1237	0.8968	0.4218
19:040404	0.9410	2.0410	0.3800	0.9985	2.4637	0.3235	0.1990	0.7846	0.4742
20:020604	0.9543	2.1039	0.4060	1.0313	2.5357	0.3552	0.1111	0.8509	0.4741
22:060006	0.9279	2.0998	0.3190	0.9853	2.5025	0.2814	0.2999	0.8659	0.7055
23:040206	0.9368	2.0809	0.3500	0.9978	2.4854	0.3171	0.1044	0.7510	0.4974
24:020406	0.9337	2.1347	0.3599	0.9916	2.5091	0.3293	0.1096	0.7521	0.3103
26:040006	0.9206	2.1803	0.3308	0.9901	2.5203	0.2719	0.2334	0.8852	0.7993
27:020208	0.9422	2.1067	0.3600	0.9913	2.4926	0.3205	0.1094	0.7500	0.3822

The uncertainties in the Mössbauer parameters for the Fe^{2+} are: $\delta = \pm 0.02$ mm/s, $\Delta E_Q = \pm 0.03$ mm/s and $\Gamma = \pm 0.04$ mm/s. For The Fe^{3+} the errors are ± 0.04 , ± 0.06 and ± 0.08 mm/s respectively.

Table 8.: Mössbauer area ratios and Fe-occupancies for the synthetic Fe-Mn-Mg olivines.

NR.	Area ratios in %			Relative occupancies in %			Absolute occupancies		
	Fe ²⁺ M1	Fe ²⁺ M2	Fe ³⁺	Fe ²⁺ M1	Fe ²⁺ M2	Fe ³⁺	x(Fe ²⁺) M1	x(Fe ²⁺) M2	x(Fe ³⁺)
1:120000	49.19	48.88	1.92	50.05	48.24	1.71	0.9950	0.9590	0.0340
4:080400	60.77	33.24	5.99	61.85	32.82	5.33	0.8198	0.4350	0.0706
5:050700	65.84	28.33	5.83	66.89	27.92	5.20	0.5541	0.2312	0.0431
6:040800	68.41	26.72	4.87	69.38	26.29	4.34	0.4593	0.1740	0.0287
7:030900	71.17	27.20	1.63	71.90	26.66	1.44	0.3573	0.1325	0.0072
8:021000	74.56	15.82	9.62	75.80	15.60	8.61	0.2512	0.0517	0.0285
11:100002	51.54	46.08	2.38	52.42	45.46	2.12	0.8684	0.7531	0.0351
12:080202	54.23	36.66	9.11	55.47	36.38	8.15	0.7351	0.4821	0.1080
13:060402	61.30	37.30	1.39	62.11	36.66	1.23	0.6174	0.3644	0.0122
14:040602	63.53	29.83	6.64	64.64	29.44	5.92	0.4283	0.1951	0.0392
15:020802	70.03	29.15	0.82	70.72	28.55	0.73	0.2344	0.0946	0.0024
17:080004	51.82	44.78	3.40	52.76	44.22	3.02	0.6993	0.5861	0.0400
18:060204	55.74	41.52	2.74	56.64	40.93	2.43	0.5630	0.4068	0.0242
19:040404	60.63	33.21	6.17	61.71	32.79	5.50	0.4089	0.2173	0.0364
20:020604	66.99	24.83	8.18	68.18	24.52	7.31	0.2259	0.0813	0.0242
22:060006	50.56	41.02	8.42	51.75	40.72	7.53	0.5144	0.4048	0.0748
23:040206	59.29	39.01	1.70	60.12	38.37	1.50	0.3984	0.2542	0.0100
24:020406	65.37	33.07	1.56	66.15	32.46	1.38	0.2192	0.1076	0.0046
26:040008	52.89	35.78	11.32	54.25	35.60	10.15	0.3594	0.2359	0.0673
27:020208	57.70	40.25	2.05	58.56	39.63	1.82	0.1941	0.1313	0.0060

For the conversion from area ratios to relative occupancies the constants are $C_1 = 0.97$ and $C_2 = 1.13$.

The relation between site populations and area ratios can be written as:

$$x_{M1}^{Fe2+} / x_{M2}^{Fe2+} = \frac{1}{C_1} \cdot A_{M1}^{Fe2+} / A_{M2}^{Fe2+} = Y_1$$

$$x_{total}^{Fe3+} / x_{total}^{Fe2+} = \frac{1}{C_2} \cdot A_{total}^{Fe3+} / A_{total}^{Fe2+} = Y_2$$

where A is an absorption peak area and x the Fe site population on M₁ or M₂. (Bancroft and Brown (1975)). The constants C₁ and C₂ are related to the ratios of the linewidths, the fractions of recoil free absorption and a saturation correction.

The site populations are then calculated as:

$$x^{Fe3+} = \frac{Y_2}{1 + Y_2}$$

$$x_{M1}^{Fe2+} = \frac{Y_1}{1 + Y_1} \cdot \left[1 - \frac{Y_2}{1 + Y_2} \right]$$

$$x_{M2}^{Fe2+} = \frac{1}{Y_1 + 1} \cdot \left[1 - \frac{Y_2}{1 + Y_2} \right]$$

We will use c₁ = 0.97. This is consistent with the value obtained by Annersten et al.(1984) (They used a slightly different formulation equivalent to C₁ = 0.98) and the measurement of fayalite (Fa - 1) of Shinno (1981). The correction is smaller than the expected uncertainty, but is included in order to avoid systematic errors as much as possible. C₂ is set according to the chemical analyses of

Shinno (1981) to 1.13. Because of the small Fe^{3+} concentrations and the relatively large uncertainties, the value of C_2 is irrelevant.

2.5.4 DISCUSSION OF THE RESULTS

Our synthetic olivines contain between 1% and 10% of the total iron as Fe^{3+} . Compared with natural olivines this fact is not surprising, as many chemical analyses (e.g. those reviewed by Deer, Howie and Zussmann (1972)) show appreciable amounts of Fe^{3+} . In connection with Mössbauer data, however, Fe^{3+} was not reported until 1981 (Shinno, 1981). This is probably due to the fact that the samples for Mössbauer analysis are often carefully selected, extremely pure phases where Fe^{3+} was systematically excluded. In synthetic olivines Fe^{3+} has not been reported before, probably because most syntheses are done at 1000 to 1400 °C with extremely low O_2 fugacities. (Shinno (1981), Annersten et al. (1984)).

2.6 CALCULATION OF INTEGRATED X-RAY INTENSITIES

Most equations and data to calculate integrated intensities can be found in the INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY, 1974 (abbreviated I.T.) The following outline is mainly influenced by Yvon et al.(1977) and Borg and Smith (1969).

2.6.1 THE DATA NEEDED FOR THE CALCULATIONS

Space group specific data

For a site $\bar{s} = (x/a, y/b, z/c) = (x', y', z')$ the equivalent positions $\bar{p}_i$ are defined by the symmetry operations for the space group:

$$\bar{p}_i = \bar{a}_i + ||T_i|| \cdot \bar{s}^T \quad i=1,2,3\dots N^{eq}$$

Where N^{eq} is the number of symmetry operations.

For $Pbnm$ the equivalent positions are: (I.T. I/151)

$$\bar{p}_1 = (0, 0, 0) + \left| \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right| \cdot \left| \begin{array}{c} x' \\ y' \\ z' \end{array} \right|$$

$$\bar{p}_2 = (1/2, 1/2, 1/2) + \left| \begin{array}{ccc} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{array} \right| \cdot \left| \begin{array}{c} x' \\ y' \\ z' \end{array} \right|$$

$$\bar{p}_3 = (0, 0, 1/2) + \left| \begin{array}{ccc} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{array} \right| \cdot \left| \begin{array}{c} x' \\ y' \\ z' \end{array} \right|$$

$$\bar{p}_4 = (1/2, 1/2, 0) + \left| \begin{array}{ccc} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{array} \right| \cdot \left| \begin{array}{c} x' \\ y' \\ z' \end{array} \right|$$

Because $Pbnm$ has a symmetry centre at the origin there are

at most 8 equivalent positions:

$\bar{p}_1, \bar{p}_2, \bar{p}_3, \bar{p}_4, -\bar{p}_1, -\bar{p}_2, -\bar{p}_3$ and $-\bar{p}_4$.

For certain sites these may not all be different if taken modulo 1. We therefore define a multiplicity factor for each site:

$$M^S = \frac{\text{number of non-identical } \bar{p}_i \text{ modulo } 1}{N^{eq}}$$

The conditions for non-extinction are also given in I.T.

I/151. For *Pbnm* they are:

$$h0l : h+l = 2n \text{ and } 0kl : k = 2n$$

Element specific data

The scattering factors f_m^0 for the atom (or ion) *m* is approximated with the analytical function:

$$f_m^0 = \left[\sum_{i=1}^4 a_i \cdot e^{-b_i \left(\frac{\sin^2 \theta}{\lambda^2} \right)} \right] + c$$

The coefficients a_i , b_i and c for each element are listed in I.T. IV/Table 2.2B. For O^{2-} they were taken from Tokonami (1965). The correction for anomalous dispersion is made by adding a real and an imaginary dispersion correction term:

$$f_m = f_m^0 + \Delta f'_m + i \cdot \Delta f''_m$$

(I.T. IV/Table 2.3.1.) They are dependent on the wavelength λ but assumed to be independent of θ .

The Lorentz-Polarisation factor (LP)

For a diffractometer powder pattern the Lorentz-Polarisation factor is (I.T. II/314):

$$(LP) = \frac{1 + \cos^2(2\theta)}{\sin\theta \cdot \sin(2\theta)}$$

Information about the individual crystal

Besides the lattice parameters a , b , c , α , β and γ we have to know for each site the atom coordinates, the occupancy factors for each element and the temperature correction factors. The numerical assumptions about these parameters is discussed in detail in chapter 2.7.

- The temperature correction factor (or Debye-Waller factor) B for a given site can either be assumed constant ($= B^{eq}$ = isotropic equivalent of the temperature correction factor) or is:

$$B = b_{11} \cdot h^2 + b_{22} \cdot k^2 + b_{33} \cdot l^2 + b_{12} \cdot h \cdot k + b_{13} \cdot h \cdot l + b_{23} \cdot k \cdot l$$

(= anisotropic temperature correction). In a structure refinement the b_{ij} are usually so-called fit parameters which should not be stressed for a strong physical interpretation. The difference in the calculated intensities using one or the other (if both are given) is too small to be important for our calculations. We will therefor use B^{eq} .

2.6.2 EQUATIONS

Summary of symbols

$a, b, c, \alpha, \beta, \gamma$: Lattice parameters

λ : Wavelength of primary X-ray

Θ : Glancing angle of reflection (hkl)

F_{hkl} : Structure factor for reflection (hkl)

M : Number of different elements in the structure

$I(m)$: Number of different sites an element m may occupy

$J(i)$: Number of equivalent positions in unit cell for site i

f_m^0 : Scattering factor for Element m . (a function of $\sin\Theta/\lambda$)

$\Delta f_m'$: real correction term for anomalous dispersion

$\Delta f_m''$: imaginary correction term for anomalous dispersion

M_i^S : Multiplicity of site i

O_{mi} : Occupancy factor for element m on site i

B_i : Temperature correction factor for site i

$x_{mij}, y_{mij}, z_{mij}$: Atom coordinates in Å for element m on j^{th} equivalent position of site i

M^P : Multiplicity of reflection (hkl)

LP: Lorentz-Polarization factor for angle Θ

The calculation of Θ for all reflections (hkl)

$$\sin^2\Theta = \frac{\lambda^2}{4 \cdot v^2} \left[(h \cdot b \cdot c \cdot \sin\alpha)^2 + (k \cdot a \cdot c \cdot \sin\beta)^2 + (l \cdot a \cdot b \cdot \sin\gamma)^2 \right. \\ + 2 \cdot k \cdot l \cdot a^2 \cdot b \cdot c \cdot (\cos\beta \cdot \cos\gamma - \cos\alpha) \\ + 2 \cdot h \cdot l \cdot a \cdot b^2 \cdot c \cdot (\cos\gamma \cdot \cos\alpha - \cos\beta) \\ \left. + 2 \cdot h \cdot l \cdot a \cdot b \cdot c^2 \cdot (\cos\alpha \cdot \cos\beta - \cos\gamma) \right]$$

Where v is the volume of the unit cell:

$$v = 2 \cdot a \cdot b \cdot c \sqrt{\sin \frac{\alpha + \beta + \gamma}{2} \cdot \sin \frac{-\alpha + \beta + \gamma}{2} \cdot \sin \frac{\alpha - \beta + \gamma}{2} \cdot \sin \frac{\alpha + \beta - \gamma}{2}}$$

For an upper 2θ limit ($2\theta^{\max}$) the maximal values for $|h|$, $|k|$ and $|l|$ are:

$$|h|^{\max} = \text{biggest integer} < \frac{\sin(2\theta^{\max}) \cdot 2 \cdot v}{\lambda \cdot b \cdot c \cdot \sin \alpha}$$

$$|k|^{\max} = \text{biggest integer} < \frac{\sin(2\theta^{\max}) \cdot 2 \cdot v}{\lambda \cdot a \cdot c \cdot \sin \beta}$$

$$|l|^{\max} = \text{biggest integer} < \frac{\sin(2\theta^{\max}) \cdot 2 \cdot v}{\lambda \cdot a \cdot b \cdot \sin \gamma}$$

We can now combine all possible h , k and l and check whether they fulfill the conditions for non-extinction and whether there are identical reflections due to the symmetry of the crystal system.

By convention a powder line is labeled with the highest index (ordered with respect to h , k and l) and the number of identical reflections is called the multiplicity of that powder line M^P .

In the orthorhombic system e.g.:

$$(0 \ 2 \ 0) = (0 \ \bar{2} \ 0) \quad M^P = 2$$

$$\text{and } (1 \ 3 \ 1) = (\bar{1} \ 3 \ 1) = (1 \ \bar{3} \ 1) = (1 \ 3 \ \bar{1})$$

$$= (\bar{1} \ 3 \ \bar{1}) = (\bar{1} \ \bar{3} \ 1) = (1 \ \bar{3} \ \bar{1}) = (\bar{1} \ \bar{3} \ \bar{1}) \quad M^P = 8$$

The structure factor and the integrated intensity

One possible way of calculating the structure factor is given below. m is used as an index for the elements, i for the sites these elements can occupy and j for their equivalent positions.

$$F_{hkl} = \sum_{m=1}^M \left[\left[(f_m^0 + \Delta f_m') + i \cdot \Delta f_m'' \right] \cdot \sum_{i=1}^{I(m)} \left[M_i^S \cdot O_{mi} \cdot e^{-B_i \frac{\sin^2 \theta}{\lambda^2}} \cdot \sum_{j=1}^{J(i)} [\cos(2\pi(h \cdot x_{mij} + k \cdot y_{mij} + l \cdot z_{mij})) + i \cdot \sin(2\pi(h \cdot x_{mij} + k \cdot y_{mij} + l \cdot z_{mij}))] \right] \right]$$

Collecting the real and imaginary terms separately:

$$S_m^R = \sum_{i=1}^{I(m)} \left[\sum_{j=1}^{J(i)} \left[M_i^S \cdot O_{mi} \cdot e^{-B_i \frac{\sin^2 \theta}{\lambda^2}} \cdot \cos(2\pi(h \cdot x_{mij} + k \cdot y_{mij} + l \cdot z_{mij})) \right] \right]$$

$$S_m^I = \sum_{i=1}^{I(m)} \left[\sum_{j=1}^{J(i)} \left[M_i^S \cdot O_{mi} \cdot e^{-B_i \frac{\sin^2 \theta}{\lambda^2}} \cdot \sin(2\pi(h \cdot x_{mij} + k \cdot y_{mij} + l \cdot z_{mij})) \right] \right]$$

$$f_m^R = f_m^0 + \Delta f_m'$$

$$f_m^I = \Delta f_m''$$

Then:

$$F_{hkl} = \sum_{m=1}^M \left[(f_m^R + i \cdot f_m^I) \cdot (S_m^R + i \cdot S_m^I) \right]$$

and

$$|F_{hkl}|^2 = \left[\sum_{m=1}^M (S_m^R \cdot f_m^R) - \sum_{m=1}^M (S_m^I \cdot f_m^I) \right]^2 + \left[\sum_{m=1}^M (S_m^I \cdot f_m^R) + \sum_{m=1}^M (S_m^R \cdot f_m^I) \right]^2$$

The integrated intensity of a powder line is defined as:

$$I_{hkl} = M^P \cdot (LP) \cdot |F_{hkl}|^2$$

This is called the absolute intensity (Hubbard et al.

(1975)). All factors that are constant for a given

diffractometer or structure are not included. The example in appendix D is for a disordered Olivine of the composition

$\text{Fe}_{0.3333}\text{Mn}_{0.6667}\text{MgSiO}_4$.

2.7 THE DETERMINATION OF MN-MG OR FE-MG SITE OCCUPANCIES BY XRD ANALYSIS

2.7.1 INTRODUCTION

If we know the structure, the lattice parameters, the positional parameters and the scattering factors for each site, we can calculate all integrated intensities as outlined in chapter 2.6. Because the scattering factor for a site occupied by Mn (or Fe) differs strongly from one occupied by Mg, the distribution of Mn (or Fe) and Mg on M1 and M2 has a noticable influence on the resulting intensities. In order to use this dependency for the determination of site occupancies, all other parameters should ideally be known. The method presented here is based on the fact that the structure and the bulk composition is known, the lattice parameters can be measured by X-ray diffraction and that the positional parameters can be approximated with a sufficient accuracy from published single crystal structure refinements. The main task in developing the method is to determine the uncertainty in the interpretation due to the use of approximate positional parameters and an unknown effective charge distribution. It was found that for each olivine at least four intensity ratios could be used for the occupancy determination. These ratios show a reasonable dependency on ordering, but remain practically independent of small errors in the positional parameters and of charge distribution. The most important

ratios are (112)/(130) and (112)/(131), which proved useful for almost all synthetic olivines. The estimated uncertainty of the method is $\pm 3\%$ for the occupancy on each site.

2.7.2 THE MEASUREMENT OF LATTICE PARAMETERS

One set of data needed to calculate integrated intensities are the lattice parameters a_0 , b_0 and c_0 . These can easily be measured from an X-ray powder diffraction profile. The internal standard was natural quartz, which in turn was standardized against Si metal. The parameters obtained for quartz are

$$a_0 = 4.9135 \pm 0.0002$$

$$c_0 = 5.4059 \pm 0.0003$$

which is in excellent agreement with the values in the ASTM-file.

The programs used for fitting were JOB9214 from the U.S. Geological Survey (Evans et al. (1963)) and the non-linear programming monitor (NLP) of the UBC computing centre. In Table 9 all measured lattice parameters are listed. Figures 12 to 15 are an attempt to visualize the ternary compositional variation of a_0 , b_0 , c_0 and volume. Each diagram has one independent compositional variable and isolines for the other two. The lines were calculated from a polynomial function fitted to the data. (See appendix F.) Although the lattice parameters for Mn-olivines show a distinct non linear dependence on the composition, the volumes are almost a linear combination of the endmember

Table 9.: The lattice parameters for the synthetic
Fe-Mn-Mg olivines

Nr.	X_{Fe}	X_{Mn}	X_{Mg}	$a_0[\text{\AA}]$	$b_0[\text{\AA}]$	$c_0[\text{\AA}]$	$\text{vol}[\text{\AA}^3]$
1	0.9940	0.0060	0.0000	4.8198	10.4839	6.0919	307.8255
4	0.6627	0.3373	0.0000	4.8420	10.5574	6.1443	314.0900
5	0.4142	0.5858	0.0000	4.8640	10.5883	6.1799	318.2741
6	0.3313	0.6687	0.0000	4.8688	10.5964	6.1944	319.5800
7	0.2485	0.7515	0.0000	4.8780	10.6051	6.2094	321.2227
8	0.1657	0.8343	0.0000	4.8890	10.6085	6.2285	323.0409
9	0.0828	0.9172	0.0000	4.8959	10.6071	6.2460	324.3629
9	0.0828	0.9172	0.0000	4.8982	10.6139	6.2486	324.8585
10	0.0000	1.0000	0.0000	4.9033	10.6030	6.2579	325.3463
10	0.0000	1.0000	0.0000	4.9030	10.6076	6.2619	325.6756
11	0.8283	0.0050	0.1667	4.8106	10.4409	6.0752	305.1390
12	0.6627	0.1707	0.1667	4.8219	10.4711	6.1001	307.9977
13	0.4970	0.3363	0.1667	4.8310	10.5045	6.1263	310.8928
14	0.3313	0.5020	0.1667	4.8428	10.5351	6.1606	314.3100
14	0.3313	0.5020	0.1667	4.8468	10.5400	6.1633	314.8539
15	0.1657	0.6676	0.1667	4.8560	10.5577	6.1875	317.2219
16	0.0000	0.8333	0.1667	4.8770	10.5683	6.2283	321.0165
17	0.6627	0.0040	0.3333	4.7998	10.3815	6.0539	301.6605
17	0.6627	0.0040	0.3333	4.7983	10.3830	6.0554	301.6846

Table continued on next page.

Table 9. (continued)

Nr.	X_{Fe}	X_{Mn}	X_{Mg}	$a_0[\text{\AA}]$	$b_0[\text{\AA}]$	$c_0[\text{\AA}]$	$\text{vol}[\text{\AA}^3]$
18	0.4970	0.1697	0.3333	4.8108	10.4218	6.0829	304.7894
19	0.3313	0.3353	0.3334	4.8171	10.4451	6.1047	307.1585
19	0.3313	0.3353	0.3334	4.8193	10.4492	6.1097	307.6712
20	0.1657	0.5010	0.3333	4.8292	10.4914	6.1473	311.4534
21	0.0000	0.6667	0.3333	4.8417	10.5155	6.1825	314.7690
22	0.4970	0.0030	0.5000	4.7914	10.3425	6.0387	299.2481
22	0.4970	0.0030	0.5000	4.7895	10.3425	6.0387	299.1294
23	0.3313	0.1687	0.5000	4.7962	10.3837	6.0710	302.3498
24	0.1657	0.3343	0.5000	4.8060	10.4184	6.0989	305.3770
25	0.0000	0.5000	0.5000	4.8133	10.4411	6.1255	307.8440
25	0.0000	0.5000	0.5000	4.8134	10.4441	6.1276	308.0444
26	0.3313	0.0020	0.6667	4.7759	10.2986	6.0235	296.2664
27	0.1657	0.1677	0.6666	4.7806	10.3311	6.0501	298.8075
28	0.0000	0.3333	0.6667	4.7857	10.3669	6.0750	301.3982
31	0.0000	0.0000	1.0000	4.7548	10.2004	5.9823	290.1467

Fig. 12: The cell parameter a_o of the Fe-Mn-Mg olivines

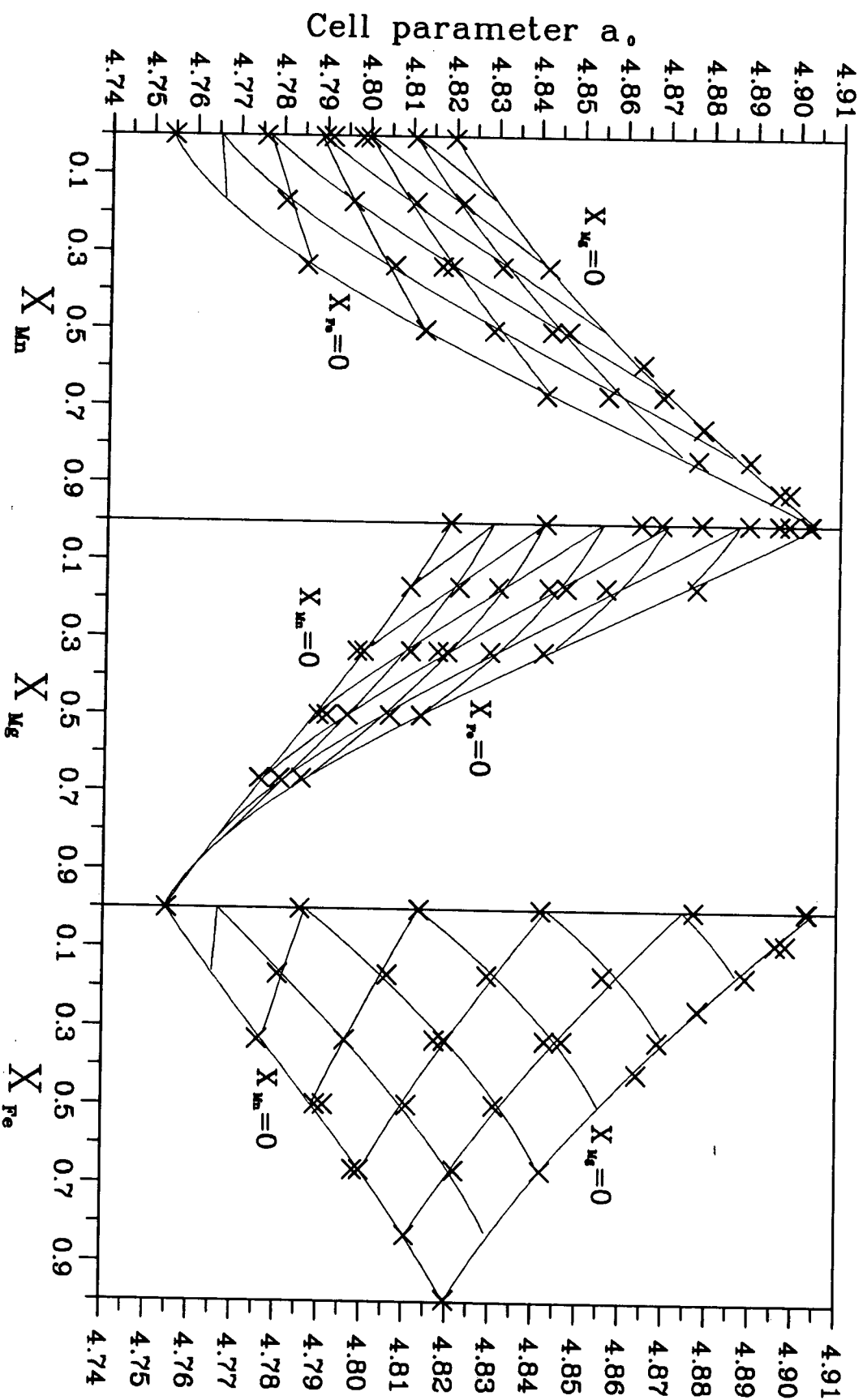


Fig. 13: The cell parameter b_0 of the Fe-Mn-Mg olivines

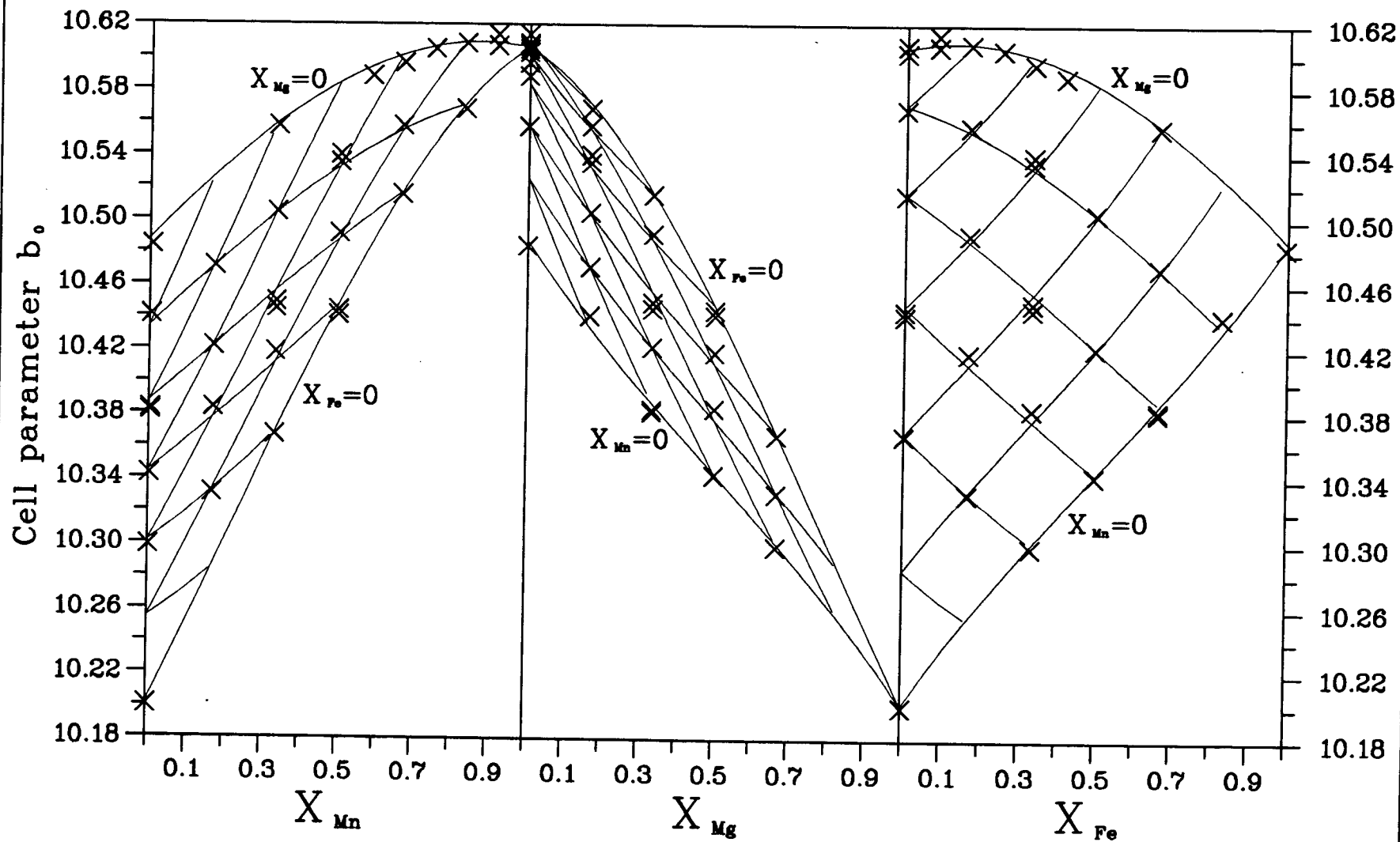


Fig. 14: The cell parameter c_0 of the Fe-Mn-Mg olivines

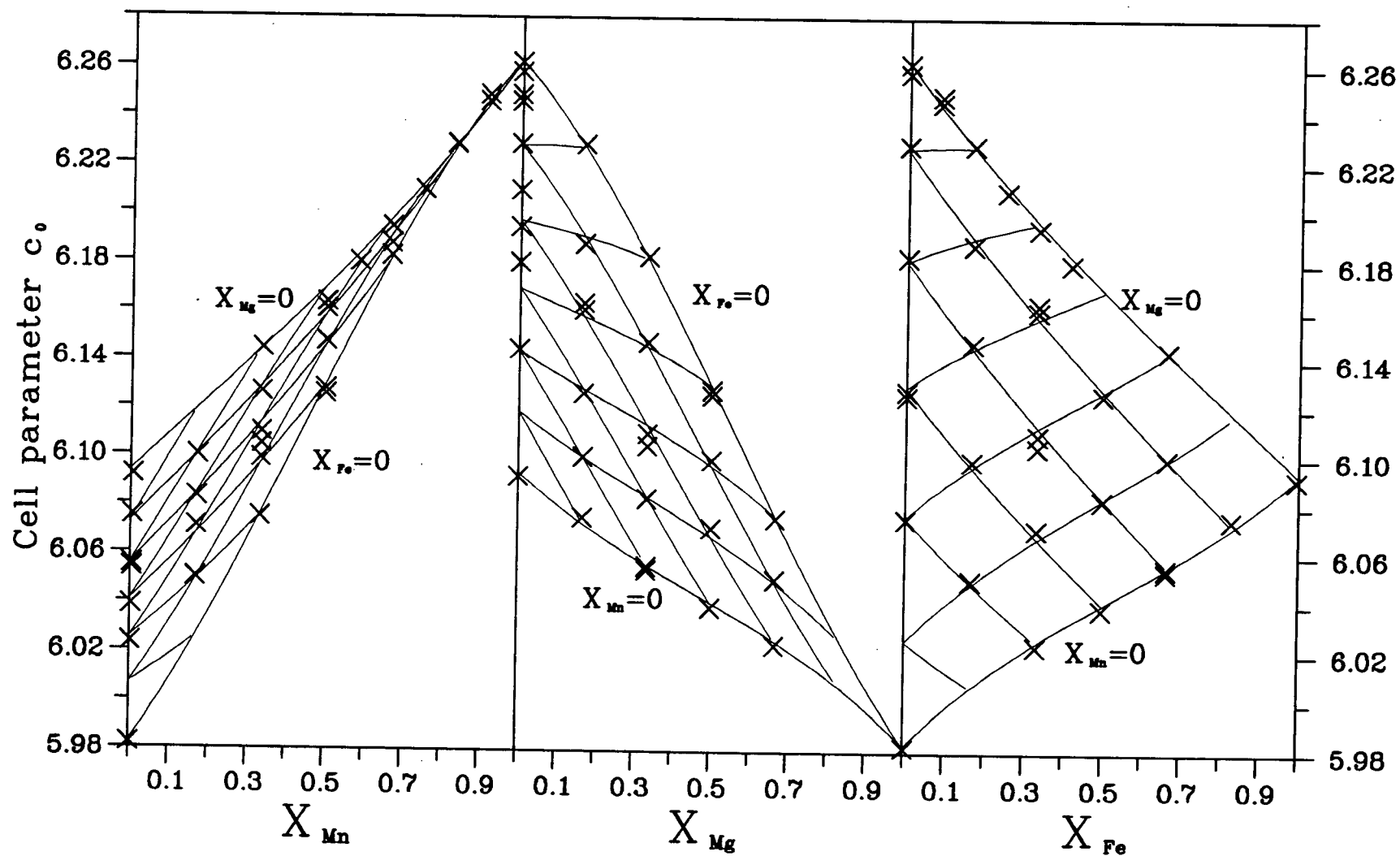
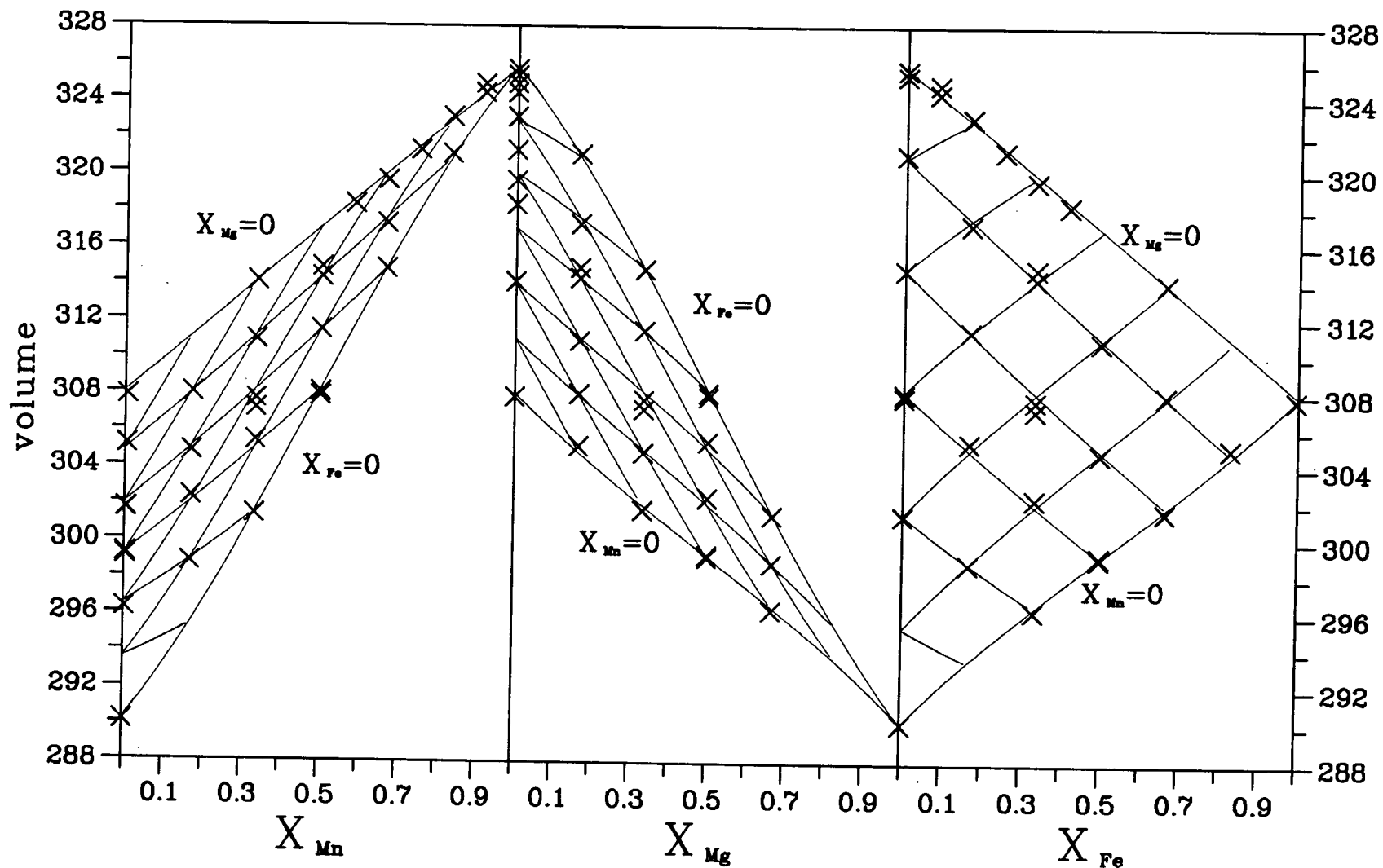


Fig. 15: The volume of the Fe-Mn-Mg olivines



volumes.

2.7.3 UNCERTAINTIES IN CALCULATED INTENSITIES DUE TO ATOM COORDINATES AND TEMPERATURE CORRECTION FACTORS

Variation of the positional parameters for Fe-Mn-Mg olivines is relatively small, as may be seen in table 10. (The literature data are tabulated in appendix F). The calculation of integrated intensities using an average value for each coordinate with an uncertainty of 0.02 - 0.05 Å, would yield intensities with uncertainties in the range of 15 - 70 %.

To avoid as much of this source of error as possible a multiple linear regression was fit to the published structure refinement data. The independent variables are the site occupancies $x_{\text{Fe}(M1)}$, $x_{\text{Mn}(M1)}$, $x_{\text{Fe}(M2)}$ and $x_{\text{Fe}(M1)}$. The result of this regression is tabulated in table 11.

To estimate the influence of each positional parameter on the resulting X-ray diffraction pattern, a primitive sensitivity analysis was performed. The estimated errors for the positional parameters were taken to be the maximal residuals from the multiple linear regression. This corresponds to $\approx 3\sigma$. Because most reported structure refinements are for compositions close to the binary joins, especially fayalite - forsterite, interpolation inside the ternary region is less certain than along the binaries. Changing one atom coordinate or one temperature correction factor at a time by the amount of the maximal residual and

Table 10.: The range of values for the positional parameters
and the temperature correction factors.

	<u>HCP</u>	<u>Range</u>	<u>var.</u>	<u>max.res.</u>
x_{M1}	0.0	0.0	0.0	0.0
y_{M1}	0.0	0.0	0.0	0.0
z_{M1}	0.0	0.0	0.0	0.0
x_{M2}	0.0	0.98510 - 0.99169	0.00659	0.0011
y_{M2}	0.25	0.27739 - 0.28030	0.00291	0.0002
z_{M2}	0.25	0.25	0.0	0.0
x_{Si}	0.375	0.42260 - 0.43122	0.00522	0.0013
y_{Si}	0.08333	0.09100 - 0.09765	0.00665	0.0002
z_{Si}	0.25	0.25	0.0	0.0
x_{O1}	0.75	0.75776 - 0.76870	0.01094	0.0003
y_{O1}	0.08333	0.08670 - 0.09363	0.00693	0.0012
z_{O1}	0.25	0.25	0.0	0.0
x_{O2}	0.25	0.20760 - 0.23010	0.02250	0.0008
y_{O2}	0.41667	0.44721 - 0.45510	0.00789	0.0012
z_{O2}	0.25	0.25	0.0	0.0
x_{O3}	0.25	0.27723 - 0.28897	0.01174	0.0004
y_{O3}	0.16667	0.15900 - 0.16563	0.00663	0.0011
z_{O3}	0.0	0.03304 - 0.04140	0.00836	0.0020

Table continued on next page.

Table 10. (continued)

	<u>Range</u>	<u>var.</u>	<u>max.res.</u>
B _{M1}	0.26 - 0.62	0.36	0.16
B _{M2}	0.22 - 0.56	0.34	0.22
B _{Si}	0.08 - 0.52	0.44	0.23
B _{O1}	0.26 - 0.70	0.44	0.22
B _{O2}	0.24 - 0.68	0.44	0.25
B _{O3}	0.28 - 0.70	0.42	0.23

HCP: "ideal" hexagonal close-packed olivine model.

(Hazen, 1976)

Range: smallest and biggest value from the literature.

var.: difference between biggest and smallest value.

max.res.: maximal residual in the multiple linear regression.

Table 11.: The result of the multiple linear regression. The constants are used to calculate the positional parameters

from known site occupancies

$$f = a_0 \cdot x_{\text{Fe}(M1)} + a_1 \cdot x_{\text{Mn}(M1)} + a_2 \cdot x_{\text{Fe}(M2)} + a_3 \cdot x_{\text{Mn}(M2)}$$

	a_0	a_1	a_2	a_3	a_4
x_{M2}	0.99065	+0.0079070	+0.0014940	-0.0132500	-0.004212
y_{M2}	0.27740	+0.0001013	+0.0013330	+0.0026840	+0.001676
x_{Si}	0.42639	+0.0045390	+0.0059540	-0.0010360	-0.004791
y_{Si}	0.09403	+0.0019040	+0.0063790	+0.0015420	-0.003984
x_{O1}	0.76575	+0.0007991	+0.0001765	+0.0017330	-0.008172
y_{O1}	0.09165	+0.0007996	+0.0082890	-0.0005220	-0.006306
x_{O2}	0.22167	-0.0115900	-0.0222700	-0.0019070	+0.011480
y_{O2}	0.44712	-0.0008320	+0.0050220	+0.0075800	+0.001551
x_{O3}	0.27732	+0.0126300	+0.0096130	-0.0011740	+0.0001291
y_{O3}	0.16306	+0.0017360	+0.0058690	+0.0000079	-0.0050850
z_{O3}	0.03314	-0.0005452	+0.0038170	+0.0057090	+0.0044400
B_{M1}	0.41954	-0.4030000	+0.2199900	+0.5038800	-0.0198600
B_{M2}	0.43665	-0.3399100	-0.0238300	+0.3529300	+0.1180900
B_{Si}	0.31248	-0.3063000	+0.0188800	+0.3729400	+0.0493900
B_{O1}	0.47866	+0.1597800	+0.0390600	-0.1653900	+0.0178700
B_{O2}	0.48532	-0.2139000	+0.0699900	+0.1610200	-0.0145500
B_{O3}	0.50677	+0.0164300	+0.0887800	+0.0331200	-0.0176900

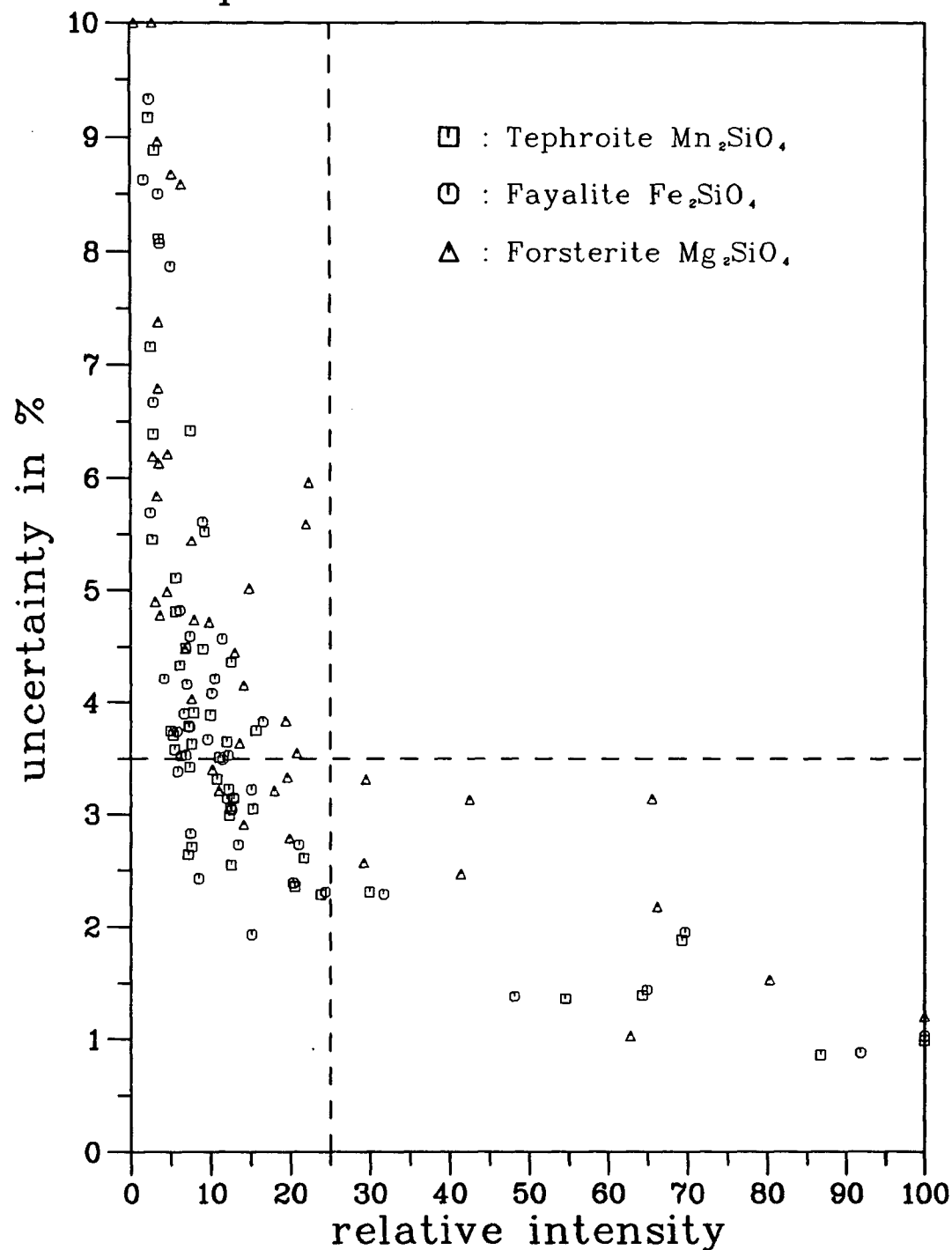
recalculating the XRD intensities provides an estimate of the error introduced in the intensity calculations by uncertainty in the positional parameters. For the three endmembers fayalite, tephroite and forsterite these errors tabulated in appendix F. The total uncertainties are also shown in fig. 16. It may be seen that all peaks with a relative intensity greater than 25 % have a total uncertainty of less than 3.5 %. This is true for all three endmembers and was also confirmed in several sample calculations of solid solutions. As a general rule, the uncertainties increase slightly with increasing Mg content.

2.7.4 UNCERTAINTIES IN CALCULATED INTENSITIES DUE TO CHARGE DISTRIBUTION.

A further factor contributing to uncertainty in the calculations is the effective charge distribution. For fayalite, tephroite and forsterite the charges on each site have been refined by Fujino et al. (1981). Their results show strong deviations from ideal ionic charges, but at present they do not allow a prediction of the charge distribution of the solid solutions. In addition, the presence of Fe^{3+} in our samples does not allow a direct comparison with their data.

The only simple way to extract site occupancies from intensity measurements is to use intensity ratios that are, within acceptable limits, independent of the effective charge distribution. In order to find these ratios we make

Fig. 16: Uncertainty of Integrated Intensities due to uncertainties in Atom coordinates and Temperature correction factors



two calculations for every sample: one assuming neutral atoms in the lattice and one with ideally charged ions. Only those ratios that differ by less than 5 % in the two calculations are used for intensity measurements. The two extreme assumptions do not span the whole range of possible charge distributions, but it was found that even very irregular charges (e.g. only M1 and half of the O3 charged) give intensity ratios between the two extreme values.

2.7.5 THE INTENSITY MEASUREMENTS AND THE OCCUPANCY INTERPRETATION

The X-ray diffraction profiles were measured on two types of diffractometer. An older (1965) Philips PW1050 goniometer and a Philips PW1710 automatic diffractometer. In the first case the peaks of interest were scanned at 2 cm/min and 0.125 deg. 2 θ /cm. The peak shapes and the background were drawn in by hand. The resulting profiles were digitized with a Talos CYBERGRAPH digitizer and the areas calculated with a polygonal approximation. The important peaks (130), (131) and (112) were usually scanned twice and each digitizing was repeated three times. The differences between the different measurements average approximately 0.5 %. If the same peak is scanned with different scales, the differences are increased to 2 %. To each peak an error is assigned which is one quarter of the background noise over the measured length plus 2 % of the measured area to account for possible systematic errors. The

total uncertainty thus assigned to the ratios varies from 3 % to 7 %, which we consider acceptable.

The measurements made with the PW1710 diffractometer were evaluated similarly, except that the digitizing is done in constant steps of $0.05^\circ 2\theta$, and that the background was approximated with a polynomial function. The measuring programs are listed in appendix G.

A final difficulty is that several peaks cannot be measured individually in a XRD profile. Instead of simple reflections it is necessary to consider groups of two or three reflections. In these cases the total uncertainty due to approximate positional parameters and temperature correction factors can be estimated from the tables in appendix F. The measuring strategy may be summarized as follows:

- The reflections or groups of reflections that may be used should have a total relative intensity greater than 25 %. This is necessary to assure that the uncertainty resulting from the approximate positional parameters and temperature correction factors is less than ≈ 3.5 %.
- For these peaks we can calculate all ratios first using uncharged atoms and then using ideally charged ions. Those ratios that remain within a range of ≈ 5 % can be used for the determination of site occupancies. Which ratios we can use must be determined separately for each individual sample.

As we can measure intensity ratios with an accuracy of $\approx 5\%$, we may predict that the maximal discrepancy between calculated and measured intensity ratios will be in the magnitude of 10% . This prediction can be tested with the three endmembers fayalite, tephroite and forsterite.

In table 12 the crucial ratios are listed together with the calculated and observed values. All differences are less than 10% . The ratios 112/130 and 112/131 are usable for all three endmembers. Not all peaks can always be measured. The reasons are that for some compositions they may not be separable from neighbouring peaks of the olivine or they overlap with graphite or silver peaks which are always present in varying amounts in the experimental products. Usually at least four usable and measurable intensity ratios were found in the solid solutions.

The solid solutions were evaluated by first measuring the intensities. Then for the whole range of possible orderings (the Fe distribution is taken from the Mössbauer measurements) the intensities were calculated in steps of $x_{\text{Mg}(\text{M2})}=0.05$ for uncharged atoms and for ideally charged ions. Those ratios that remain within 5% for both calculations were used. Comparing with the measurements and assuming a 10% tolerance, each ratio yields a range of possible occupancies. This range is not a true absolute bracket and therefore the final interpretation is taken as the weighted mean $\pm 1\sigma$ of the midpoints of the all ranges, the weight being the reciprocal of the width of the range.

Table 12.: The differences between calculated and observed integrated intensity ratios for fayalite, tephroite and forsterite.

1)	calc.	obs.	diff [%]
<u>fayalite</u>			
122/111+120	0.37672	0.38649	2.59
222+240+123/111+120	222+.. not measured		
022+041/130	0.45960	0.49389	7.46
112/130	1.08995	1.10898	1.75
222+240+123/130	222+.. not measured		
112/022+040	2.37152	2.24539	5.62
222+240+123/022+040	222+.. not measured		
112/131	1.54171	1.66188	7.79
200+041/131	0.43868	0.44257	0.89
<u>tephroite</u>			
222+240+123/111+120	1.52454	1.55106	1.74
200+041/121+022	2.35904	2.33459	1.05
112/130	1.15534	1.17306	1.70
222+240+123/130	1.07927	1.05567	2.24
131/022+040	1.65471	1.68087	1.58
112/022+040	2.57255	2.45424	4.82
112/131	1.55468	1.46011	6.48

Table 12. (continued)

<u>forsterite</u>			
212+002/020	1.08861	1.09177	0.29
200+041/020	200+.. not measured		
210/111+120	0.35267	0.34161	3.24
222+240+123/111+120	3.12378	2.95109	5.85
131/121+002	3.30228	3.03487	8.81
112/130	1.59151	1.62960	2.39
210/130	0.16209	0.17813	9.89
112/131	1.24503	1.26579	1.67
222+240+123/210	8.85752	8.63869	2.53

1): ratios predicted to have a difference between calculated and measured values smaller than 10 %.

The calculated values are for uncharged atoms.

As may be seen in the following example, this coincides roughly with the range where all useful measured ratios are within 10% of the calculated ones. (Table 13.) All measured intensities are compared with the calculated ones in fig. 17.

2.7.6 EXAMPLE OF A SITE OCCUPANCY DETERMINATION

The measured intensities for MnMgSiO_4 are listed together with the other results in table 14. The reflections with intensities greater than 25% and not overlapping with peaks from other phases are (130), (131), (112), (121), (122) and (222). In table 13 the result of the calculations is summarized. The five usable ratios are also plotted in figure 18 and 19. The boxes on the curves represent the ranges where the observed values are within 10% of the calculated ones. The (110) reflection could not be observed and is assumed to have a relative intensity less than $\approx 1\%$. It is interesting to note that this is also consistent with the interpretation of $x_{\text{Mn}}(\text{M1}) = 0.336$ because much smaller or larger values would result in a more intense (110) reflection.

Fig. 17: Comparison of calculated and measured integrated intensities for tephroite, fayalite and forsterite

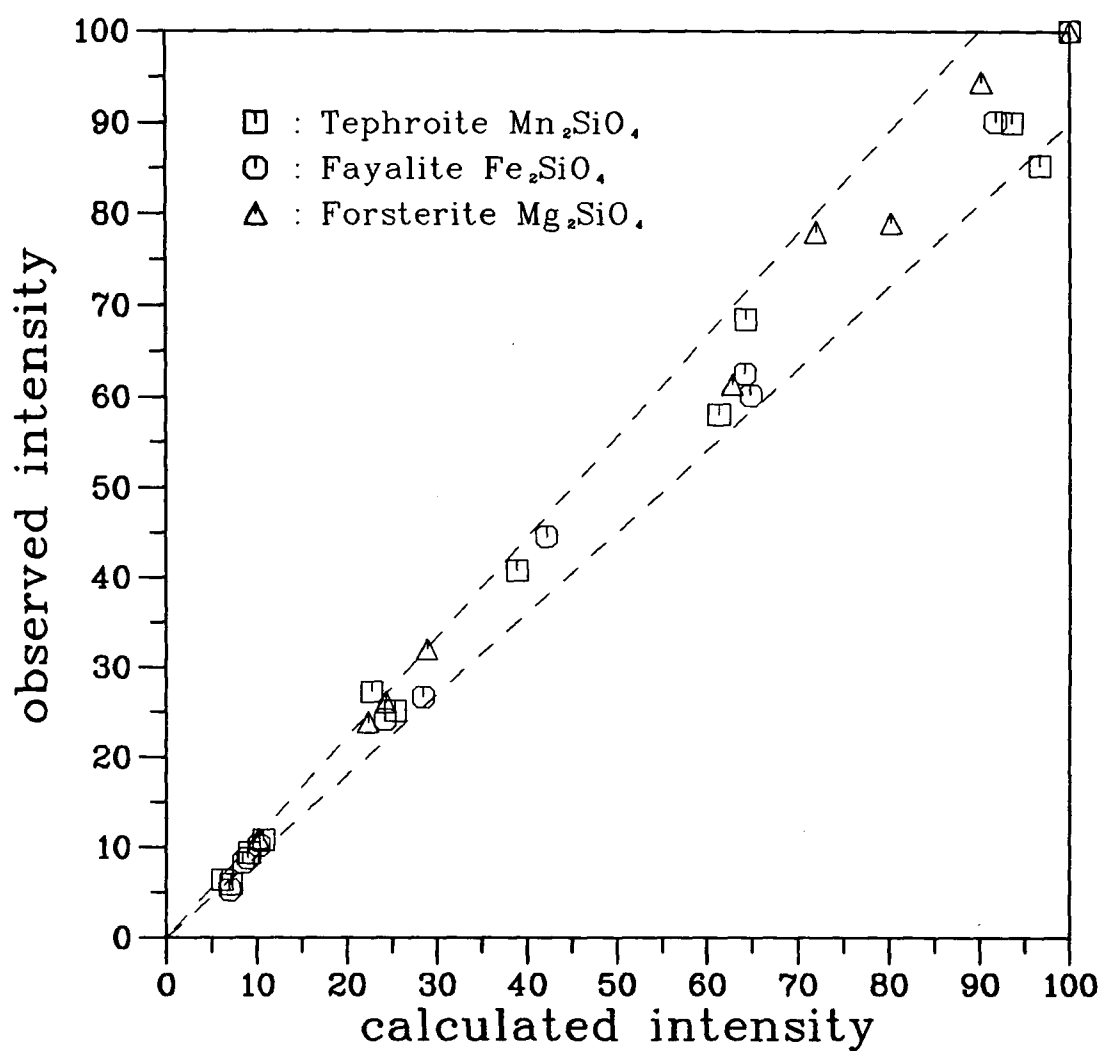


Table 13.: Example: The site occupancy for MnMgSiO_4

<u>reflex</u>	<u>uncharged</u>	<u>charged</u>	<u>diff</u>	<u>comments</u>
	$x_{\text{Mn}}(\text{M1})$	$x_{\text{Mn}}(\text{M1})$		
130/121	0.354±0.036	0.317±0.035	0.037	O.K.
131/121	0.387±0.074	0.354±0.068	0.033	O.K.
112/121	0.356±0.034	0.337±0.030	0.019	O.K.
122/121	0.421±0.042	0.291±0.042	0.130	too big diff.
222/121	0.361±0.048	0.298±0.042	0.063	too big diff.
131/130	0.326±0.069	0.285±0.065	0.041	O.K.
112/130	0.420±0.420	0.572±0.373	0.152	too flat
122/130	0.131±0.131	0.438±0.184	0.307	too big diff.
222/130	0.360±0.204	0.428±0.206	0.068	too flat
112/131	0.327±0.059	0.321±0.054	0.006	O.K.
122/131	0.461±0.103	0.192±0.106	0.269	too big diff.
222/131	0.304±0.104	0.212±0.099	0.092	too big diff.
122/112	0.173±0.124	0.478±0.122	0.305	too big diff.
222/112	0.367±0.139	0.474±0.132	0.107	too big diff.
121 : 121+002	122 : 122+140	222 : 222+240+123		
10 % bracket.....				0.329±0.022
weighted mean.....				0.336±0.024

Fig. 18: Intensity ratios versus site occupancy for $\text{Mn}_6\text{Mg}_6\text{Si}_6\text{O}_{24}$ (ratios < 1)

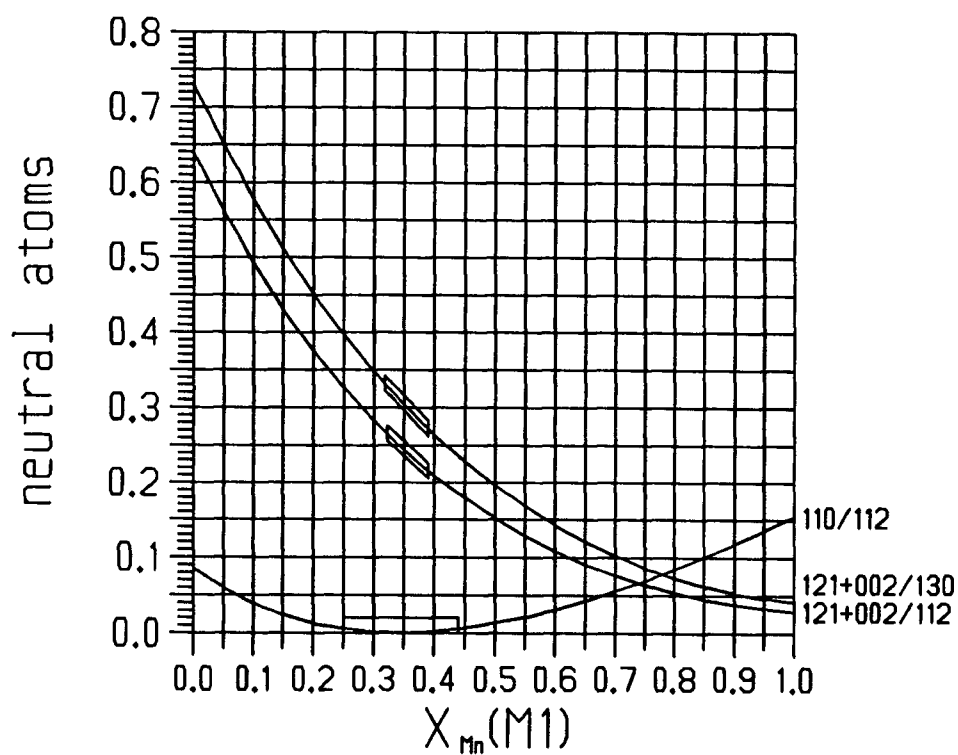
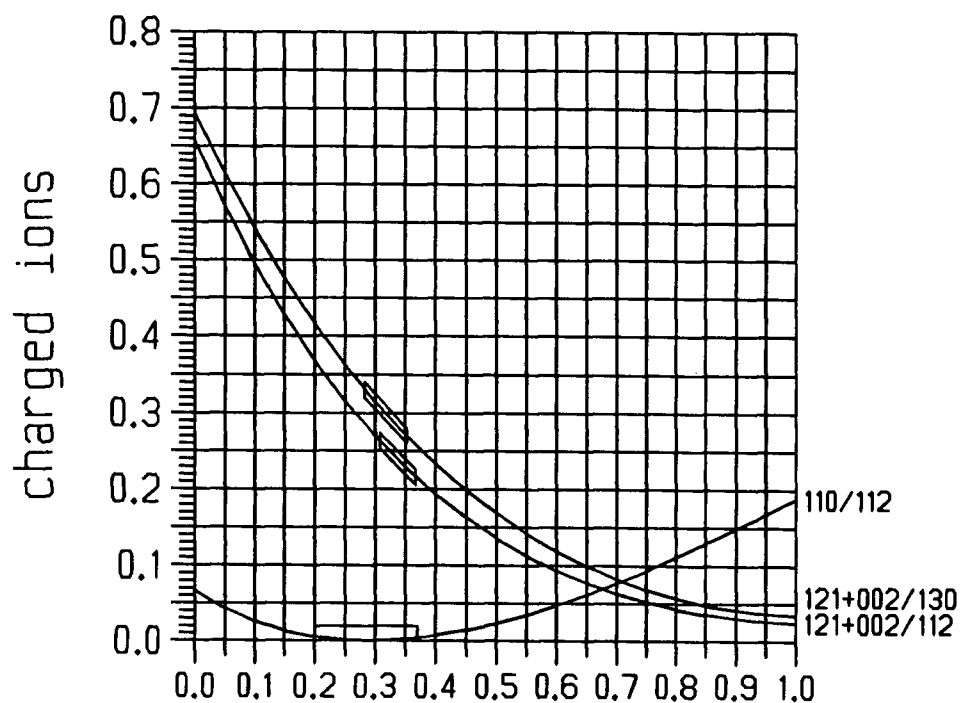


Fig. 19: Intensity ratios versus site occupancy for $\text{Mn}_6\text{Mg}_6\text{Si}_6\text{O}_{24}$ (ratios > 1)

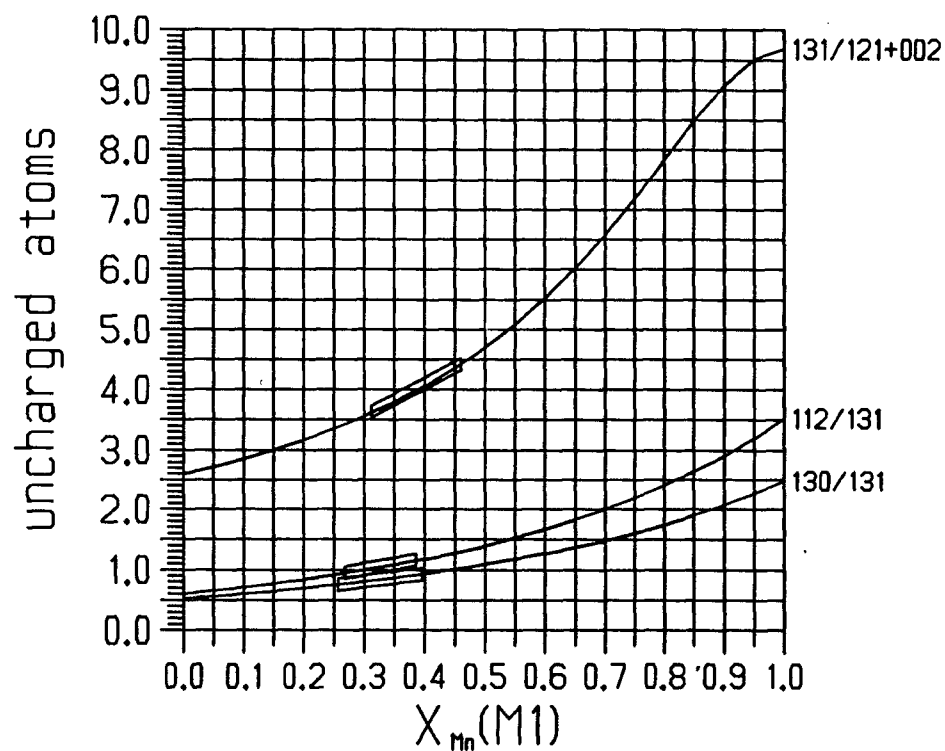
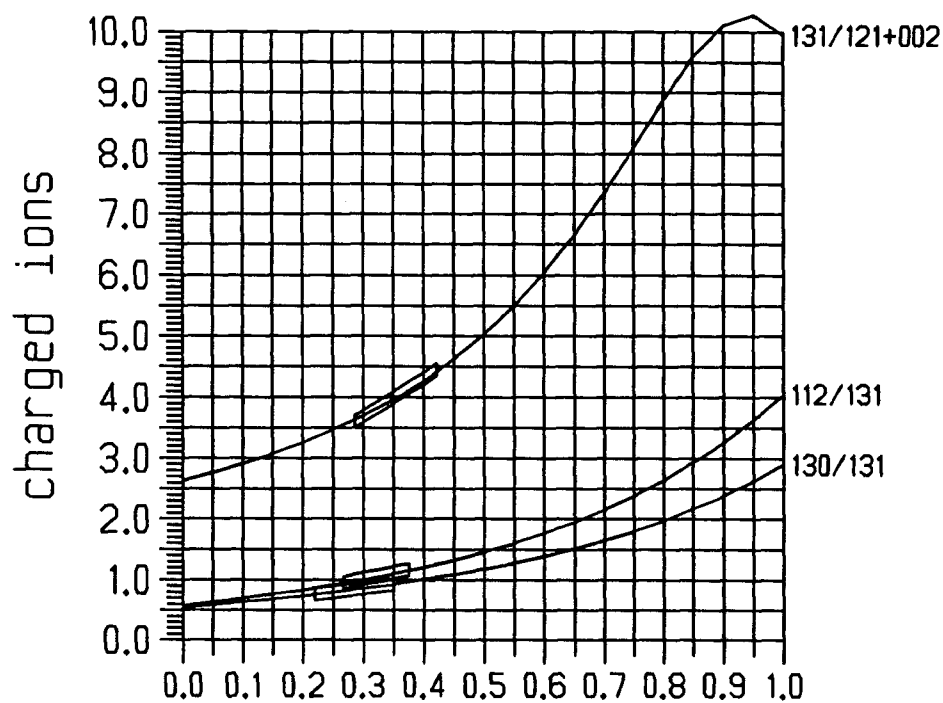


Table 14.: (continued)

	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>	<u>31</u>
020	2.7	7.8	4.1	10.2	23.8
110	<0.5	<0.5	<0.5	<1	<0.5
021	----	----	----	----	68.7
101	----	----	----	----	26.4
111+120	44.0	27.7	33.4	56.9	32.0
121+002	23.6	12.9	18.4	27.0	26.0
130	79.6	68.4	66.6	80.1	61.4
022+040	14.5	10.1	4.3	12.1	----
131	95.2	68.2	78.9	90.5	79.0
112	100.0	100.0	100.0	100.0	100.0
200+041	26.0	16.4	44.5	18.8	11.4
210	24.8	9.6	11.5	9.2	10.9
122+140	49.8	55.3	58.5	50.1	78.0
211+220	----	----	----	----	19.8
222+240+123	102.6	111.1	117.5	105.1	77.4
152	----	10.2	----	----	----

25:00.06.06	26:04.00.08	27:02.02.08	28:00.04.08
31:00.00.12			

Table 15.: Site occupancies for the synthetic Fe-Mn-Mg olivines

NR.	x_{Fe}	x_{Mn}	x_{Mg}	Fe(M1)	Fe(M2)	Mn(M1)	Mn(M2)	Mg(M1)	Mg(M2)	$\ln(K_D)^1$	$\ln(K_D)^2$	$\ln(K_D)^3$	method
1:120000	0.9940	0.0060	0.0000	0.9950	0.9930	0.003*	0.009*	0.0000	0.0000	—	—	—	M
calc.:				0.9974	0.9906	0.0026	0.0094	0.0000	0.0000				
4:080400	0.6627	0.3373	0.0000	0.8198	0.5056	0.1811	0.4944	0.0000	0.0000	1.4876	—	—	M
calc.:				0.8010	0.5244	0.1990	0.4756	0.0000	0.0000				
5:050700	0.4142	0.5858	0.0000	0.5541	0.2743	0.4459	0.7257	0.0000	0.0000	1.1902	—	—	M
calc.:				0.5655	0.2629	0.4345	0.7371	0.0000	0.0000				
6:040800	0.3310	0.6687	0.0000	0.4593	0.2027	0.5407	0.7973	0.0000	0.0000	1.2063	—	—	M
calc.:				0.4679	0.1943	0.5320	0.8058	0.0000	0.0000				
7:030900	0.2485	0.7515	0.0000	0.3573	0.1397	0.6427	0.8603	0.0000	0.0000	1.3207	—	—	M
calc.:				0.3623	0.1347	0.6377	0.8653	0.0000	0.0000				
8:021000	0.1657	0.8343	0.0000	0.2512	0.0802	0.7488	0.9198	0.0000	0.0000	1.3474	—	—	M
calc.:				0.2484	0.0830	0.7516	0.9170	0.0000	0.0000				
11:100002	0.8283	0.0050	0.1667	0.8684	0.7882	0.002*	0.008*	0.1276	0.2058	—	0.5749	—	M
11:100002	0.8283	0.0050	0.1667	0.8490	0.8076	0.002*	0.008*	0.1470	0.1864	—	0.2875	—	PW
calc.:				0.8435	0.8131	0.0022	0.0078	0.1544	0.1790				
12:080202	0.6626	0.1707	0.1667	0.7351	0.5901	0.0871	0.2543	0.1778	0.1556	1.2912	0.0863	-1.2048	M,D
calc.:				0.7407	0.5845	0.0870	0.2544	0.1722	0.1612				
13:060402	0.4970	0.3363	0.1667	0.6174	0.3766	0.2110	0.4616	0.1716	0.1618	1.2772	0.4355	-0.8416	M,PW
calc.:				0.6079	0.3861	0.2008	0.4718	0.1913	0.1421				
14:040602	0.3313	0.5020	0.1667	0.4283	0.2343	0.3400	0.6640	0.2317	0.1017	1.2726	-0.2202	-1.4928	M,PW
14:040602	0.3313	0.5020	0.1667	0.4283	0.2343	0.3510	0.6530	0.2207	0.1127	1.2240	-0.0689	-1.2929	M,D
calc.:				0.4399	0.2227	0.3496	0.6544	0.2105	0.1229				

Table 15. (continued)

NR.	x _{Fe}	x _{Mn}	x _{Mg}	Fe(M1)	Fe(M2)	Mn(M1)	Mn(M2)	Mg(M1)	Mg(M2)	ln(K _D) ¹	ln(K _D) ²	ln(K _D) ³	method
15:020802	0.1657	0.6676	0.1667	0.2344	0.0970	0.5480	0.7872	0.2176	0.1158	1.2445	0.2515	-0.9930	M, PW
calc.:				0.2361	0.0953	0.5354	0.7997	0.2284	0.1050				
16:001002	0.0000	0.8333	0.1667	0.0000	0.0000	0.7600	0.9066	0.2400	0.0934	—	—	-1.1201	PW
16:001002	0.0000	0.8333	0.1667	0.0000	0.0000	0.7770	0.8896	0.2230	0.1104	—	—	-0.8384	D
calc.:				0.0000	0.0000	0.7559	0.9107	0.2441	0.0893				
17:080004	0.6627	0.0040	0.3333	0.6993	0.6261	0.002 [*]	0.006 [*]	0.2977	0.3689	—	0.3250	—	M
17:080004	0.6627	0.0040	0.3333	0.6970	0.6284	0.002 [*]	0.006 [*]	0.3000	0.3666	—	0.3041	—	PW
calc.:				0.6847	0.6407	0.0018	0.0062	0.3135	0.3531				
18:060204	0.4970	0.1697	0.3333	0.5691	0.4294	0.0922	0.2472	0.3403	0.3263	1.2679	0.2396	-1.0282	M, D
calc.:				0.5630	0.4310	0.0877	0.2517	0.3493	0.3173				
19:040404	0.3313	0.3353	0.3334	0.4089	0.2537	0.2030	0.4676	0.3881	0.2787	1.3117	0.1462	-1.1655	M, D
calc.:				0.4100	0.2526	0.2025	0.4681	0.3874	0.2794				
20:020604	0.1657	0.5010	0.3333	0.2259	0.1055	0.3650	0.6370	0.4091	0.2575	1.3183	0.2984	-1.0198	M, PW
calc.:				0.2222	0.1092	0.3524	0.6496	0.4254	0.2412				
21:000804	0.0000	0.6667	0.3333	0.0000	0.0000	0.5300	0.8034	0.4700	0.1966	—	—	-1.2875	D
calc.:				0.0000	0.0000	0.5393	0.7941	0.4673	0.2059				
22:060006	0.4970	0.0030	0.5000	0.5144	0.4796	0.001 [*]	0.005 [*]	0.4831	0.5169	—	0.1377	—	M
22:060006	0.4970	0.0030	0.5000	0.5015	0.4925	0.001 [*]	0.005 [*]	0.4960	0.5040	—	0.0341	—	PW
calc.:				0.5209	0.4731	0.0013	0.0047	0.4778	0.5222				
23:040206	0.3313	0.1687	0.5000	0.3984	0.2642	0.0900	0.2474	0.5116	0.4884	1.4319	0.3643	-1.0576	M, PW
calc.:				0.3803	0.2823	0.0882	0.2492	0.5315	0.4685				

Table 15. (continued)

NR.	x _{Fe}	x _{Mn}	x _{Mg}	Fe(M1)	Fe(M2)	Mn(M1)	Mn(M2)	Mg(M1)	Mg(M2)	ln(K _D) ¹	ln(K _D) ²	ln(K _D) ³	method
24:020406	0.1657	0.3343	0.5000	0.2192	0.1122	0.2140	0.4546	0.5668	0.4332	1.4231	0.4009	-1.0222	M, PW
calc.:				0.2074	0.1240	0.2042	0.4644	0.5883	0.4116				
25:000606	0.0000	0.5000	0.5000	0.0000	0.0000	0.3360	0.6640	0.6640	0.3360	—	—	-1.3623	PW
calc.:				0.0000	0.0000	0.3552	0.6448	0.6448	0.3552				
26:040008	0.3313	0.0020	0.6667	0.3594	0.3032	0.001*	0.003*	0.6391	0.6943	—	0.2529	—	M
26:040008	0.3313	0.0020	0.6667	0.3625	0.3001	0.001*	0.003*	0.6360	0.6974	—	0.2811	—	PW
calc.:				0.3521	0.3105	0.0009	0.0031	0.6469	0.6865				
27:020208	0.1657	0.1677	0.6667	0.1941	0.1373	0.0960	0.2394	0.7099	0.6233	1.2600	0.2161	-1.0439	M, PW
calc.:				0.1927	0.1390	0.0882	0.2455	0.7190	0.6155				
28:000408	0.0000	0.3333	0.6667	0.0000	0.0000	0.2000	0.4666	0.8000	0.5334	—	—	-1.2525	D
calc.:				0.0000	0.0000	0.2059	0.4607	0.7941	0.5393				

*: For these samples the occupancies for Mn are estimated

$$1: (k_D)_1 = (Fe(M1) \cdot Mn(M2)) / (Fe(M2) \cdot Mn(M1))$$

$$2: (k_D)_2 = (Fe(M1) \cdot Mg(M2)) / (Fe(M2) \cdot Mg(M1))$$

$$3: (k_D)_3 = (Mn(M1) \cdot Mg(M2)) / (Mn(M2) \cdot Mg(M1))$$

method: M: Mössbauer spectroscopy, D: XRD intensities using old diffractometer, PW: XRD intensities using Philips PW1710.

The calculated values are according to 'model 2' described in chapter 2.8.

2.7.7 THE SITE OCCUPANCIES OF THE SYNTHETIC FE-MN-MG

OLIVINES

In Table 14 all measured integrated intensities are listed. Knowing the site distribution of Fe from the Mössbauer spectroscopy, the Mn-Mg distribution was determined as described above. In addition, the binary fayalite-forsterite series was also analyzed with this method, in order to compare the results with the Mössbauer data. The measured Fe^{3+} was assigned to M2 as discussed in chapter 2.5.3. The final result with the M1 and M2 occupancies of all synthetic olivines is presented in table 15. For the ternary compositions the uncertainties in the Fe and Mn site distribution are highly correlated. Because the Fe and Mn have similar scattering factors, the XRD method provides information on Fe+Mn versus Mg occupancies. An overestimation of the Fe occupancy in the Mössbauer spectroscopy will result in an underestimation of the Mn occupancy on the same site in the XRD method.

2.8 THERMODYNAMIC MODEL FOR THE TERNARY FE-MN-MG OLIVINE

SOLID SOLUTIONS AT 850 °C

2.8.1 INTRODUCTION

The general framework for the mixing model of the olivines is chosen to be the "speciation model" of Brown and Greenwood (in preparation). (See also chapter 1.2.2.) This model is a generalization of all site mixing models and therefore very appropriate for our problem. Because three cations (Fe, Mn and Mg) can be distributed on two sites (M1 and M2) the complete structural variation using two-site species can be described with nine species. Among these there are 6 independent reactions:



For an ideal speciation model, the activity of each species is equal to its concentration and the reaction constants become:

$$K_1 = \frac{x_{\text{FeMn}}^2}{x_{\text{FeFe}} \cdot x_{\text{MnMn}}} \quad K_2 = \frac{x_{\text{MnFe}}^2}{x_{\text{FeFe}} \cdot x_{\text{MnMn}}}$$

$$K_3 = \frac{x_{\text{FeMg}}^2}{x_{\text{FeFe}} \cdot x_{\text{MgMg}}} \quad K_4 = \frac{x_{\text{MgFe}}^2}{x_{\text{FeFe}} \cdot x_{\text{MgMg}}}$$

$$K_5 = \frac{x_{\text{MnMg}}^2}{x_{\text{MnMn}} \cdot x_{\text{MgMg}}} \quad K_6 = \frac{x_{\text{MgMn}}^2}{x_{\text{MnMn}} \cdot x_{\text{MgMg}}}$$

2.8.2 MODEL ASSUMING INDEPENDENT SITE MIXING

If the ordering in the olivines is assumed to be a pure site preference then the probability of finding for example Fe on a specific M1-site is equal to $x_{\text{Fe}}(\text{M1})$, independent of what the nearest neighbours are. We may therefore write:

$$x_{(\text{FeMn})} = x_{\text{Fe}}(\text{M1}) \cdot x_{\text{Mn}}(\text{M2})$$

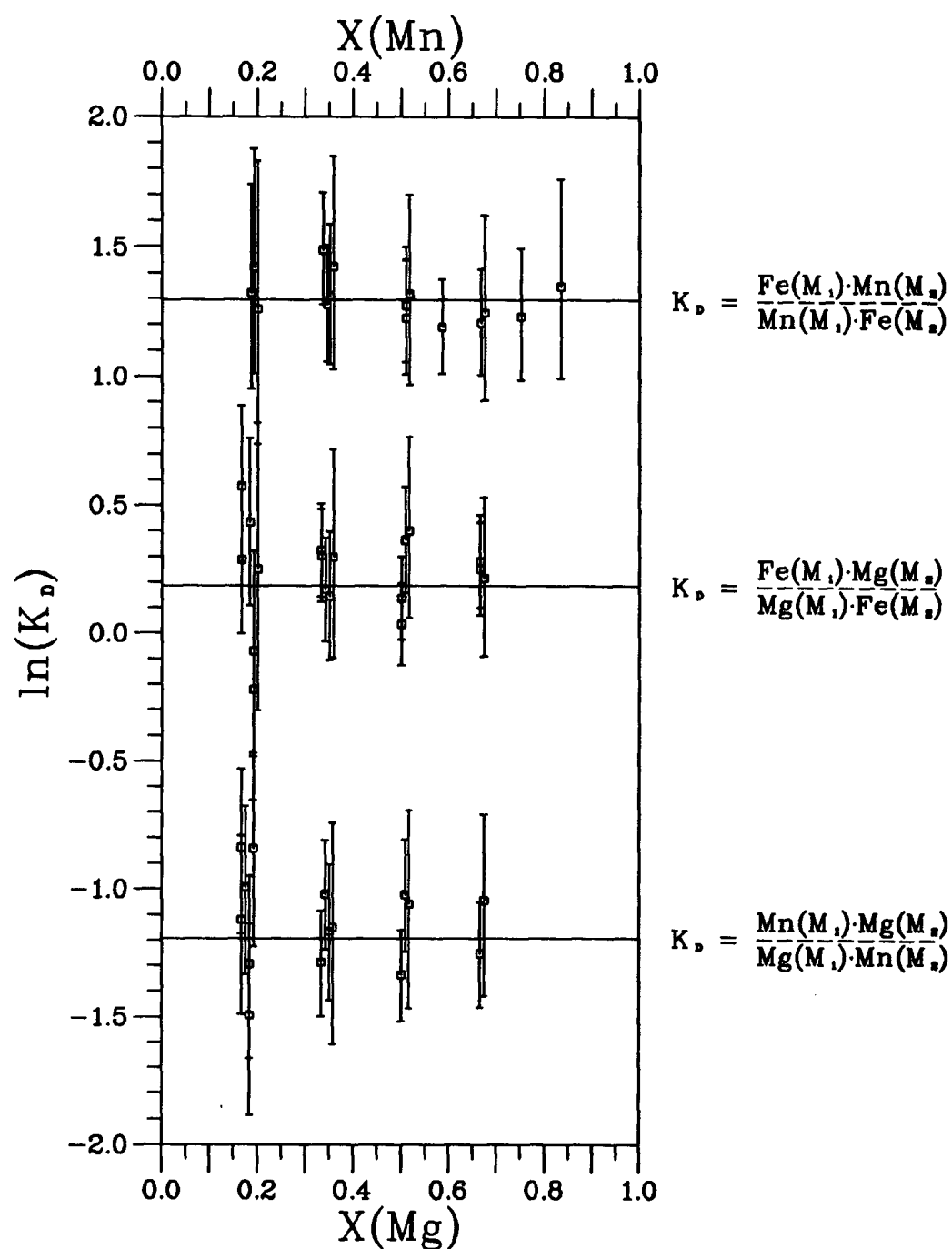
This assumption is quite frequently used to approximate the activities of endmembers in solutions with ideal site mixing. (e.g. Wood and Fraser (1972)). The implication for a speciation model is that only two independent reaction constants remain:

$$K_1 = K_2^{-1} = K_D(\text{Fe-Mn}) = \frac{x_{\text{Fe}}(\text{M1}) \cdot x_{\text{Mn}}(\text{M2})}{x_{\text{Fe}}(\text{M2}) \cdot x_{\text{Mn}}(\text{M1})}$$

$$K_3 = K_4^{-1} = K_D(\text{Fe-Mg}) = \frac{x_{\text{Fe}}(\text{M1}) \cdot x_{\text{Mg}}(\text{M2})}{x_{\text{Fe}}(\text{M2}) \cdot x_{\text{Mg}}(\text{M1})}$$

$$K_5 = K_6^{-1} = K_D(\text{Mn-Mg}) = \frac{x_{\text{Mn}}(\text{M1}) \cdot x_{\text{Mg}}(\text{M2})}{x_{\text{Mn}}(\text{M2}) \cdot x_{\text{Mg}}(\text{M1})}$$

Fig. 20: The observed $\ln(K_p)$ values for the synthetic Fe-Mn-Mg olivines



where $k_5 = k_3/k_1$, because $K_D(\text{Mn-Mg}) = \frac{K_D(\text{Fe-Mg})}{K_D(\text{Fe-Mn})}$

We can therefore predict the thermodynamic properties of the ternary solution, knowing only two binaries. As an example we may assume we had only the ten site occupancy measurements on the fayalite-forsterite and on the fayalite-tephroite join. A fit to the data yields $\ln(K_D(\text{Fe-Mg})) = 0.237$ and $\ln(K_D(\text{Fe-Mn})) = 1.326$. We can now calculate $\ln(K_D(\text{Mn-Mg})) = -1.089$. Considering how few data were used, this is an excellent prediction.

A fit to all data, assuming $k_5 = K_3/k_1$, yields:

$$\ln(k_1) = \ln(k_D(\text{Fe-Mn})) = 1.332$$

$$\ln(k_3) = \ln(k_D(\text{Fe-Mg})) = 0.206$$

model 1

$$\ln(k_5) = \ln(k_D(\text{Mn-Mg})) = -1.126$$

2.8.3 A SLIGHTLY MORE GENERAL MODEL

The most general ideal model would assume as the only constraint that all k 's are constant. A first attempt to fit the data under these conditions failed to converge ($\ln(k_3)$ growing infinite) and was later not repeated because the uncertainties of the data do not really justify too complicated a mixing model.

The only extension we will allow is that the k_D 's are not equal to the k values, but that the relations $k_1 = k_2^{-1}$,

$k_3=k_4^{-1}$ and $k_5=k_6^{-1}$ still hold. This assumption is equivalent to the statement that any internal reaction where the site occupancies remain the same has a $\Delta_r G$ of zero. ($k_r = 1$). For the binaries, k_D will still be equal to k but the k_D values vary with increasing concentration of the third cation. The improvement over the independent site mixing model is that the data of the three binaries are much better taken into account. The k values obtained are:

$$\ln(k_1) = -\ln(k_2) = 1.295$$

$$\ln(k_3) = -\ln(k_4) = 0.185$$

model 2

$$\ln(k_5) = -\ln(k_6) = -1.193$$

This model is represented by the horizontal lines in Fig.20.

2.8.4 FITTING THE MODELS TO THE DATA

With the uncertainties given in table 15, there is no problem to fit a model which is consistent with all data. For the "best fit" the following function was minimized:

$$\sum_{i=1}^n \text{SQRT} \left[\left[(x_{\text{Fe}}^{\text{obs}}(M1) - x_{\text{Fe}}^{\text{calc}}(M1)) \right]_i^2 + \left[(x_{\text{Mn}}^{\text{obs}}(M1) - x_{\text{Mn}}^{\text{calc}}(M1)) \right]_i^2 + \left[(x_{\text{Mg}}^{\text{obs}}(M1) - x_{\text{Mg}}^{\text{calc}}(M1)) \right]_i^2 \right]$$

The distribution of species was calculated with the program THERIAK described in part one of the present thesis. The minimization of the above function was made with the same

gradient method as used for the G-minimization of solution phases in THERIAK, except that the derivatives were calculated by finite differences.

The calculated occupancies are compared with the measured ones in Table 15.

2.9 CONCLUSIONS

Using integrated powder diffraction intensities, we can measure the site distribution of two elements, provided their scattering factors are sufficiently different. The method presented yields uncertainties for the occupancies in the order of 0.03. Combined with Mössbauer data it was possible to determine the site distributions of Fe, Mn and Mg in olivines. Theoretically the method is not restricted to olivines, and it might provide useful information if it were applied to other systems, e.g. the orthopyroxenes. Because the precision of the method is limited, it may be important for experimental petrologists to concentrate on the growth of larger crystals, so that single crystal structure refinements are possible. Larger and homogeneous crystals would also be very desirable as microprobe standards. To obtain smaller uncertainties dealing with fine grained samples, it may be necessary to investigate using newer methods, like CHEXE (Smyth and Taftø (1982)) or the effects of anomalous dispersion (Waseda (1984)). A further unresolved problem is that the knowledge of site occupancies describes only long-range ordering, and it

should therefore be an aim for future investigations to recognize also short-range ordering.

In order to incorporate the knowledge of occupancies into a thermodynamic model, we need a versatile site mixing model and a robust method for calculating chemical equilibria. The model used to describe the olivine solid solutions in my thesis is the "speciation" model according to Brown and Greenwood (in preparation). This model considers each configuration of a small structural unit as a species, similar to the ones used in gas mixing models. (Compare also chapters 2.8.1. and 1.2.2.). The method for computing chemical equilibria presented in the first part of my thesis ("THERIAK"), uses a non-linear programming technique (step 1 of the algorithm), which is specially designed to be used with non-ideal "speciation" models. The combination "THERIAK"/"speciation" provides therefore a powerful tool for modelling even very complex mineral equilibria.

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APPENDIX A: DESCRIPTION OF INPUT FOR THE PROGRAM THERIAK

A.1 PROBLEM INPUT

The minimum input consists of two lines (the first and the last). These provide information about the temperature, the pressure, the bulk composition, the desired output and the phases to be considered.

first line:

TC P

TC: Temperature in °C

P : Pressure in bars

last line:

PRTCODE	FORMULA	USE
---------	---------	-----

PRTCODE: Allows a choice between different outputs:

<-1: print information about selected or rejected phases
from the data-base. NO EQUILIBRIUM CALCULATED

=-1: print composition, considered phases and solution
models. NO EQUILIBRIUM CALCULATED

= 0: short output (stable paragenesis)

= 1: long output (composition, considered phases, solution
models, stable paragenesis, activities of all
considered phases

FORMULA: Bulk composition in the form:

component(value) component(value)...

the values can be any numbers, but should be positive to avoid unpredictable results. The maximum length of FORMULA is 170 characters, it may contain single blanks and must be separated from PRTCODE and USE by at least two blanks.

USE: Code for selecting data from the data-base.

For more information see A.2.2.

Two examples of minimum input:

	700	3000	
-2	SI(1.0)	AL(2.0)	O(5.0) N
	550.00	2000.0	
1	MN(1)	SI(8)	CA(2) O(19) *

optional input

Between the first and the last line, optional lines may be inserted. They contain one or more statements in the form:

parameter=value

separated by at least two blanks. The first eight of the following possible parameters define the sizes of arrays and structures. They can be changed at execution time only in the PL/1 version. In FORTRAN these have to be changed before compilation of the program.

<u>parameter</u>	<u>default</u>	
COMAX	15	Maximum number of components. (Can be less than the number of components in the database)
PHMAX	100	Maximum number of considered non-solution phases.
SOMAX	10	Maximum number of considered solution phases.
EMMAX	6	Maximum number of endmembers for each solution phase.
SITEMAX	5	Maximum number of different sites for ideal site mixing model.
MAMAX	7	Maximum number of margules parameters for each solution phase.
MPOLMAX	3	Maximum degree of polynom for margules equation.

CALMAX	150	Maximum number of phases to be kept simultaneously in matrix $ X $.
LO1MAX	80	Maximum number of iterations for the calculation. If LO1MAX < 0 then the number of iterations will be exactly $ LO1MAX $.
TEST	10^{-8}	The calculations will stop, if the absolute sum of all non-positive g_i after the linear programming section is smaller than $ TEST $. If TEST < 0 then the program prints a short summary for each iteration.
EQUALX	10^{-5}	Two phases of the same solution are considered equal if $\sum \Delta x_i < EQUALX$.
PGAS	1	The pressure for fluid phases is $P*PGAS$.
LPP	60	Lines per page. (has an effect only in the PL/1 version).
DELXMIN	10^{-7}	Δ_{min} : smallest possible stepsize. = precision for calculating x_i 's in non-ideal solutions.
DELXSCAN	1	Grid width for scanning non-ideal solution phases for initial guess.
DELXSTAR	0.02	Δ_{init} : initial stepsize.
STEPSTAR	2	Maximum number of steps, if initial guess results from a scan.

STEPMAX	3	Maximum number of steps if initial guess is a previous minimum.
GCMAX	100	Maximum number of ΔG function calls per step. (= maximum m in stepsize procedure)

Examples for optional input:

```
TEST=-1E-7   LO1MAX=200   GCMAX=15
MPOLMAX=4    MAMAX=32    EMAX=10
```

A.2 THE DATA-BASE

The format of the data-base follows closely the one used by E.H. Perkins, R.G. Berman and T.H. Brown for the calculation of phase diagrams. The first few lines of the data-base contain general information on the components to be used :

```
NC    R
COMP(1) COMP(2) ... ... COMP(8)
...
COMP( ) COMP( )... ... COMP(NC)
MOLWT(1) MOLWT(2) ... ... MOLWT(8)
...
MOLWT( ) MOLWT( ) ... ... MOLWT(NC)
```

NC: Number of components used in the data-base.

R : Gas constant [J/mol]

COMP*N*(*i*) : Components. (Format = 8A8)

MOLWT(*i*) : Molecular weights. (Format = 8F8.2)

The rest of the data-base is organized in sections. Each section begins with a line having the string '***' as the first three non-blank characters. The text of that line is scanned for a string defining the section.

The sections recognized by the program are:

*** ... MINERAL DATA ...

*** ... GAS DATA ...

These two are treated identically. They contain the phase definitions and the information to calculate $\Delta_f G$ for variable pressures and temperatures.

*** ... SOLUTION DATA ...

Definitions of solutions and solution models.

*** ... MARGULES ...

This section contains Margules parameters for non-ideal solution phases.

Other sections (e.g. *** ... COMMENTS ...) will be skipped by the program. Principally the sections can be in any order and may appear more than once. But it is obvious that if we define a solution phase, its endmembers must have been read in previously. Similarly the Margules parameters for a solution phase can only be assigned properly after the solution phase is defined.

Any line anywhere, which is empty or begins with a '!' is considered a comment line and is skipped.

A.2.1 SECTION *** ... MINERAL DATA ...

Each phase is defined with one phase definition line and any number of data lines.

phase definition line

NAME FORMULA ABBREV [CODE]

The four strings are separated by at least two blanks. They all may contain single blanks.

NAME : Name of the phase. (maximum 16 characters)

FORMULA : Chemical formula of the phase in the form:

 component(value) component(value) ...

The components have to be the same as defined at the beginning of the data-base. The values can be negative.

ABBREV : Abbreviation for phase (maximum 8 characters)

CODE : [optional] (maximum 15 characters)

Each character in CODE defines a group to which the phase belongs. If the first character is a '*' then the phase is considered "special".

For more details see A.2.2.

A line within this section is recognized to be a phase definition line if it contains at least one '(' (left

paranthesis) and is not a comment line.

Examples of phase definition lines:

HIGH ALBITE	NA(1)AL(1)SI(3)O(8)	H-ALB	N
ALMANDINE	FE(3) AL(2) SI(3) O(12)	alm	

Data lines

The thermodynamic data for a phase follow the phase definition line in any order. The first three non-blank characters identify the content of the input line. These three characters must be within the first five columns of the line. Columns 6 to 80 contain at most five fields of 15 columns with numerical data. (FORMAT = A5,5F15.4)

1. Standard state information. (25 °C, 1 bar). $\Delta_f G^\circ$ is not used and its field can be left blank.

ST	$\Delta_f G^\circ$ [J/mol]	$\Delta_f H^\circ$ [J/mol]	S° [J/K·mol]	V° [cm ³ /mol]
----	----------------------------	----------------------------	---------------------	----------------------------------

2. Heat capacity information:

$$cp = k1 + k2 \cdot T + k3/T^2 + k4/\sqrt{T} + k5 \cdot T^2 + k6/T + k7 \cdot \sqrt{T} + k8/T^3 + k9 \cdot T^3 \quad [\text{J/mol}]$$

CP1	k1	k4	k3	k8	
CP2	k6	k2	k5	k7	k9
CP3	k1	k2	k3		

3. Equation of state for gases (used to calculate $\int V dp$). If the $\Delta_f G$ calculation shows that the phase is liquid the name of the phase will be changed to: name(LIQ).

$$a = a_0 + a_1 \cdot T \text{ [J} \cdot \text{cm}^3] \quad b = b_0 + b_1 \cdot T \text{ [cm}^3]$$

$$\text{Van der Waals: } P = (R \cdot T)/(V-b) + a/V^2$$

$$\text{Redlich-Kwong: } P = (R \cdot T)/(V-b) - a/(\sqrt{T} \cdot V \cdot (V+b))$$

$$\text{VDW} \quad a_0 \quad a_1 \quad b_0 \quad b_1$$

$$\text{R-K} \quad a_0 \quad a_1 \quad b_0 \quad b_1$$

4. Lambda transitions. Between the limits T_{ref} and T_{tr} a Cp-like function is added:

$$Cp_{\text{tr}} = (T - \Delta T) \cdot [l_1 + l_2 \cdot (T - \Delta T)]^2$$

$$\text{where } T_{\text{ref}} = T_{\text{ref}}^0 + \Delta T$$

$$T_{\text{tr}} = T_{\text{tr}}^0 + \Delta T$$

$$\text{and } \Delta T = (P - P_0) \cdot T_q$$

In addition ΔH_{tr} , ΔV_{tr} , $(\delta V/\delta T)$ and $(\delta V/\delta P)$ are considered.

$$\text{TR1} \quad T_{\text{tr}}^0 \quad T_{\text{ref}}^0 \quad l_1 \quad l_2 \quad \Delta H_{\text{tr}}$$

$$\text{TR2} \quad T_q \quad \Delta V_{\text{tr}} \quad (\delta V/\delta T) \quad (\delta V/\delta P)$$

5. Disorder contributions to $\Delta_f G$ can be approximated by adding a Cp-like function between the limits T_0 and T_d .

$$\text{dis} = d1 + d2 \cdot T + d3/T^2 + d4/\sqrt{T} + d5 \cdot T^2 + d6/T + d7 \cdot \sqrt{T} \\ + d8/T^3 + d9 \cdot T^3 \quad [\text{J/mol}]$$

The volume is taken from the shape of the enthalpy function and is scaled to the data by the variable V_{ad} .

D1	d1	d4	d3	v_{ad}	d6
D2	d2	d5	T_o	T_d	

6. Special phases: $\Delta_f G$ at p and T is calculated in an external subroutine. All other data lines will be ignored. (Used e.g. to calculate $\Delta_f G$ for water and steam according to Haar et al.(1982)). The Keyword can be maximal 10 characters long. (See also A.3)

SPC	Keyword
-----	---------

7. To the $\Delta_f G$ defined by the standard state, C_p 's etc. we can add any combination of previously calculated $\Delta_f G$'s. This is useful e.g. for polymorphs or buffers.

COM	name[value]	name[value]	...
-----	-------------	-------------	-----

A.2.2 USE AND CODE (SELECTING PHASES)

The phases in the data-base may be divided into different groups. Each group is coded as one character (e.g.:A,B,C,D). The variable CODE in the data-base [optional] defines for each phase to which groups it belongs. When the program is run we can specify in the variable USE all groups that should be considered. If USE = '*' then all groups are considered, including those with no CODE defined.

special phases:

If The first character of CODE is a '*' then the phase is "special" (e.g. a buffer) and does not belong to a specific group. It will only be considered if mentioned in USE after a comma. The first comma in USE is a delimiter between the group names and the special phases.

If the first character of CODE is a '+' then $\Delta_f G$ of this phase will be calculated even if its composition is outside the compositional space. In that case this phase can still be used to define $\Delta_f G$ of other phases, but will itself not be considered for the equilibrium assemblage.

In general a phase will be considered if:

1.

The group code is matching

2.

no phase with identical name is already considered

3.

its components are a subsystem of the bulk components

4.

enough data to calculate $\Delta_f G$ is provided.

Examples for USE and CODE:

	<u>CODE</u>	<u>USE</u>	<u>Considered phases</u>
Phase 1	A	A	1,4
Phase 2	BC	B	2
Phase 3	C	C	2,3,4
Phase 4	AC	AB	1,2,4
Phase 5		AC	1,2,3,4
Phase 6	*QFM	BC	2,3,4
Phase 7	*CB	ABC	1,2,3,4
		*	1,2,3,4,5
		AB,QFM	1,2,4,6
		AB,QFM,CB	1,2,4,6,7
		ABC ,CB	1,2,3,4,5,7
		A,CB	1,4,7

A.2.3 SECTION *** ... SOLUTION DATA ...

A solution phase is defined by one definition line followed by any number of endmember lines.

solution definition line

SOLNAME (MODELL)[/DIV] N M₁ M₂ ... M_n

A line within this section is recognized to be a solution definition line if it contains the string ' (' (blank,blank,left parenthesis) and is not a comment line.

SOLNAME : Name for solution (maximum 16 characters)

MODELL : This string is scanned for certain keywords:

SKIP : The solution phase will not be considered.

IDEAL : An ideal solution model is assumed. ($a_i = x_i$). This is also the default if no keyword is recognized.

SITE : An ideal site mixing model is used.

N : Number of different sites (integer, can be zero).

M_i : Multiplicity of site i (integer). It is assumed that the endmembers have the site i occupied by M_i identical elements or element groups.

EXT : The activities of the endmembers are defined in an external subroutine. All other keywords (except SKIP and MARGULES) N and M have no influence. (See also A.4.)

MARGULES : This keyword states, that there may be Margules parameters defined for this phase. They will only be added if this keyword appears in MODELL.

/DIV : If a slash follows immediately the (MODELL), then the number following it is used to calculate fractional multiplicities. All multiplicities are divided by DIV.

Comments: N, M_i and DIV are integers by definition, but read as real. If decimal fractions are entered the program will calculate accordingly, but print a wrong model.

N and M_i are not optional. if not used at least N=0 has to be defined.

Endmember lines

EMNAME E_1 E_2 ... E_n

EMNAME : Name of the endmember. (maximum 16 characters). The endmember will be added to the solution if a considered phase with the same name exists.

E_i : Element on site i . (Maximum 8 characters). The element names do not have to correspond to a compositional element. They are only used to find out which endmembers have which sites occupied by the same element or element group.

Examples:

GAS PHASE	(IDEAL)	0
CARBON DIOXYDE		
STEAM		
OXYGEN		
CARBON MONOXYDE		

HIGH FELDSPARS	(IDEAL,MARGULES)	0
HIGH ALBITE		
HIGH SANIDINE		

GARNETS	(SITE)	2	3	2
PYROPE	MG	AL		
ALMANDINE	FE	AL		
SPESSARTINE	MN	AL		
GROSSULAR	CA	AL		
ANDRADITE	CA	FE		

For the above examples the program will print the models as shown on the following page.

Examples of printed models

SOLUTION PHASES:

1 GAS PHASE : SOLUTION MODELL: IDEAL ONE SITE MIXING

1 CARBON DIOXYDE (29) $A(\text{CO}_2) = X(\text{CO}_2)$

2 STEAM (96) $A(\text{H}_2\text{O}) = X(\text{H}_2\text{O})$

3 OXYGEN (73) $A(\text{O}_2) = X(\text{O}_2)$

4 CARBON MONOXYDE (30) $A(\text{CO}) = X(\text{CO})$

2 HIGH FELDSPARS : SOLUTION MODELL: IDEAL ONE SITE MIXING + MARGULES TYPE EXCESS FUNCTION

1 HIGH ALBITE (14) $A(\text{H-ALB}) = X(\text{H-ALB})$

2 HIGH SANIDINE (88) $A(\text{H-SAN}) = X(\text{H-SAN})$

MARGULES PARAMETERS: $W(112) = 18948.06$ $W(122) = 10322.68$

3 GARNET : SOLUTION MODELL: "IDEAL" 2 SITE MIXING

1 PYROPE (81) $A(\text{PYROPE}) = [X(\text{PYROPE})]^3 [X(\text{PYROPE}) + X(\text{ALM}) + X(\text{SPESS}) + X(\text{GROSS})]^2$

2 ALMANDINE (15) $A(\text{ALM}) = [X(\text{ALM})]^3 [X(\text{PYROPE}) + X(\text{ALM}) + X(\text{SPESS}) + X(\text{GROSS})]^2$

3 SPESSARTINE (94) $A(\text{SPESS}) = [X(\text{SPESS})]^3 [X(\text{PYROPE}) + X(\text{ALM}) + X(\text{SPESS}) + X(\text{GROSS})]^2$

4 GROSSULAR (50) $A(\text{GROSS}) = [X(\text{GROSS}) + X(\text{ANDR})]^3 [X(\text{PYROPE}) + X(\text{ALM}) + X(\text{SPESS}) + X(\text{GROSS})]^2$

5 ANDRADITE (18) $A(\text{ANDR}) = [X(\text{GROSS}) + X(\text{ANDR})]^3 [X(\text{ANDR})]^2$

A.2.4 SECTION *** ... MARGULES ...

The Margules parameters are grouped in subsystems (binary, ternary etc.). Each subsystem is defined by a definition line, followed by any number of parameter lines.

Margules definition line

EMNAME1 - EMNAME2 - ...

A line within this section is recognized to be a definition line if it contains the string ' - ' (blank, minus, blank)

EMNAME_n : Name of n^{th} endmember in subsystem.

parameter lines

$k_1 k_2 k_3 \dots$ WH WS WV WCP

The number of k_i 's defines the degree of the polynomial in the Margules equation. This does not have to be the same for all parameters.

$WG = WH - T \cdot WS + p \cdot WV + \dots$

$G^{\text{Ex}} = WG \cdot x(k_1) \cdot x(k_2) \cdot x(k_3) \dots$

where the k_i 's refer to the indices in the definition line.

Example:

HIGH ALBITE - HIGH SANIDINE

112	32098.8	16.1356	0.46903	0
122	26470.9	19.3807	0.38702	0

A.3 CALCULATION OF $\Delta_f G$ IN AN EXTERNAL SUBROUTINE

If $\Delta_f G$ is to be calculated in an external subroutine, (data line: SPC Keyword), then the program calls a subroutine named GSPEC. The parameters transmitted are: NAME(name of phase), P(pressure), PGAS(pressure of fluid phases), T(temperature), CASE(=Keyword) and G($\Delta_f G$). The subroutine calculates G (or may read it from a terminal) and returns control to the main program.

Example of GSPEC in PL/1:

```

GSPEC:PROCEDURE(NAME,P,PGAS,T,CASE,G);
DCL (NAME) CHAR(16) VARYING;
DCL (CASE) CHAR(10) VARYING;
DCL (P,PGAS,T,G) DECIMAL FLOAT(16);
DCL (WHAAR) ENTRY;
G=0.0;
IF CASE='HAAR' THEN CALL WHAAR(NAME,PGAS,T,G);
RETURN;
END GSPEC;
```

A.4 CALCULATION OF ACTIVITIES IN AN EXTERNAL SUBROUTINE

If the model of a solution phase contains the string 'EXT' then three subroutines (or three entry-points) will be called:

1. PSOLINI. In this subroutine we define for a given solution phase the number and the names of the endmembers.
2. PSOLMOD. This subroutine returns a string to be printed, and which describes the activity according to solution name and endmember number. (optional)
3. PSOLCAL. For each endmember the activity is calculated.

The solution has to be defined in the data-base, but may have fewer endmembers and in a different order than the same solution in the external subroutines.

The calling parameters are relatively complex, but to add a new solution phase to the already existing subroutines, only few lines have to be inserted:

Example (for PL/1)

in PSOLINI:

```
IF SOLNAME='name of solution phase'
THEN DO; N=number of endmembers;
      NAME(1)='name of endmember 1';
      NAME(2)='name of endmember 2';
      .....
      NAME(n)='name of endmember n';
END;
```



```
in PSOLMOD: (Default: MODELL='NOT EXPLICITLY DEFINED';)
```

```
IF SOLNAME='name of solution phase'
THEN DO; IF K=1 THEN MODELL='activity of endmember 1';
          IF K=2 THEN MODELL='activity of endmember 2';
          .....
          IF K=n THEN MODELL='activity of endmember n';
END;
```

```
in PSOLCAL: The independent variables in the formulas
             can be: P,T,X(1),X(2),...X(n)
```

```
IF SOLNAME='name of solution phase'
THEN DO; A(1)=formula for activity of endmember 1;
          A(2)=formula for activity of endmember 2;
          .....
          A(n)=formula for activity of endmember n;
END;
```

APPENDIX B: LISTING OF PROGRAM THERIAK

The major COMMON blocks are only listed in the main routine.

```
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
LOGICAL*4 MORE
INTEGER*4 I001,I002,I1,I2,II,COMAY,LLL,LPP
REAL*8 FAR001(11),FF,MOLGEW(COMAX)
CHARACTER*250 CH001,CH002,SYREC
CHARACTER*8 CAR001(11)
C-----COMMON BLOCK FOR SAVING INPUT DATA
INTEGER*4 INDATA(12,PHMAX)
COMMON /DAIN/ INDATA
REAL*8 REDATA(75,PHMAX)
COMMON /DARE/ REDATA
CHARACTER*16 CHDATA(PHMAX)
COMMON /DACH/ CHDATA
LOGICAL*4 LODATA(5,PHMAX)
COMMON /DALO/ LODATA
C-----GLOBAL COMMON BLOCK
REAL*8 P,PGAS,PRAT,P0,R,RT,T,TC,T0
COMMON /SURE/ P,PGAS,PRAT,P0,R,RT,T,TC,T0
C-----COMMON BLOCK FOR DATABASE
INTEGER*4 CHMCOD(COMAX),DIM,LUSE,NC,NPAR
COMMON /ININ/ CHMCOD,DIM,LUSE,NC,NPAR
REAL*8 CHE(COMAX),CHEM(COMAX),GGK(PHMAX),BULK(COMAX)
COMMON /INRE/ CHE,CHEM,GGK,BULK
CHARACTER*250 REC
CHARACTER*170 FORMUL
CHARACTER*60 MODCOD
CHARACTER*25 CH,USE
CHARACTER*16 MANAM(EMAX),SONAM
CHARACTER*8 ALPDIV(SOMAX+1),FORM,OXYDE(COMAX)
CHARACTER*5 SITEL(SOMAX+1,EMAX,SITMAX)
CHARACTER*3 RECODE
COMMON /INCH/ MANAM,SONAM,ALPDIV,FORM,OXYDE,
>SITEL,RECODE,REC,FORMUL,MODCOD,CH,USE
LOGICAL*4 GENUG(8),MARCOD(SOMAX+1),NULL(PHMAX+1)
COMMON /INLO/ GENUG,MARCOD,NULL
C-----COMMON BLOCK FOR G-CALCULATION
INTEGER*4 NLANDA,NCOM,ICOM(10)
COMMON /GCIN/ NLANDA,NCOM,ICOM
REAL*8 AAT,AA0,ASPK(4),BBT,BB0,BSPK(4),DHTR(4),DVDP(4),
>DVDT(4),DVTR(4),D1,D2,D3,D4,D5,D6,D7,D8,D9,GR,G0R,H0R,
>K1,K2,K3,K4,K5,K6,K7,K8,K9,SQT,SQT0,S0R,TDMAX,TD0,TEQ(4),
>TQ1B(4),TRE(4),TT,TT0,VADJ,V0R,FFCOM(10)
COMMON /GCRE/ AAT,AA0,ASPK,BBT,BB0,BSPK,DHTR,DVDP,
>DVDT,DVTR,D1,D2,D3,D4,D5,D6,D7,D8,D9,GR,G0R,H0R,
>K1,K2,K3,K4,K5,K6,K7,K8,K9,SQT,SQT0,S0R,TDMAX,TD0,TEQ,
>TQ1B,TRE,TT,TT0,VADJ,V0R,FFCOM
```

```

      CHARACTER*16 CASE,NAM
      COMMON /GCCH/ CASE,NAM
      LOGICAL*4 DIS,RDK,VDW,LIQ,SPC,COM
      COMMON /GCLO/ DIS,RDK,VDW,LIQ,SPC,COM
C-----COMMON BLOCK FOR THERIAK
      INTEGER*4 EM(SOMAX+1,EMAX),EMBCOD(SOMAX+1,EMAX),EMCODE(0:CALMAX),
> EMNR(PHMAX),EMSOL(PHMAX),EQEM(SOMAX+1,EMAX,SITMAX,EMAX),GCMAX,
> INDX(SOMAX+1,MAMAX,MPOMAX),LOO1,LO1MAX,NEMBAS(SOMAX+1),
> NEND(SOMAX+1),NEQEM(SOMAX+1,EMAX,SITMAX),NMARG(SOMAX+1),NPHA,
> NSITE(SOMAX+1),NSOL,NUMMER(0:CALMAX),NUN,NUN2,
> POLY(SOMAX+1,MAMAX),
> PRTCOD,QQ(SOMAX+1,MAMAX,EMAX),STPMAX,STPSTA,SUGG(0:CALMAX),SUGNR
      COMMON /THIN/ EM,EMBCOD,EMCODE,EMNR,EMSOL,EQEM,GCMAX,INDX,LOO1,
> LO1MAX,NEMBAS,NEND,NEQEM,NMARG,NPHA,NSITE,NSOL,NUMMER,NUN,NUN2,
> POLY,PRTCOD,QQ,STPMAX,STPSTA,SUGG,SUGNR
      REAL*8 ALPHA(SOMAX+1),DXMIN,DXSCAN,DXSTAR,EQUALX,G(0:CALMAX),
> GG(PHMAX),NN(0:CALMAX),SITMUL(SOMAX+1,SITMAX),TEST,
> WG(SOMAX+1,MAMAX),WH(SOMAX+1,MAMAX),WS(SOMAX+1,MAMAX),
> WV(SOMAX+1,MAMAX),WCP(SOMAX+1,MAMAX),
> X(0:CALMAX,COMAX),XEM(0:CALMAX,EMAX),XX(PHMAX,COMAX)
      COMMON /THRE/ ALPHA,DXMIN,DXSCAN,DXSTAR,EQUALX,G,GG,NN,SITMUL,
> TEST,WG,WH,WS,WV,WCP,X,XEM,XX
      CHARACTER*16 NAME(PHMAX),SOLNAM(SOMAX+1)
      CHARACTER*8 ABK(PHMAX),CHNAME(COMAX)
      CHARACTER*1 MODELL(SOMAX+1)
      COMMON /THCH/ NAME,SOLNAM,ABK,CHNAME,MODELL
      LOGICAL*4 PRTLOG(8)
      COMMON /THLO/ PRTLOG
C-----END OF COMMON VARIABLES
C----
      CHARACTER*3 YESNO
C----
      DATA CAR001/'PGAS','LO1MAX','EQUALX','TEST','DELXMIN',
* 'DELXSCAN','DELXSTAR','STEPSTAR','STEPMAX','GCMAX','LPP'/
      DATA FAR001/1.0D0,80.0,1D-5,1D-8,1D-7,
* 1.0D0,2D-2,2.0,3.0,100.0,60.0/
      COMAY=COMAX
      LLL=0
C-----READ T AND P FROM UNIT 5
      MORE=.TRUE.
      READ (UNIT=9,FMT='(A250)') SYREC
      CALL GELI(SYREC,TC)
      CALL GELI(SYREC,P)
C-----READ OOPTIONAL NEW DEFAULT VALUES FROM UNIT 9
C-----THE FOLLOWING RECORD IS STORED IN SYREC
      1001 IF (MORE) THEN
          READ (UNIT=9,FMT='(A250)') SYREC
          MORE=(INDEX(SYREC,(').EQ.0)
          IF (MORE) THEN
              DO 501,I2=1,11
                  I002=INDEX(CAR001(I2), ' ')
                  IF (I002.EQ.0) I002=9
                  I001=INDEX(SYREC,CAR001(I2)(1:I002-1))
                  IF (I001.NE.0) THEN

```

```

CH002=SYREC(I001:)
I001=INDEX(CH002,'=')
CH001=CH002(I001+1:)
CALL FIBLA(CH001,I001)
CH002=CH001(I001:)
I001=INDEX(CH002,' ')
CH001=CH002(1:I001-1)
READ (UNIT=CH001,FMT='(BN,D16.0)') FAR001(I2)
END IF
501 CONTINUE
END IF
ELSE
GOTO 1
END IF
COTO 1001
1 PRAT=FAR001(1)
LO1MAX=IDINT(FAR001(2))
EQUALX=FAR001(3)
TEST=FAR001(4)
DXMIN=FAR001(5)
DXSCAN=FAR001(6)
DXSTAR=FAR001(7)
STPSTA=IDINT(FAR001(8))
STPMAX=IDINT(FAR001(9))
CCMAX=IDINT(FAR001(10))
LPP=IDINT(FAR001(11))
IF (DXMIN.LE.0.0) DXMIN=1D-7
IF (DXSCAN.LT.0.001) DXSCAN=1.0D-3
IF (DXSCAN.GT.1.0) DXSCAN=1.0D0
IF (DXSTAR.LE.0.0) DXSTAR=DXSCAN/10.0D0
IF (LPP.LT.30) LPP=30
C-----
C-----READ NC AND R FROM UNIT 8
READ (UNIT=8,FMT='(A250)') REC
CALL GELI(REC,FF)
NC=IDINT(FF)
IF (NC.GT.COMAX) THEN
WRITE (UNIT=6,FMT='(' COMAX='',I5/' NC='',I5') COMAX,NC
STOP
END IF
CALL GELI(REC,R)
T0=298.15D0
P0=1.0D0
TT0=T0*T0
SQT0=DSQRT(T0)
C-----READ ELEMENTS AND MOLGEW FROM UNIT 8
DO 502,I=1,NC,8
I001=MIN0(NC,I+7)
502 READ (UNIT=8,FMT='(8A8)') (OXYDE(II),II=I,I001)
DO 503,I=1,NC,8
I001=MIN0(NC,I+7)
503 READ (UNIT=8,FMT='(8F8.2)') (MOLGEW(II),II=I,I001)
C-----
C-----READ PRTCOD, FORMUL AND USE FROM SYREC

```

```

C-----SET UP FIRST NUN COLUMNS OF MATRIX
      CALL GELI(SYREC,FF)
      PRTCOD=IDINT(FF)
      DO 650,I=1,8
650  PRTLOG(I)=.FALSE.
      IF (PRTCOD.LE.-2) PRTLOG(1)=.TRUE.
      IF (PRTCOD.EQ.-1) THEN
        DO 652,I=2,5
652  PRTLOG(I)=.TRUE.
      END IF
      IF (PRTCOD.EQ.0) THEN
        DO 654,I=5,6
654  PRTLOG(I)=.TRUE.
      END IF
      IF (PRTCOD.GE.1) THEN
        DO 656,I=2,8
656  PRTLOG(I)=.TRUE.
      END IF
      CALL TAXI(SYREC,FORMUL)
      CALL TAXI(SYREC,USE)
      CALL CHEMIE(COMAY,NC,OXYDE,FORMUL,CHEM)
      LUSE=INDEX(USE,' ')-1
      IF (PRTCOD.EQ.0) TEST=DABS(TEST)
      CALL DBREAD
      IF (PRTLOG(1)) STOP
      CLOSE(UNIT=9)
C      WRITE (7,FMT='(I4)') NUN
C      WRITE (7,FMT='(7A10)') (CHNAME(I),I=1,NUN)
C      WRITE (7,FMT='(I4)') NPHA
C      WRITE (7,FMT='(5A20)') (NAME(I),I=1,NPHA)
C      WRITE (7,FMT='(I4)') NSOL
C      DO 550,I=1,NSOL
C      WRITE (7,FMT='(A20,I4)') SOLNAM(I),NEND(I)
C      WRITE (7,FMT='(10I5)') (EM(I,II),II=1,NEND(I))
C 550 CONTINUE
C      IF (PRTLOG(2).OR.PRTLOG(3).OR.PRTLOG(4)) CALL PRININ
      IF (PRTLOG(5)) THEN
        WRITE (UNIT=6,FMT=140) TEST,LO1MAX,EQUALX,DXMIN
140  FORMAT ('0TEST =',1PE11.4,8X,'LO1MAX =',I4,13X,'EQUALX =',
          *1PE11.4,6X,'DELXMIN =',1PE11.4)
        WRITE (UNIT=6,FMT=141) DXSCAN,DXSTAR,STPSTA,STPMAX,GCMAX
141  FORMAT (' DELXSCAN =',1PE11.4,4X,'DELXSTAR =',1PE11.4,4X,
          *'STEPSTAR =',I4,11X,'STEPMAX =',I4,12X,'GCMAX =',I5)
      END IF
      CALL GRECAL
C-----START LOOPING
2111 WRITE (6,2010)
2010 FORMAT (' PRINT PARAMETERS:')
      YESNO='NO '
      IF (PRTLOG(2)) YESNO='YES'
      WRITE (6,2012) YESNO
2012 FORMAT (' BEFORE CALCULATION: PRINT BULK COMPOSITION: ',A3)
      YESNO='NO '
      IF (PRTLOG(3)) YESNO='YES'

```

```

        WRITE (6,2013) YESNO
2013  FORMAT (21X,'PRINT CONSIDERED PHASES: ',A3)
        YESNO='NO '
        IF (PRTLOG(4)) YESNO='YES'
        WRITE (6,2014) YESNO
2014  FORMAT (21X,'PRINT SOLUTION MODELS: ',A3)
        YESNO='NO '
        IF (PRTLOG(6)) YESNO='YES'
        WRITE (6,2016) YESNO
2016  FORMAT (' AFTER CALCULATION: PRINT STABLE ASSEMBLAGE: ',A3)
        YESNO='NO '
        IF (PRTLOG(7)) YESNO='YES'
        WRITE (6,2017) YESNO
2017  FORMAT (20X,'PRINT COMPOSITIONS OF STABLE PHASES: ',A3)
        YESNO='NO '
        IF (PRTLOG(8)) YESNO='YES'
        WRITE (6,2018) YESNO
2018  FORMAT (20X,'PRINT ACTIVITIES OF ALL PHASES: ',A3)
        WRITE (UNIT=6,FMT=2020) P,PGAS,TC,T
2020  FORMAT ('0P =',F9.2,' bar    P(Gas) =',F9.2,' bar    T =',
        *F8.2,' C    = ',F8.2,' K')
        WRITE (6,2022) CHNAME(1),CHEM(CHMCD(1))
2022  FORMAT ('0BULK COMPOSITION: ',A8,1X,F11.6)
        DO 605,I=2,NUN
        WRITE (6,2023) CHNAME(I),CHEM(CHMCD(I))
2023  FORMAT (19X,A8,1X,F11.6)
        605  CONTINUE
        WRITE (6,2000)
2000  FORMAT ('0TP:NEW T AND P/' BULK:NEW BULK',
        >/' PARA: NEW PARAMETERS/' THER: CALL THERIAK'/)
        READ (UNIT=5,FMT='(A170)',END=2099) CH001
        IF (CH001.EQ.'TP') THEN
        WRITE (6,2001)
2001  FORMAT (' ENTER NEW T AND P')
        READ (5,*,END=2099) TC,P
        CALL GRECAL
        END IF
        IF (CH001.EQ.'BULK') THEN
        WRITE (6,2002)
2002  FORMAT (' ENTER NEW FORMULA.:')
        READ (UNIT=5,FMT='(A170)',END=2099) FORMUL
        CALL CHEMIE(COMAY,NC,OXYDE,FORMUL,CHE)
        MORE=.FALSE.
        DO 601,I=1,NC
        IF (CHE(I).EQ.0.0D0.NEQV.CHEM(I).EQ.0.0D0) MORE=.TRUE.
        CHEM(I)=CHE(I)
        601  CONTINUE
        IF (MORE) THEN
        WRITE (6,FMT='('' RE-READ DATABASE'')')
        CALL DBREAD
        CALL GRECAL
        ELSE
        DO 602,I=1,NUN
        602  BULK(I)=CHE(CHMCD(I))

```

```

END IF
END IF
IF (CH001.EQ.'PARA') THEN
WRITE (6,2030)
2030 FORMAT (' PRINT BULK COMPOSITION?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(2)=.TRUE.
ELSE
PRTLOG(2)=.FALSE.
END IF
WRITE (6,2031)
2031 FORMAT (' PRINT CONSIDERED PHASES ?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(3)=.TRUE.
ELSE
PRTLOG(3)=.FALSE.
END IF
WRITE (6,2032)
2032 FORMAT (' PRINT SOLUTION MODELS ?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(4)=.TRUE.
ELSE
PRTLOG(4)=.FALSE.
END IF
WRITE (6,2033)
2033 FORMAT (' PRINT STABLE ASSEMBLAGE ?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(6)=.TRUE.
ELSE
PRTLOG(6)=.FALSE.
END IF
WRITE (6,2034)
2034 FORMAT (' PRINT COMPOSITIONS OF STABLE PHASES ?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(7)=.TRUE.
ELSE
PRTLOG(7)=.FALSE.
END IF
WRITE (6,2035)
2035 FORMAT (' PRINT ACTIVITIES OF ALL PHASES ?')
READ (UNIT=5,FMT='(A3)') YESNO
IF (YESNO(1:1).EQ.'Y') THEN
PRTLOG(8)=.TRUE.
ELSE
PRTLOG(8)=.FALSE.
END IF
END IF
IF (CH001.EQ.'THER') THEN
CALL CALSTR

```

```

      IF (PRTLOG(2).OR.PRTLOG(3).OR.PRTLOG(4)) CALL PRININ
      CALL THERIA
      END IF
      GOTO 2111
2099 CONTINUE
      END
C-----
C*****
      SUBROUTINE DBREAD
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
      LOGICAL*4 IDCODE,FILEND
      INTEGER*4 I001,I,I1,I2,I5
      CHARACTER*3 SECTIO
C-----COMMON BLOCK FOR SAVING INPUT DATA
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      REWIND (UNIT=8)
      NUN=0
      DO 505,I=1,NC
      IF (CHEM(I).NE.0.0D0) THEN
      NUN=NUN+1
      IF (NUN.GT.COMAX) THEN
      WRITE (UNIT=6,FMT='(' COMAX=',15)' NUN=',15') COMAX,NUN
      STOP
      END IF
      CHMCO(NUN)=I
      END IF
505 CONTINUE
      IF (NUN.LE.0) THEN
      WRITE (UNIT=6,FMT='(' NUN=',15)' NUN
      STOP
      END IF
      DO 507,I=1,NUN
      I001=INDEX(OXYDE(CHMCO(I)), ' ')
      NAME(I)=' '//OXYDE(CHMCO(I))(1:I001-1)//' '
      ABK(I)=OXYDE(CHMCO(I))
      DO 506,I1=1,COMAX
506 XX(I,I1)=0.0D0
      XX(I,I)=1.0D0
      EMSOL(I)=0
      EMNR(I)=0
      BULK(I)=CHEM(CHMCO(I))
507 CHNAME(I)=OXYDE(CHMCO(I))
      NPHA=NUN
      SUGNR=NUN
C-----
C-----START READING DATABASE
C-----
      FILEND=.FALSE.

```



```

      NSOL=0
      GOTO 5011
C-----START END-FILE ACTION
5010 RECODE='***'
      FILEND=.TRUE.
      REC='** ENDFILE **'
      GOTO 5012
C-----END OF END-FILE ACTION
5011 DO 508,I=1,8
      508 GENUG(I)=.FALSE.
      SECTIO='BAH'
1002 RECODE=' '
C-----SKIP BLANK AND COMMENT RECORDS
1003 IF (RECODE.NE.' ' .AND.RECODE(1:1).NE.'!') GOTO 3
      READ (UNIT=8,FMT='(A250)',END=5010) REC
      CALL FIBLA(REC,I1)
      IF (I1.NE.0) RECODE=REC(I1:I1+2)
      GOTO 1003
C-----
      3 IDCODE=.FALSE.
      IF (SECTIO.EQ.'MIN') IDCODE=(INDEX(REC,'(').NE.0)
      IF (SECTIO.EQ.'SOL') IDCODE=(INDEX(REC,'(').NE.0)
      IF (SECTIO.EQ.'MAR') IDCODE=(INDEX(REC,' - ').NE.0)
5012 IF (RECODE.EQ.'***'.OR.IDCODE) THEN
      IF (GENUG(1)) THEN
      IF (SECTIO.EQ.'MIN') THEN
      CALL MINFIN
      CALL DASAVE(NPHA)
      END IF
      IF (SECTIO.EQ.'SOL') CALL SOLFIN
      DO 518,I=1,8
518 GENUG(I)=.FALSE.
      END IF
      IF (RECODE.EQ.'***') THEN
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT='(''0'',A132)') REC
      IF (FILEND.OR.INDEX(REC,'END').NE.0.OR.
      *INDEX(REC,'FINISH').NE.0) GOTO 999
      SECTIO='BAH'
      IF (INDEX(REC,'MINERAL DATA').NE.0.OR.
      *INDEX(REC,'GAS DATA').NE.0) SECTIO='MIN'
      IF (INDEX(REC,'SOLUTION DATA').NE.0) SECTIO='SOL'
      IF (INDEX(REC,'MARGULES').NE.0) THEN
      DO 519,IS=1,NSOL
519 IF (MARCOD(IS)) GOTO 5
      5 IF (IS.LE.NSOL) THEN
      SECTIO='MAR'
      ELSE
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT=105)
105 FORMAT (1X,'NO SOLUTION PHASE IS EXPECTING MARGULES-PARAMETERS')
      END IF
      ELSE
      IF (SECTIO.EQ.'BAH'.AND.PRTLOG(1)) WRITE (UNIT=6,FMT=106)
106 FORMAT (1X,'SECTION NOT READ: DATA NOT RECOGNIZED BY THERIAK')
      END IF

```

```

ELSE
  IF (SECTION.EQ.'MIN') CALL MINNEW
  IF (SECTION.EQ.'SOL') CALL SOLNEW
  IF (SECTION.EQ.'MAR') CALL MARNEW
END IF
ELSE
  IF (GENUG(1)) THEN
    IF (SECTION.EQ.'MIN') CALL MINDAT
    IF (SECTION.EQ.'SOL') CALL SOLDAT
    IF (SECTION.EQ.'MAR') CALL MARDAT
  END IF
END IF
GOTO 1002

C-----
C-----END OF READING DATABASE
  999 RETURN
  END

C-----
C*****
  SUBROUTINE GRECAL
    INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
    PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
    INTEGER*4 I001,I,II,IS
C-----COMMON BLOCK FOR SAVING INPUT DATA
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
    T=TC+273.15D0
    IF (T.LE.0.0) THEN
      WRITE (UNIT=6,FMT='('' T ='',F8.2)') T
      STOP
    END IF
    IF (P.LT.0.0) THEN
      WRITE (UNIT=6,FMT='('' P ='',F9.2)') P
      STOP
    END IF
    PGAS=P*PRAT
    RT=R*T
    TT=T*T
    SQT=DSQRT(T)
    DO 601,II=1,NUN
601  GGK(II)=0.0D0
    DO 600,II=(NUN+1),NPHA
      I001=II
      CALL DAREST(I001)
      NAM=NAME(II)
      IF (SPC) THEN
        CALL GSPEC(NAM,P,PGAS,T,CASE,GR)
      ELSE
        LIQ=.FALSE.
      CALL GCALC

```

```

      END IF
      DO 650,I=1,NCOM
      IF (COM) THEN
      DO 650,I=1,NCOM
      GR=GR+FCOM(I)*CGK(ICOM(I))
      END IF
      CGK(II)=GR
      600 CONTINUE
      DO 610,IS=1,NSOL
      DO 610,I=1,NMARG(IS)
      WG(IS,I)=WH(IS,I)+WCP(IS,I)*(T-T0)
      >-(WS(IS,I)+DLOC(T/T0)*WCP(IS,I))*T+WW(IS,I)*P
      610 CONTINUE
      RETURN
      END
C-----C
      SUBROUTINE FIBLA(CH,II)
      CHARACTER*(*) CH
      INTEGER*4 II,LAE
      LAE=LEN(CH)
      DO 501,I=1,LAE
      DO 501 IF (CH(I:I).NE.' ') GOTO 1
      1 II=I
      IF (II.EQ.LAE+1) II=0
      RETURN
      END
C-----C
      SUBROUTINE CELI(CH,FF)
      CHARACTER*(*) CH
      CHARACTER*250 CH001
      CHARACTER*16 CH016
      REAL*8 FF
      INTEGER*4 I001,LAE
      LAE=LEN(CH)
      I001=INDEX(CH001,' ')
      CH016=CH(I001:1)
      READ (UNIT=CH016,FMT='(BN,D16.0)') FF
      CH=CH001(I001:)
      RETURN
      END IF
      CH001=CH(I001:)
      I001=INDEX(CH001,' ')
      CH016=CH001(1:I001-1)
      READ (UNIT=CH016,FMT='(BN,D16.0)') FF
      CH=CH001(I001:)
      RETURN
      END
C-----C
      SUBROUTINE TAXI(REC,CHST)
      CHARACTER*(*) REC
      CHARACTER*250 CH001
      CHARACTER*(*) CHST
      INTEGER*4 I1

```

```

CALL FIBLA(REC,I1)
IF (I1.EQ.0) THEN
  CHST=' '
  RETURN
END IF
CH001=REC(I1:)
I1=INDEX(CH001,' ')
CHST=CH001(1:I1-1)
REC=CH001(I1:)
RETURN
END

```

C-----

C*****

```

SUBROUTINE CHEMIE(COMAY,NC,OXYDE,FORMUL,CHE)
  INTEGER*4 I,I1,I2,I3,NC,COMAY
  CHARACTER*170 FORMUL,CH170
  CHARACTER*8 ELE,OXYDE(COMAY)
  REAL*8 CHE(COMAY),FF
  DO 501,I=1,COMAY
501 CHE(I)=0.0
  CALL FIBLA(FORMUL,I1)
1001 IF (I1.EQ.0) GOTO 2
  I2=INDEX(FORMUL,'(')
  I3=INDEX(FORMUL,')')
  IF (I2.LE.I1) I2=I1+1
  IF (I3.LE.I2+1) I3=I2+2
  ELE=FORMUL(I1:I2-1)
  DO 502,I=1,NC
502 IF (ELE.EQ.OXYDE(I)) GOTO 1
  1 IF (I.EQ.NC+1) THEN
    WRITE (UNIT=6,FMT=100) FORMUL,ELE
100 FORMAT (' *** ',A170" *** ELE= ',A8)
    STOP
  END IF
  CH170=FORMUL(I2+1:I3-1)
  READ (UNIT=CH170,FMT='(BN,D16.0)') FF
  CHE(I)=CHE(I)+FF
  CH170=FORMUL
  FORMUL=CH170(I3+1:)
  CALL FIBLA(FORMUL,I1)
  GOTO 1001
  2 RETURN
END

```

C-----

C*****

```

SUBROUTINE MINNEW
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES

```

```

INTEGER*4 COMAY,I,II,I001
CHARACTER*60 REJECT
CHARACTER*15 USECOD
COMAY=COMAX
CALL TAXI(REC,NAM)
CALL TAXI(REC,FORMUL)
CALL TAXI(REC,FORM)
CALL TAXI(REC,USECOD)
IF (USECOD.EQ.' ') USECOD='N'
GENUG(1)=.FALSE.
NULL(NPHA+1)=.FALSE.
CALL CHEMIE(COMAY,NC,OXYDE,FORMUL,CHE)
DO 520,I=1,LUSE
IF (GENUG(1).OR.USE(I:I).EQ.',') GO TO 9
520 GENUG(1)=(INDEX(USECOD,USE(I:I)).NE.0.OR.USE.EQ.'*')
9 IF (USECOD(1:1).EQ.'*') THEN
USECOD(1:1)=' '
I001=INDEX(USECOD,' ')
GENUG(1)=(INDEX(USE,USECOD(1:I001-1)).NE.0)
END IF
IF (.NOT.GENUG(1))
*REJECT='CODE NOT MATCHING : '//USECOD/'"'
DO 521,II=1,NPHA
IF (.NOT.GENUG(1)) GO TO 10
IF (NAM.EQ.NAME(II)) THEN
GENUG(1)=.FALSE.
REJECT='DEFINED MORE THAN ONCE IN DATABASE'
END IF
521 CONTINUE
10 DO 522,II=1,NC
IF (.NOT.GENUG(1)) GO TO 11
GENUG(1)=(CHE(II).EQ.0.0.OR.CHEM(II).NE.0.0)
IF (.NOT.GENUG(1).AND.USECOD(1:1).EQ.'+') THEN
DO 702,I=1,NC
702 CHE(I)=0.0D0
GENUG(1)=.TRUE.
NULL(NPHA+1)=.TRUE.
GOTO 11
END IF
IF (.NOT.GENUG(1)) REJECT='COMPOSITION OUTSIDE DEFINED SPACE'
522 CONTINUE
11 IF (GENUG(1)) THEN
GOR=0.0D0
HOR=0.0D0
SOR=0.0D0
VOR=0.0D0
AA0=0.0D0
AAT=0.0D0
BB0=0.0D0
BBT=0.0D0
K1=0.0D0
K2=0.0D0
K3=0.0D0
K4=0.0D0

```

```

      K5=0.0D0
      K6=0.0D0
      K7=0.0D0
      K8=0.0D0
      K9=0.0D0
      NLANDA=0
      NCOM=0
      DO 523,I=1,10
      ICOM(I)=0
523  FFCOM(I)=0.0D0
      DO 517,I=1,4
      ASPK(I)=0.0D0
      BSPK(I)=0.0D0
      TQ1B(I)=0.0D0
      TEQ(I)=0.0D0
      DVDT(I)=0.0D0
      DVDP(I)=0.0D0
      TRE(I)=0.0D0
      DHTR(I)=0.0D0
517  DVTR(I)=0.0D0
      TD0=0.0D0
      TDMAX=0.0D0
      VADJ=0.0D0
      D1=0.0D0
      D2=0.0D0
      D3=0.0D0
      D4=0.0D0
      D5=0.0D0
      D6=0.0D0
      D7=0.0D0
      D8=0.0D0
      D9=0.0D0
      CASE=' '
      RDK=.FALSE.
      VDW=.FALSE.
      SPC=.FALSE.
      COM=.FALSE.
      DIS=.FALSE.
      ELSE
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT=107) NAM,REJECT
107  FORMAT (' ----->',A16,' : ',A60)
      END IF
      RETURN
      END
C-----
C*****
      SUBROUTINE MINDAT
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK

```

C-----END OF COMMON VARIABLES

```

      INTEGER*4 I
      IF (RECODE.EQ.'ST ') THEN
        READ (UNIT=REC,FMT='(5X,4D15.0)') G0R,H0R,S0R,V0R
        GENUG(2)=.TRUE.
        V0R=V0R/10.0D0
      END IF
      IF (RECODE.EQ.'R-K') THEN
        READ (UNIT=REC,FMT='(5X,4D15.8)') AA0,AAT,BB0,BBT
        RDK=.TRUE.
        VDW=.FALSE.
      END IF
      IF (RECODE.EQ.'VDW') THEN
        READ (UNIT=REC,FMT='(5X,4D15.8)') AA0,AAT,BB0,BBT
        VDW=.TRUE.
        RDK=.FALSE.
      END IF
      IF (RECODE.EQ.'CP1') THEN
        READ (UNIT=REC,FMT='(5X,4D15.0)') K1,K4,K3,K8
        GENUG(3)=.TRUE.
      END IF
      IF (RECODE.EQ.'CP3') THEN
        READ (UNIT=REC,FMT='(5X,3D15.0)') K1,K2,K3
        GENUG(3)=.TRUE.
      END IF
      IF (RECODE.EQ.'CP2') THEN
        READ (UNIT=REC,FMT='(5X,5D15.0)') K6,K2,K5,K7,K9
      END IF
      IF (RECODE.EQ.'D1') THEN
        READ (UNIT=REC,FMT='(5X,5D15.0)') D1,D4,D3,VADJ,D6
        DIS=.TRUE.
      END IF
      IF (RECODE.EQ.'D2') THEN
        READ (UNIT=REC,FMT='(5X,4D15.0)') D2,D5,TD0,TDMAX
      END IF
      IF (RECODE.EQ.'SPC') THEN
        CALL TAXI(REC,CH)
        CALL TAXI(REC,CASE)
        SPC=.TRUE.
        GENUG(2)=.TRUE.
        GENUG(3)=.TRUE.
      END IF
      IF (RECODE.EQ.'COM') THEN
        CALL TAXI(REC,CH)
        CALL TAXI(REC,FORMUL)
        COM=.TRUE.
      END IF
      IF (RECODE.EQ.'TR1') THEN
        NLANDA=NLANDA+1
        I=NLANDA
        READ (UNIT=REC,FMT='(5X,5D15.0)') TQ1B(I),TRE(I),ASPK(I),
        *BSPK(I),DHTR(I)
      END IF
      IF (RECODE.EQ.'TR2') THEN

```

```

      IF (NLANDA.GT.0) THEN
      I=NLANDA
      READ (UNIT=REC,FMT='(5X,4D15.0)') TEQ(I),DVTR(I),DVDT(I),
      *DVDP(I)
      END IF
      END IF
      RETURN
      END
C-----
C*****
      SUBROUTINE MINFIN
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 I,IX,I001,I1,I2
      REAL*8 FF
      CHARACTER*170 MODEL1
      CHARACTER*16 EMNAM
      IF (GENUG(1).AND.GENUG(2).AND.GENUG(3)) THEN
      NPHA=NPHA+1
      IF (NPHA.GT.PHMAX.OR.NPHA.GT.CALMAX) THEN
      WRITE (UNIT=6,FMT=100) PHMAX,CALMAX,NPHA
100  FORMAT (' PHMAX=',I5/ ' CALMAX=',I5/ ' NPHA=',I5)
      STOP
      END IF
      IF (COM) THEN
      NCOM=0
      CALL FIBLA(FORMUL,I1)
2001 IF (I1.EQ.0) GOTO 71
      I2=INDEX(FORMUL,'I')
      IX=INDEX(FORMUL,'J')
      IF (I2.LE.I1) I2=I1+1
      IF (IX.LE.I2+1) IX=I2+2
      EMNAM=FORMUL(I1:I2-1)
      DO 701,I=1,(NPHA-1)
701 IF (EMNAM.EQ.NAME(I)) GOTO 72
72 IF (I.EQ.NPHA) THEN
      WRITE (UNIT=6,FMT=300) FORMUL,EMNAM
300  FORMAT (' *** ',A170/ ' *** NAME= ',A16)
      STOP
      END IF
      MODEL1=FORMUL(I2+1:IX-1)
      READ (UNIT=MODEL1,FMT='(BN,D16.0)') FF
      NCOM=NCOM+1
      ICOM(NCOM)=I
      FFCOM(NCOM)=FF
      MODEL1=FORMUL
      FORMUL=MODEL1(IX+1:)
      CALL FIBLA(FORMUL,I1)

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```

      GOTO 2001
      END IF
71  CONTINUE
      SUGNR=SUGNR+1
      NAME(NPHA)=NAM
      ABK(NPHA)=FORM
      DO 705,I=1,NUN
705  XX(NPHA,I)=CHE(CHMCO(I))
      EMSOL(NPHA)=0
      EMNR(NPHA)=0
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT='(1X,A16," O.K.")' ) NAM
      ELSE
      IF (PRTLOG(1)) WRITE(UNIT=6,FMT=101) NAM
101  FORMAT (' ----->',A16,' : NOT ENOUGH DATA')
      END IF
      RETURN
      END
C-----
C*****
      SUBROUTINE SOLNEW
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 I,K
      REAL*8 FF
      K=NSOL+1
      NEND(K)=0
      CALL TAXI(REC,SONAM)
      CALL TAXI(REC,MODCOD)
      IF (INDEX(MODCOD,'SKIP').NE.0) THEN
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT=108) SONAM
108  FORMAT (' ----->',A16,' : EXPLICITLY EXCLUDED')
      GOTO 40
      END IF
      CALL GELI(REC,FF)
      NSITE(K)=IDINT(FF)
      IF (NSITE(K).GT.SITMAX) THEN
      WRITE (UNIT=6,FMT=109) SITMAX,K,NSITE(K)
109  FORMAT (' SITMAX=',I5/1X,I5,' : NSITE=',I5)
      STOP
      END IF
      DO 523,I=1,NSITE(K)
523  CALL GELI(REC,SITMUL(K,I))
      GENUG(1)=.TRUE.
      40  CONTINUE
      RETURN
      END
C-----
C*****

```

```

SUBROUTINE SOLDAT
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
  INTEGER*4 I,II,III,K
  CHARACTER*16 EMNAM
  K=NSOL+1
  II=NEND(K)+1
  CALL TAXI(REC,EMNAM)
  DO 526,I=1,NSITE(K)
    CALL TAXI(REC,CH)
526  SITEL(K,II,I)=CH
    DO 527,III=1,NPHA
527  IF (NAME(III).EQ.EMNAM.AND.(.NOT.NULL(III))) GO TO 15
15  IF (III.LE.NPHA) THEN
    NEND(K)=NEND(K)+1
    IF (NEND(K).GT.EMAX) THEN
      WRITE (UNIT=6,FMT=110) EMAX,K,NEND(K)
110  FORMAT (' EMAX=',I5/1X,I5,' : NEND=',I5)
      STOP
    END IF
    EM(K,NEND(K))=III
    IF (PRTLOG(1)) WRITE (UNIT=6,FMT=111) SONAM,EMNAM
111  FORMAT (1X,A16,': ',A16,' O.K.')
    ELSE
    IF (PRTLOG(1)) WRITE (UNIT=6,FMT=112) SONAM,EMNAM
112  FORMAT (1X,A16,' ----->',A16,' NOT A CONSIDERED PHASE')
    END IF
    RETURN
  END
C-----
C*****
  SUBROUTINE SOLFIN
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
  INTEGER*4 I,II,IE,IR001(EMAX),I001,I002,I003,I1,K
  REAL*8 FF
  K=NSOL+1
  IF (NEND(K).GT.1) THEN
    NSOL=K
    IF (NSOL.GT.SOMAX) THEN
      WRITE (UNIT=6,FMT='('' SOMAX=',I5/'' NSOL=',I6)') SOMAX,NSOL
    STOP

```

```

END IF
ALPHA(K)=1.0D0
ALPDIV(K)=' '
I1=INDEX(MODCOD,'/')
IF (I1.NE.0) ALPDIV(K)=MODCOD(I1:)
IF (NSITE(K).EQ.0.AND.INDEX(MODCOD,'SITE').NE.0) MODCOD=' '
IF (INDEX(MODCOD,'SITE').EQ.0.AND.INDEX(MODCOD,'EXT').EQ.0)
* MODELL(K)='I'
IF (INDEX(MODCOD,'SITE').NE.0) THEN
I=1
DO 509,I001=1,EMAX
DO 509,I002=1,SITMAX
NEQEM(K,I001,I002)=0
DO 509,I003=1,EMAX
509 EQEM(K,I001,I002,I003)=0
MODELL(K)='S'
1007 IF (I.GT.NSITE(K)) GO TO 7
DO 514,IE=1,NEND(K)
DO 512,II=1,NEND(K)
IF (SITE(K,IE,I).EQ.SITE(K,II,I)) THEN
NEQEM(K,IE,I)=NEQEM(K,IE,I)+1
EQEM(K,IE,I,NEQEM(K,IE,I))=II
END IF
512 CONTINUE
IF (NEQEM(K,IE,I).EQ.NEND(K)) THEN
SITMUL(K,I)=SITMUL(K,NSITE(K))
DO 513,I001=1,EMAX
513 SITE(K,I001,I)=SITE(K,I001,NSITE(K))
NSITE(K)=NSITE(K)-1
I=I-1
GO TO 6
END IF
514 CONTINUE
6 I=I+1
GO TO 1007
7 IF (NSITE(K).EQ.1) THEN
MODELL(K)='I'
ALPHA(K)=SITMUL(K,1)
END IF
END IF
IF (INDEX(MODCOD,'EXT').NE.0) THEN
MODELL(K)='F'
DO 515,IE=1,NEND(K)
515 MANAM(IE)=NAME(EM(K,IE))
CALL SOLINI(SONAM,NEND(K),MANAM,NEMBAS(K),IR001)
DO 710,IE=1,NEMBAS(K)
710 EMBCOD(K,IE)=IR001(IE)
IF (NEMBAS(K).LT.0) THEN
WRITE (UNIT=6,FMT=102) SONAM,NAME(EM(K,-NEMBAS(K)))
102 FORMAT (1X,A16,' :THERE IS NO DATA FOR ',A16,
*' IN SUBROUTINE')
STOP
END IF
END IF

```

```

      IF (MODELL(K).EQ.'I') SITMUL(K,1)=ALPHA(K)
      IF ((MODELL(K).EQ.'I'.OR.MODELL(K).EQ.'S').AND.
      *ALPDIV(K).NE.' ') THEN
      CALL GELI(ALPDIV(K)(2:),FF)
      ALPHA(K)=ALPHA(K)/FF
      END IF
      SOLNAM(NSOL)=SONAM
      DO 516,I=1,NEND(NSOL)
      EMSOL(EM(NSOL,I))=NSOL
516  EMNR(EM(NSOL,I))=I
      IF (PRTLOG(1)) THEN
      WRITE (UNIT=6,FMT=103) SONAM,(NAME(EM(K,I)),I=1,NEND(K))
103  FORMAT (1X,A16,' O.K., ENDMEMBERS: ',100(5(2X,A16)/35X))
      END IF
      MARCOD(NSOL)=(INDEX(MODCOD,'MARGULES').NE.0)
      NMARG(NSOL)=0
      ELSE
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT=104) SONAM
104  FORMAT (' ----->',A16,' : LESS THAN TWO ENDMEMBERS')
      END IF
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT='('' ''')
      RETURN
      END

C-----
C*****
      SUBROUTINE MARNEW
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 I
      DO 524,I=2,254
524  IF (REC(I-1:I+1).EQ.' - ') REC(I-1:I+1)=' '
      DO 525,I=1,EMAX
      CALL TAXI(REC,MANAM(I))
525  IF (MANAM(I).EQ.' ') GO TO 13
13  DIM=I-1
      NPAR=0
      IF (DIM.GT.1) GENUG(1)=.TRUE.
      RETURN
      END

C-----
C*****
      SUBROUTINE MARDAT
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR G-CALCULATION

```

C-----COMMON BLOCK FOR THERIAK

C-----END OF COMMON VARIABLES

```

      INTEGER*4 I,IIND(MPOMAX),IND(MPOMAX),POL,IS,I001,K
      REAL*8 WWCP,WWH,WWWS,WWW
      LOGICAL*4 CODE
      NPAR=NPAR+1
      CALL TAXI(REC,CH)
      POL=INDEX(CH,' ')-1
      READ (UNIT=CH,FMT='(10011)') (IIND(I),I=1,POL)
      CALL GELI(REC,WWH)
      CALL GELI(REC,WWWS)
      CALL GELI(REC,WWW)
      CALL GELI(REC,WWCP)
      DO 532,IS=1,NSOL
      IF (MARCOD(IS)) THEN
      CODE=.TRUE.
      DO 529,I=1,DIM
      IF (.NOT.CODE) GO TO 17
      DO 528,K=1,NEND(IS)
528 IF (MANAM(I).EQ.NAME(EM(IS,K))) GO TO 16
      16 IND(I)=K
      CODE=(K.NE.NEND(IS)+1)
529 CONTINUE
      17 IF (CODE) THEN
      NMARG(IS)=NMARG(IS)+1
      IF (NMARG(IS).GT.MAMAX) THEN
      WRITE (UNIT=6,FMT=113) MAMAX,IS,NMARG(IS)
113 FORMAT (' MAMAX=',I5/1X,I5,' : NMARG=',I5)
      STOP
      END IF
      POLY(IS,NMARG(IS))=POL
      IF (POL.GT.MPOMAX) THEN
      WRITE (UNIT=6,FMT=114) MPOMAX,IS,POL
114 FORMAT (' MPOMAX=',I5/1X,I5,' : POL=',I5)
      STOP
      END IF
      DO 530,I001=1,EMAX
530 QQ(IS,NMARG(IS),I001)=0
      DO 531,I=1,POL
      INDX(IS,NMARG(IS),I)=IND(IIND(I))
531 QQ(IS,NMARG(IS),IND(IIND(I)))=QQ(IS,NMARG(IS),IND(IIND(I)))+1
      WH(IS,NMARG(IS))=WWH
      WS(IS,NMARG(IS))=WWWS
      WV(IS,NMARG(IS))=WWW
      WCP(IS,NMARG(IS))=WWCP
C      WC(IS,NMARG(IS))=WWH+WWCP*(T-T0)-(WWWS+DLOG(T/T0)*WWCP)*T+WWW*P
      IF (PRTLOG(1)) WRITE (UNIT=6,FMT='(1X,A16," : MARGULES-",
      *"PARAMETER ",10011)') SOLNAM(IS),(IIND(I),I=1,POL)
      END IF
      END IF
532 CONTINUE
      RETURN
      END

```

C-----

```

C*****
      SUBROUTINE GCALC
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR G-CALCULATION
C-----END OF COMMON VARIABLES
      REAL*8 CPRDT,CPRTDT,TD,VD
      INTEGER*4 I,I001
      CPRDT=K1*(T-T0)+K2*(TT-TT0)/2.0D0
      *-K3*(1.0D0/T-1.0D0/TT)+2D0*K4*(SQT-SQT0)
      *+K5*(TT*T-TT0*T0)/3.0D0+K6*DLOG(T/T0)
      *+K7*(T*SQT-T0*SQT0)*2.0D0/3.0D0
      *-K8*(1.0D0/(TT)-1.0D0/(TT0))/2.0D0
      *+K9*(TT*TT-TT0*TT0)/4.0D0
      CPRTDT=K1*DLOG(T/T0)+K2*(T-T0)
      *-K3*(1.0D0/(TT)-1.0D0/(TT0))/2.0D0
      *-2D0*K4*(1.0D0/SQT-1.0D0/SQT0)
      *+K5*(TT-TT0)/2.0D0-K6*(1.0D0/T-1.0D0/TT)
      *+2D0*K7*(SQT-SQT0)
      *-K8*(1.0D0/(TT*T)-1.0D0/(TT0*T0))/3.0D0
      *+K9*(TT*T-TT0*T0)/3.0D0
      GR=H0R+CPRDT-T*(S0R+CPRTDT)
      IF (RDK.OR.VDW) THEN
      CALL GAS
      ELSE
      GR=GR+V0R*(P-P0)
      END IF
      DO 510,I=1,NLANDA
      I001=I
510 CALL LANDA(I001)
      IF (DIS.AND.TD0.NE.0.0D0.AND.TDMAX.NE.0.0D0.AND.T.GT.TD0) THEN
      TD=DMIN1(T,TDMAX)
      CPRDT=D1*(TD-TD0)+D2*(TD*TD-TD0*TD0)/2.0D0
      *-D3*(1.0D0/TD-1.0D0/TD0)+2D0*D4*(DSQRT(TD)-DSQRT(TD0))
      *+D5*(TD**3-TD0**3)/3.0D0+D6*DLOG(TD/TD0)
      *+D7*(TD*DSQRT(TD)-TD0*DSQRT(TD0))*2.0D0/3.0D0
      *-D8*(1.0D0/(TD*TD)-1.0D0/(TD0*TD0))/2.0D0
      *+D9*(TD**4-TD0**4)/4.0D0
      CPRTDT=D1*DLOG(TD/TD0)+D2*(TD-TD0)
      *-D3*(1.0D0/(TD*TD)-1.0D0/(TD0*TD0))/2.0D0
      *-2D0*D4*(1.0D0/DSQRT(TD)-1.0D0/DSQRT(TD0))
      *+D5*(TD*TD-TD0*TD0)/2.0D0-D6*(1.0D0/TD-1.0D0/TD0)
      *+2D0*D7*(DSQRT(TD)-DSQRT(TD0))
      *-D8*(1.0D0/(TD**3)-1.0D0/(TD0**3))/3.0D0
      *+D9*(TD**3-TD0**3)/3.0D0
      IF (DABS(VADJ).GT.10.0D0) THEN
      VD=CPRDT/(10.0D0*VADJ)
      ELSE
      VD=0.0D0
      END IF
      GR=GR+CPRDT-(T*CPRTDT)+VD*(P-1.0D0)
      END IF

```

```

      RETURN
      END
C-----
C*****
      SUBROUTINE GAS
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR G-CALCULATION
      REAL*8 AA,BB,DGGAS
      COMMON /GORE/ AA,BB,DGGAS
C-----END OF COMMON VARIABLES
      REAL*8 KUB,KUC,KUD,OFT,VREF,VOL,VGAS,VFL,X1,X2,X2I,X3,F001
      AA=AA0+T*AAT
      BB=BB0+T*BBT
      IF (PGAS.LE.0.0D0) THEN
      WRITE (UNIT=6,FMT='(' PGAS=',',F8.2)') PGAS
      STOP
      END IF
      IF (RDK) THEN
      OFT=P0*SQT
      KUB=-10.0D0*RT/P0
      KUC=AA/OFT-BB*BB+BB*KUB
      KUD=-AA*BB/OFT
      END IF
      IF (VDW) THEN
      KUB=-BB-10.0D0*RT/P0
      KUC=AA/P0
      KUD=-AA*BB/P0
      END IF
      CALL KUBIK(KUB,KUC,KUD,X1,X2,X2I,X3)
      IF (X2I.NE.0.0D0) THEN
      VREF=X1
      ELSE
      VREF=DMAX1(X1,X2,X3)
      END IF
      IF (RDK) THEN
      OFT=PGAS*SQT
      KUB=-10.0D0*RT/PGAS
      KUC=AA/OFT-BB*BB+BB*KUB
      KUD=-AA*BB/OFT
      END IF
      IF (VDW) THEN
      KUB=-BB-10.0D0*RT/PGAS
      KUC=AA/PGAS
      KUD=-AA*BB/PGAS
      END IF
      CALL KUBIK(KUB,KUC,KUD,X1,X2,X2I,X3)
      IF (X2I.NE.0.0D0) THEN
      VOL=X1
      ELSE
      VGAS=DMAX1(X1,X2,X3)
      VFL=DMIN1(X1,X2,X3)

```

```

DGGAS=-1D0
F001=PGAS
IF (VFL.GT.BB) CALL DELGAS(VFL,VGAS,PGAS,F001)
IF (DGGAS.GT.0.0D0) THEN
  LIQ=.TRUE.
  VOL=VFL
ELSE
  VOL=VGAS
END IF
END IF
CALL DELGAS(VREF,VOL,P0,PGAS)
GR=GR+DGGAS
RETURN
END

C-----
C*****
      SUBROUTINE DELGAS(V1,V2,P1,P2)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
        *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR G-CALCULATION
      REAL*8 AA,BB,DGGAS
      COMMON /GORE/ AA,BB,DGGAS
C-----END OF COMMON VARIABLES
      REAL*8 V1,V2,P1,P2
      IF (RDK) DGGAS=V2*P2-V1*P1-10*RT*DLOG((V2-BB)/(V1-BB))
      *+(AA/(SQT*BB))*DLOG(V2*(V1+BB)/(V1*(V2+BB)))
      IF (VDW) DGGAS=V2*P2-V1*P1-10*RT*DLOG((V2-BB)/(V1-BB))
      *-AA*(1.0/V2-1.0/V1)
      DGGAS=DGGAS/10.0
      RETURN
      END

C-----
C*****
      SUBROUTINE KUBIK(B,C,D,X1,X2,X2I,X3)
      REAL*8 B,C,D,Q,P,R,PI,PHI3,FF,X1,X2,X2I,X3
      PI=3.14159263538979D0
      IF (C.EQ.0.0D0.AND.D.EQ.0.0D0) THEN
        X1=-B
        X2=0.0D0
        X2I=0.0D0
        X3=0.0D0
        RETURN
      END IF
      Q=((2.D0*B*B*B)/(27.D0)-(B*C)/(3.D0)+D)/2.D0
      P=(3.D0*C-B*B)/(9.D0)
      FF=DABS(P)
      R=DSQRT(FF)
      FF=R*Q
      IF (FF.LT.0.0D0) R=-R
      FF=Q/(R*R*R)
      IF (P.GT.0.0D0) THEN
        PHI3=DLOG(FF+DSQRT(FF*FF+1.D0))/3.D0

```



```

X1=-R*(DEXP(PHI3)-DEXP(-PHI3))-B/(3.D0)
X2I=1D0
ELSE
IF (Q*Q+P*P*P.GT.0.0D0) THEN
PHI3=DLOG(FF+DSQRT(FF*FF-1.D0))/3.D0
X1=-R*(DEXP(PHI3)+DEXP(-PHI3))-B/(3.D0)
X2I=1D0
ELSE
PHI3=DATAN(DSQRT(1.D0-FF*FF)/FF)/3.D0
X1=-2.D0*R*DCOS(PHI3)-B/(3.D0)
X2=2.D0*R*DCOS(PI/3.D0-PHI3)-B/(3.D0)
X2I=0.0D0
X3=2.D0*R*DCOS(PI/3.D0+PHI3)-B/(3.D0)
END IF
END IF
RETURN
END

```

C-----

C*****

```

SUBROUTINE LANDA(K)
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)

```

C-----GLOBAL COMMON BLOCK

C-----COMMON BLOCK FOR G-CALCULATION

C-----END OF COMMON VARIABLES

```

REAL*8 A11,B11,C11,D11,CTR,T9,TR9,DHSPK,DSSPK,GSPK,
*AASP,ABSP,CCTR,TEQK
INTEGER*4 K
TEQK=TEQ(K)*(P-1.0D0)+TQ1B(K)
CTR=TQ1B(K)-TEQK
TR9=TRE(K)-CTR
IF (T.GT.TEQK) THEN
T9=TEQK
ELSE
T9=T
END IF
D11=BSPK(K)*BSPK(K)
AASP=ASPK(K)*ASPK(K)
ABSP=ASPK(K)*BSPK(K)
CCTR=CTR*CTR
A11=AASP*CTR+2.0D0*ABSP*CCTR+D11*CCTR*CTR
B11=AASP+4.0D0*ABSP*CTR+3.0D0*D11*CCTR
C11=2.0D0*ABSP+3.0D0*CTR*D11
DHSPK=A11*(T9-TR9)+B11*(T9*T9-TR9*TR9)/2.0D0
*+C11*(T9**3-TR9**3)/3.0D0+D11*(T9**4-TR9**4)/4.0D0
DSSPK=A11*(DLOG(T9)-DLOG(TR9))+B11*(T9-TR9)
*+C11*(T9*T9-TR9*TR9)/2.0D0+D11*(T9**3-TR9**3)/3.0D0
IF ((T9+CTR).LT.298.15D0) THEN
DHSPK=0.0D0
DSSPK=0.0D0
END IF
GSPK=DHSPK-T9*DSSPK
IF (T.GT.TEQK) GSPK=GSPK-(DHTR(K)/TQ1B(K)+DSSPK)*(T-TEQK)

```

```

GSPK=GSPK+DVDT(K)*(P-1.0D0)*(T9-298.15D0)
*+(DVDP(K)/2.0D0)*(P*P-1.0D0)-DVDP(K)*(P-1.0D0)
GR=GR+GSPK
RETURN
END

```

C-----

C*****

```

SUBROUTINE DASAVE(N)
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)

```

C-----COMMON BLOCK FOR SAVING INPUT DATA

C-----COMMON BLOCK FOR G-CALCULATION

C-----END OF COMMON VARIABLES

```

INTEGER*4 N,I,J

```

```

INDATA(1,N)=NLANDA

```

```

INDATA(2,N)=NCOM

```

```

DO 500,I=1,10

```

```

500 INDATA(I+2,N)=ICOM(I)

```

C-----

```

REDATA(1,N)=G0R

```

```

REDATA(2,N)=H0R

```

```

REDATA(3,N)=S0R

```

```

REDATA(4,N)=V0R

```

```

REDATA(5,N)=AA0

```

```

REDATA(6,N)=AAT

```

```

REDATA(7,N)=BB0

```

```

REDATA(8,N)=BBT

```

```

REDATA(9,N)=K1

```

```

REDATA(10,N)=K2

```

```

REDATA(11,N)=K3

```

```

REDATA(12,N)=K4

```

```

REDATA(13,N)=K5

```

```

REDATA(14,N)=K6

```

```

REDATA(15,N)=K7

```

```

REDATA(16,N)=K8

```

```

REDATA(17,N)=K9

```

```

DO 600,I=1,4

```

```

J=9*(I-1)

```

```

REDATA(J+18,N)=ASPK(I)

```

```

REDATA(J+19,N)=BSPK(I)

```

```

REDATA(J+20,N)=TQ1B(I)

```

```

REDATA(J+21,N)=TEQ(I)

```

```

REDATA(J+22,N)=DVDT(I)

```

```

REDATA(J+23,N)=DVDP(I)

```

```

REDATA(J+24,N)=TRE(I)

```

```

REDATA(J+25,N)=DHTR(I)

```

```

600 REDATA(J+26,N)=DVTR(I)

```

```

REDATA(54,N)=TD0

```

```

REDATA(55,N)=TDMAX

```

```

REDATA(56,N)=VADJ

```

```

REDATA(57,N)=D1

```

```

REDATA(58,N)=D2

```

```

REDATA(59,N)=D3

```

```

      REDATA(60,N)=D4
      REDATA(61,N)=D5
      REDATA(62,N)=D6
      REDATA(63,N)=D7
      REDATA(64,N)=D8
      REDATA(65,N)=D9
      DO 610,I=1,10
610  REDATA(I+65,N)=FFCOM(I)
C-----
      CHDATA(N)=CASE
C-----
      LODATA(1,N)=RDK
      LODATA(2,N)=VDW
      LODATA(3,N)=SPC
      LODATA(4,N)=COM
      LODATA(5,N)=DIS
      RETURN
      END
C-----
C*****
      SUBROUTINE DAREST(N)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----COMMON BLOCK FOR SAVING INPUT DATA
C-----COMMON BLOCK FOR G-CALCULATION
C-----END OF COMMON VARIABLES
      INTEGER*4 N,I,J
      NLANDA=INDATA(1,N)
      NCOM=INDATA(2,N)
      DO 500,I=1,10
500  ICOM(I)=INDATA(I+2,N)
C-----
      G0R=REDATA(1,N)
      H0R=REDATA(2,N)
      S0R=REDATA(3,N)
      V0R=REDATA(4,N)
      AA0=REDATA(5,N)
      AAT=REDATA(6,N)
      BB0=REDATA(7,N)
      BBT=REDATA(8,N)
      K1=REDATA(9,N)
      K2=REDATA(10,N)
      K3=REDATA(11,N)
      K4=REDATA(12,N)
      K5=REDATA(13,N)
      K6=REDATA(14,N)
      K7=REDATA(15,N)
      K8=REDATA(16,N)
      K9=REDATA(17,N)
      DO 600,I=1,4
      J=9*(I-1)
      ASPK(I)=REDATA(J+18,N)
      BSPK(I)=REDATA(J+19,N)

```

```

TQ1B(I)=REDATA(J+20,N)
TEQ(I)=REDATA(J+21,N)
DVDT(I)=REDATA(J+22,N)
DVDP(I)=REDATA(J+23,N)
TRE(I)=REDATA(J+24,N)
DHTR(I)=REDATA(J+25,N)
600 DVTR(I)=REDATA(J+26,N)
TD0=REDATA(54,N)
TDMAX=REDATA(55,N)
VADJ=REDATA(56,N)
D1=REDATA(57,N)
D2=REDATA(58,N)
D3=REDATA(59,N)
D4=REDATA(60,N)
D5=REDATA(61,N)
D6=REDATA(62,N)
D7=REDATA(63,N)
D8=REDATA(64,N)
D9=REDATA(65,N)
DO 610,I=1,10
610 FFCOM(I)=REDATA(I+65,N)
C-----
CASE=CHDATA(N)
C-----
RDK=LODATA(1,N)
VDW=LODATA(2,N)
SPC=LODATA(3,N)
COM=LODATA(4,N)
DIS=LODATA(5,N)
RETURN
END
C-----
C*****
SUBROUTINE CALSTR
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
C-----COMMON BLOCK FOR DATABASE
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
INTEGER*4 N,I
DO 500,N=1,NPHA
DO 600,I=1,NUN
600 X(N,I)=XX(N,I)
NN(N)=0.0D0
GG(N)=GCK(N)
G(N)=GGK(N)
NUMMER(N)=N
EMCODE(N)=0
IF (NULL(N)) THEN
SUGG(N)=-N
ELSE
SUGG(N)=N
END IF

```

```

      DO 605,I=1,EMAX
605  XEM(N,I)=0.0D0
500  CONTINUE
      DO 505,N=1,NUN
      SUGG(N)=-N
505  NN(N)=BULK(N)
      SUGNR=NPHA
      RETURN
      END

```

C-----

C*****

```

      SUBROUTINE PRININ
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)

```

C-----GLOBAL COMMON BLOCK

C-----COMMON BLOCK FOR DATABASE

C-----COMMON BLOCK FOR G-CALCULATION

C-----COMMON BLOCK FOR THERIAK

C-----END OF COMMON VARIABLES

```

      INTEGER*4 I,II,IE,IS,IL00,IL02,N
      REAL*8 NNPC,SUMME
      CHARACTER*250 CH001
      CHARACTER*170 MODEL1,MODEL2
      CHARACTER*20 MODEL0
      WRITE (UNIT=6,FMT=120) P,PGAS,TC,T
      WRITE (UNIT=7,FMT=120) P,PGAS,TC,T
120  FORMAT ('1P =',F9.2,' bar   P(Gas) =',F9.2,' bar   T =',
      *F8.2,' C   = ',F8.2,' K')
      IF (PRTLOG(2)) THEN
      WRITE (UNIT=6,FMT=119)
      WRITE (UNIT=7,FMT=119)
119  FORMAT('0COMPOSITION:',8X,'N',10X,'MOL%'' ' ')
      SUMME=0.0
      DO 540,I=1,NUN
540  SUMME=SUMME+DABS(NN(I))
      DO 541,I=1,NUN
      NNPC=(NN(I)/SUMME)*100.
      WRITE (UNIT=6,FMT=121) I,CHNAME(I),NN(I),NNPC
      WRITE (UNIT=7,FMT=121) I,CHNAME(I),NN(I),NNPC
121  FORMAT (1X,I3,2X,A8,1X,F11.6,2X,F11.6)
      IF (CHNAME(I)(5:6).EQ.' ') THEN
      CH=CHNAME(I)
      CHNAME(I)=' '//CH
      END IF
541  CONTINUE
      END IF
      IF (PRTLOG(3)) THEN
      I001=MIN0(15,NUN)
      WRITE (UNIT=6,FMT=122) (CHNAME(I),I=1,I001)
      WRITE (UNIT=7,FMT=122) (CHNAME(I),I=1,I001)
122  FORMAT ('0CONSIDERED PHASES:',15X,'G',7X,15(A5,1X))
      DO 542,I001=16,NUN,15
      WRITE (UNIT=7,FMT=123) (CHNAME(I),I=I001,MIN0(I001+14,NUN))

```

```

542 WRITE (UNIT=6,FMT=123) (CHNAME(I),I=I001,MIN0(I001+14,NUN))
123 FORMAT (42X,15(A5,1X))
    WRITE (UNIT=6,FMT='('' '')')
    WRITE (UNIT=7,FMT='('' '')')
    DO 545,K=1,NPHA
    WRITE (UNIT=CH001,FMT=124) K,NAME(K),GG(K)
124 FORMAT (1X,I3,2X,A16,1X,':',2X,F13.2)
    DO 544,I001=1,NUN,15
    DO 543,I=I001,MIN0(I001+14,NUN)
    I002=42+MOD(I-1,15)*6
    IF (XX(K,I).EQ.0.0) THEN
    WRITE (UNIT=CH001(I002+3:),FMT='(''-'')')
    ELSE
    WRITE (UNIT=CH001(I002:),FMT='(F6.2)') XX(K,I)
    END IF
543 CONTINUE
    WRITE (UNIT=6,FMT='(A133)') CH001
    WRITE (UNIT=7,FMT='(A133)') CH001
544 CH001=' '
545 CONTINUE
    END IF
    IF (PRTLOG(4)) THEN
    IF (NSOL.NE.0) THEN
    WRITE (UNIT=6,FMT='(''0SOLUTION PHASES:''')')
    WRITE (UNIT=7,FMT='(''0SOLUTION PHASES:''')')
    END IF
    DO 600,IS=1,NSOL
    WRITE (UNIT=CH001,FMT=130) IS,SOLNAM(IS)
130 FORMAT ('0',I3,2X,A16,' :',12X,'SOLUTION MODELL: ')
    IF (MODELL(IS).EQ.'I') WRITE (UNIT=CH001(54:),FMT=131)
131 FORMAT ('IDEAL ONE SITE MIXING')
    IF (MODELL(IS).EQ.'S') WRITE (UNIT=CH001(54:),FMT=132) NSITE(IS)
132 FORMAT ('"IDEAL"',I3,' SITE MIXING')
    IF (MODELL(IS).EQ.'F') WRITE (UNIT=CH001(54:),FMT=133)
133 FORMAT ('FROM EXTERNAL SUBROUTINE')
    IF (NMARG(IS).NE.0) THEN
    DO 550,I001=250,1,-1
550 IF (CH001(I001:I001).NE.' ') GO TO 20
    20 WRITE (UNIT=CH001(I001+2:),FMT=134)
134 FORMAT ('+ MARGULES TYPE EXCESS FUNCTION')
    END IF
    WRITE (UNIT=6,FMT='(A133)') CH001
    WRITE (UNIT=7,FMT='(A133)') CH001
    CH=' '
    I001=INDEX(SOLNAM(IS),' ')
    DO 551,I002=1,I001-1
551 CH(I002:I002)='- '
    WRITE (UNIT=6,FMT='(6X,A16)') CH
    WRITE (UNIT=7,FMT='(6X,A16)') CH
    DO 599,IE=1,NEND(IS)
    MODEL1=' '
    MODEL2=' '
    MODEL0='A'//ABK(EM(IS,IE))
    I001=INDEX(MODEL0,' ')

```

```

MODEL0(I001:)=') ='
IL00=I001+2
IF (MODELL(IS).EQ.'I') THEN
MODEL2='X('//MODEL0(3:IL00-2)
IL02=IL00-2
WRITE (UNIT=CH,FMT='(F15.0)') SITMUL(IS,1)
CALL FIBLA(CH,I001)
I002=INDEX(CH,'.')
CH(I002:)=ALPDIV(IS)
I002=I002+INDEX(ALPDIV(IS),' ')-1
IF (CH(I001-1:I002).NE.' 1 ') THEN
MODEL1(IL02+1:)=CH(I001:I002-1)
IL02=IL02+(I002-I001)
END IF
END IF
IF (MODELL(IS).EQ.'S') THEN
IL02=0
DO 552,I=1,NSITE(IS)
MODEL2(IL02+1:)= 'I'
IL02=IL02+1
DO 553,II=1,NEQEM(IS,IE,I)
MODEL2(IL02+1:)= ' X('//ABK(EM(IS,EQEM(IS,IE,I,II)))
I001=INDEX(MODEL2(IL02+1:),' ')
IL02=IL02+I001-1
MODEL2(IL02+1:)=') +'
IL02=IL02+3
553 CONTINUE
MODEL2(IL02:)= 'I'
WRITE (UNIT=CH,FMT='(F16.0)') SITMUL(IS,I)
CALL FIBLA(CH,I001)
I002=INDEX(CH,'.')
CH(I002:)=ALPDIV(IS)
I002=I002+INDEX(ALPDIV(IS),' ')-1
IF (CH(I001-1:I002).NE.' 1 ') THEN
MODEL1(IL02+1:)=CH(I001:I002-1)
IL02=IL02+(I002-I001)+1
END IF
552 CONTINUE
END IF
IF (MODELL(IS).EQ.'F') THEN
DO 554,I=1,NEMBAS(IS)
I001=1
554 IF (EMBCOD(IS,I).EQ.IE) GO TO 21
21 CONTINUE
CALL SOLMOD(SOLNAM(IS),I001,MODEL2)
IL02=INDEX(MODEL2,' ')-1
END IF
DO 555,I=1,IL02,85
K=MIN0(85,IL02-I+1)
N=IL00+37
CH001=' '
WRITE (UNIT=CH001(N+1:),FMT='(A85)') MODEL1(I:)
WRITE(UNIT=6,FMT='(A133)') CH001
WRITE(UNIT=7,FMT='(A133)') CH001

```

```

CH001=' '
IF (I.EQ.1) THEN
  WRITE (UNIT=CH001,FMT=135) IE,NAME(EM(IS,IE)),EM(IS,IE),
  *MODEL0(I:)
135 FORMAT (6X,I3,2X,A16,1X,'('I3,')',3X,A15)
END IF
  WRITE (UNIT=CH001(N+1:),FMT='(A85)') MODEL2(I:)
  WRITE(UNIT=6,FMT='(A133)') CH001
  WRITE(UNIT=7,FMT='(A133)') CH001
555 CONTINUE
599 CONTINUE
  IF (NMARG(IS).GT.0) WRITE (UNIT=CH001,FMT=136)
136 FORMAT ('0',5X,'MARGULES PARAMETERS:')
  DO 558,I001=1,NMARG(IS),3
  DO 557,I=I001,MIN0(I001+2,NMARG(IS))
  I002=30+MOD(I-1,3)*28
  CH001(I002:I002+1)='W('
  I002=I002+2
  DO 556,K=1,POLY(IS,I)
  WRITE (UNIT=CH001(I002:I002),FMT='(I1)') INDX(IS,I,K)
556 I002=I002+1
  WRITE (UNIT=CH001(I002:),FMT=137) WG(IS,I)
137 FORMAT ('') =',F13.2)
557 CONTINUE
  WRITE (UNIT=6,FMT='(A133)') CH001
  WRITE (UNIT=7,FMT='(A133)') CH001
558 CH001=' '
  WRITE (UNIT=6,FMT='(''0'')')
  WRITE (UNIT=7,FMT='(''0'')')
600 CONTINUE
  END IF
  RETURN
END

C-----
C*****
SUBROUTINE THERIA
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
  *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
  INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
  >STEM(SOMAX+1),TRY
  REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
  >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
  >DXEND,DXLAST(SOMAX+1,EMAX)
  COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
  COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
  >MUE,VEKTOR,XXEM,DXEND,DXLAST
  INTEGER*4 I,II,IX,I001,K,LOO2
  REAL*8 FF,FX,SUMME
  CHARACTER*20 CH
  LOGICAL*4 CODE

```



```

NMAX=NPHA
GTOT=100.0D0
GTEST=DABS(TEST)
TRY=1
IF (LO1MAX.LT.0) THEN
  GTEST=-100.D0
  LO1MAX=-LO1MAX
END IF
IF (NMAX.GT.CALMAX) THEN
  WRITE (UNIT=6,FMT=142) CALMAX,NMAX
142 FORMAT (' CALMAX=',I5' NMAX=',I5)
  STOP
END IF
DO 500,I=1,NUN
  IF (NN(I).EQ.0.0D0) THEN
    DO 502,II=NUN+1,NMAX
      IF (X(II,I).NE.0.0D0) G(II)=1D25
502 CONTINUE
    END IF
500 CONTINUE
    DO 650,LOO1=1,LO1MAX
      IF (GTOT.LE.GTEST) THEN
        TRY=TRY+1
        IF (TRY.GT.2) GO TO 25
        DO 410,I=1,NSOL
410 STEM(I)=1
          END IF
          IF (TEST.LT.0.0D0) THEN
            WRITE (UNIT=6,FMT='(" ")')
            WRITE (UNIT=7,FMT='(" ")')
          END IF
          IF (LOO1.GT.1) THEN
            CALL ADDPH
          ELSE
            DO 400,I=1,NUN
400 G(I)=1D20
              END IF
              DO 602,II=1,NUN
                IX=I
                FX=DABS(X(I,I))
                DO 601,II=I+1,NUN
                  IF (DABS(X(II,I)).GT.FX) THEN
                    IX=II
                    FX=DABS(X(II,I))
                  END IF
241 CONTINUE
                I001=I
                IF (IX.NE.I) CALL COLCHG(I001,IX)
242 CALL REDUCE(I001)
                CODE=.TRUE.
                DO 640,LOO2=1,25
                  IF (.NOT.CODE) GO TO 24
                  CODE=.FALSE.
                  DO 630,K=(NUN+1),NMAX

```

```

      IF (SUGG(K).LT.0) GOTO 630
      SUMME=0D0
      DO 603,I=1,NUN
603  SUMME=SUMME+G(I)*X(K,I)
      IF (SUMME-G(K).GT.0D0) THEN
        DO 604,I=1,NUN
604  IF (X(K,I).GT.0D0) GO TO 23
      23 IF (I.LT.NUN+1) THEN
        FX=NN(I)/X(K,I)
        IX=I
        DO 605,I=(IX+1),NUN
        IF (X(K,I).GT.0D0) THEN
          FF=NN(I)/X(K,I)
          IF (FF.LT.FX) THEN
            FX=FF
            IX=I
          END IF
        END IF
605  CONTINUE
        DO 606,I=1,NUN
606  NN(I)=NN(I)-FX*X(K,I)
        NN(K)=FX
        NN(IX)=0D0
        I001=K
        CALL COLCHG(K,IX)
        CALL REDUCE(IX)
        CODE=.TRUE.
        END IF
      END IF
630  CONTINUE
640  CONTINUE
      24 GTOT=0.0D0
      DO 641,I=1,NUN
641  GTOT=GTOT+DABS(G(I))
      CALL CLEAN
      IF (TEST.LT.0.0D0) THEN
        I001=LOO2-1
        CH='-----'
        WRITE (UNIT=6,FMT=150) LOO1,I001,GTOT,CH
        WRITE (UNIT=7,FMT=150) LOO1,I001,GTOT,CH
150  FORMAT (' LOO1  =',I4,4X,'LOO2  =',I4,4X,'G(-)  =',1PE12.5,2X,A17)
        CALL PRTSTR(1,NUN)
      END IF
650  CONTINUE
      25 CALL PRTCAL
      RETURN
      END
C-----
C*****
      SUBROUTINE CLEAN
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
        *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK

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```

C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      > STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      > MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      > DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
      > MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 K,II
      IF (LOO1.EQ.1) THEN
        DO 500,K=1,NMAX
500  IF (SUGG(K).LT.0) G(K)=0.0D0
        GTOT=100.0D0
        END IF
        DO 501,K=(NUN+1),NMAX
        DO 501,II=1,NUN
501  G(K)=G(K)-X(K,II)*G(II)
        DO 502,K=1,NUN
502  G(K)=0.0D0
        DO 503,II=1,NSOL
          LOMIN1(II)=LOCMIN(II)
          LOCMIN(II)=0
503  STEM(II)=0
          K=1
1001 IF (K.GT.NMAX) GO TO 1
          IF (NUMMER(K).GT.0) THEN
            IF (EMSOL(NUMMER(K)).CT.0.AND.K.LE.NUN)
              * STEM(EMSOL(NUMMER(K)))=STEM(EMSOL(NUMMER(K)))+1
            DO 504,II=1,NUN
504  X(K,II)=XX(NUMMER(K),II)
            GG(NUMMER(K))=G(K)
            ELSE
              IF (K.GT.NUN.AND.(GTOT.GT.GTEST.OR.TRY.EQ.1)) THEN
                IF (NUMMER(K).EQ.0) THEN
                  CALL COLCHG(K,NMAX)
                  NMAX=NMAX-1
                  K=K-1
                END IF
              ELSE
                CALL XSOL(K)
                IF (K.LE.NUN) THEN
                  LOCMIN(EMCODE(K))=LOCMIN(EMCODE(K))+1
                  DXLAST(EMCODE(K),LOCMIN(EMCODE(K)))=DELXXX(K)
                  DO 505,II=1,NEND(EMCODE(K))
505  MINCOM(EMCODE(K),LOCMIN(EMCODE(K)),II)=XEM(K,II)
                  END IF
                END IF
              END IF
              K=K+1
              GO TO 1001
            1 RETURN
          END

```

```

C-----
C*****
      SUBROUTINE ADDPH
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
        *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
      >MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 IS,I1,START,I001,I002
      DO 502,IS=1,NSOL
      I001=IS
      IF (NMARG(IS).GT.0.OR.MODELL(IS).NE.'I') THEN
      IF (STEM(IS).EQ.0.AND.LOMIN1(IS).EQ.LOCMIN(IS)) THEN
      I1=MIN0(1,LOCMIN(IS))
      ELSE
      I1=-NEND(IS)
      END IF
      DO 501,START=I1,LOCMIN(IS)
      GNOM=0
      I002=START
      CALL MARMIN(I001,I002)
501 CALL NEWPH(I001)
      ELSE
      CALL MING(I001)
      CALL NEWPH(I001)
      END IF
502 CONTINUE
      RETURN
      END
C-----
C*****
      SUBROUTINE NEWPH(IS)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
        *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,

```

```

>MUE,VEKTOR,XXEM,DXEND,DXLAST
  INTEGER*4 IS,I
  NMAX=NMAX+1
  SUGNR=SUGNR+1
  IF (NMAX.GT.CALMAX) THEN
    WRITE (UNIT=6,FMT=100) CALMAX,NMAX
100 FORMAT (' CALMAX=',I5,' NMAX=',I5)
    STOP
  END IF
  NN(NMAX)=0.0D0
  G(NMAX)=GSOL
  NUMMER(NMAX)=0
  EMCODE(NMAX)=IS
  DELXXX(NMAX)=DXEND
  DO 501,I=1,NEND(IS)
501 XEM(NMAX,I)=XXEM(I)
  SUGG(NMAX)=SUGNR
  CALL XSOL(NMAX)
  I=NMAX
  IF (TEST.LT.0.0D0) CALL PRTSTR(NMAX,I)
  RETURN
END

C-----
C*****
  SUBROUTINE XSOL(K)
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
  INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
  >STEM(SOMAX+1),TRY
  REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
  >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
  >DXEND,DXLAST(SOMAX+1,EMAX)
  COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
  COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
  >MUE,VEKTOR,XXEM,DXEND,DXLAST
  INTEGER*4 I,K,N
  DO 501,N=1,NUN
  X(K,N)=0.0D0
  DO 501,I=1,NEND(EMCODE(K))
  X(K,N)=X(K,N)+XEM(K,I)*XX(EM(EMCODE(K),I),N)
501 CONTINUE
  RETURN
END

C-----
C*****
  SUBROUTINE MING(IS)
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK

```

C-----COMMON BLOCK FOR THERIAK

C-----END OF COMMON VARIABLES

```

    INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
    >STEM(SOMAX+1),TRY
    REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
    >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
    >DXEND,DXLAST(SOMAX+1,EMAX)
    COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
    COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
    >MUE,VEKTOR,XXEM,DXEND,DXLAST
    INTEGER*4 IS,I
    REAL*8 GMIN,SUMME,RTA
    RTA=RT*ALPHA(IS)
    GMIN=GG(EM(IS,1))
    DO 501,I=2,NEND(IS)
501  GMIN=DMIN1(GMIN,GG(EM(IS,I)))
    SUMME=0.0D0
    DO 502,I=1,NEND(IS)
    XXEM(I)=1D0/DEXP(DMIN1(150D0,(GG(EM(IS,I))-GMIN)/(RTA)))
502  SUMME=SUMME+XXEM(I)
    DO 503,I=1,NEND(IS)
503  XXEM(I)=XXEM(I)/SUMME
    GSOL=0.0D0
    DO 504,I=1,NEND(IS)
504  GSOL=GSOL+XXEM(I)*GG(EM(IS,I))+RTA*XXEM(I)*DLOG(XXEM(I))
    RETURN
    END

```

C-----

C*****

```

    SUBROUTINE MARMIN(IS,START)
    INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
    PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
    *MAMAX=31,MPOMAX=4,CALMAX=200)

```

C-----GLOBAL COMMON BLOCK

C-----COMMON BLOCK FOR THERIAK

C-----END OF COMMON VARIABLES

```

    INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
    >STEM(SOMAX+1),TRY
    REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
    >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
    >DXEND,DXLAST(SOMAX+1,EMAX)
    COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
    COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
    >MUE,VEKTOR,XXEM,DXEND,DXLAST
    INTEGER*4 I,IS,START,STEP,STEP2,NSTEP,L3,L1,I1,I001,I002
    REAL*8 XXSC(EMAX),GSC,XXX(3,EMAX),GGG(3),AR001(EMAX),
    *AR002(EMAX),SUMME,F001,FN,FF,FX
    CHARACTER*133 CH001
    IF (START.EQ.0) THEN
    DO 501,I=1,(NEND(IS)-1)
501  XXSC(I)=0.0D0
    XXSC(NEND(IS))=1.0D0
    GSOL=GG(EM(IS,NEND(IS)))
    DO 502,I001=1,NEND(IS)

```

```

502 XXEM(I001)=XXSC(I001)
    SUMME=0.0D0
1001 XXSC(NEND(IS)-1)=XXSC(NEND(IS)-1)+DXSCAN
    SUMME=SUMME+DXSCAN
    XXSC(NEND(IS))=1.0D0-SUMME
    DO 503,I=(NEND(IS)-1),2,-1
    IF (XXSC(NEND(IS)).GE.0.0D0) GO TO 1
    XXSC(I-1)=XXSC(I-1)+DXSCAN
    SUMME=SUMME+DXSCAN
    DO 504,II=I,(NEND(IS)-1)
    SUMME=SUMME-XXSC(I)
504 XXSC(I)=0.0D0
503 XXSC(NEND(IS))=1.0D0-SUMME
    1 IF (XXSC(NEND(IS)).LT.0.0D0) THEN
        GO TO 10
    ELSE
        CALL GNONID(IS,XXSC,GSC)
        IF (GSC.LT.GSOL) THEN
            DO 505,I001=1,NEND(IS)
505 XXEM(I001)=XXSC(I001)
            GSOL=GSC
            END IF
            END IF
            GO TO 1001
10 DELTAX=DXSTAR
    NSTEP=STPSTA
    END IF
    IF (START.LT.0) THEN
        II=-START
        DO 701,I=1,NEND(IS)
701 XXEM(I)=0.0D0
        XXEM(II)=1.0D0
        GSOL=GG(EM(IS,II))
        DELTAX=DXSTAR
        NSTEP=STPSTA
        END IF
        IF (START.GT.0) THEN
            DO 506,I=1,NEND(IS)
506 XXEM(I)=MINCOM(IS,START,I)
            GSOL=0.0D0
            DELTAX=DXLAST(IS,START)
            NSTEP=STPMAX
            END IF
            IF (TEST.LT.0.0D0) THEN
                WRITE (UNIT=CH001,FMT=100) DELTAX
100 FORMAT (' START: DELTAX = ',1PE12.5)
                DO 512,I001=1,NEND(IS),10
                DO 511,I=I001,MIN0(I001+9,NEND(IS))
                I002=34+MOD(I-1,10)*10
511 WRITE (UNIT=CH001(I002:),FMT='(F8.6)') XXEM(I)
                WRITE (UNIT=6,FMT='(A133)') CH001
                WRITE (UNIT=7,FMT='(A133)') CH001
512 CH001=' '
            END IF

```

```

DO 513,I=1,NEND(IS)
513 XXX(1,I)=XXEM(I)
GGG(1)=GSOL
L1=1
IF (TRY.GT.1.AND.GTOT.LE.GTEST) NSTEP=500
DO 516,STEP=1,MIN0(2,NSTEP)
DO 514,I001=1,NEND(IS)
514 AR002(I001)=XXX(STEP,I001)
CALL MUECAL(IS,AR002)
CALL STEEP(IS)
L1=STEP+1
CALL ETC(IS,AR002,GGG(STEP),AR001,GGG(L1))
DO 515,I001=1,NEND(IS)
515 XXX(L1,I001)=AR001(I001)
516 CONTINUE
DO 525,STEP=3,NSTEP
IF (DELTAX.LE.DXMIN) GO TO 15
L3=MOD(STEP-1,3)+1
L1=MOD(STEP,3)+1
DO 517,I001=1,NEND(IS)
AR001(I001)=XXX(L1,I001)
517 AR002(I001)=XXX(L3,I001)
CALL MUECAL(IS,AR002)
GSC=0.0D0
DO 518,I=1,NEND(IS)
518 GSC=GSC+MUE(I)*XXX(L1,I)
CALL DISTAN(IS,AR001,AR002)
DELTAX=DISTA
IF (DELTAX.GT.DXMIN) THEN
IF (GSC.LT.GGG(L3)) THEN
CALL STEEP(IS)
DELTAX=DELTAX/2.0D0
ELSE
SUMME=0.0D0
DO 519,I=1,NEND(IS)
VEKTOR(I)=XXX(L3,I)-XXX(L1,I)
519 SUMME=SUMME+VEKTOR(I)*VEKTOR(I)
SUMME=DSQRT(SUMME)
IF (SUMME.GT.0.0D0) THEN
DO 520,I=1,NEND(IS)
520 VEKTOR(I)=VEKTOR(I)/SUMME
END IF
END IF
CALL ETC(IS,AR002,GGG(L3),AR001,GGG(L1))
DO 521,I001=1,NEND(IS)
521 XXX(L1,I001)=AR001(I001)
END IF
525 CONTINUE
15 CALL DISTAN(IS,AR001,XXEM)
STEP2=0
IF (DISTA.LT.DXMIN) THEN
DELTAX=DXSTAR
STEP=2-STEP
FN=NEND(IS)

```



```

      FX=DSQRT((FN-1.0D0)/FN)
      FF=-DSQRT(1.0D0/(FN*(FN-1.0D0)))
      DO 526,I=1,NEND(IS)
526  VEKTOR(I)=FF
      DO 530,STEP2=1,NEND(IS)
      IF (STEP2.NE.1) VEKTOR(STEP2-1)=FF
      VEKTOR(STEP2)=FX
      F001=DXMIN
      CALL VECADD(IS,AR001,F001,XXSC)
      CALL GNONID(IS,XXSC,GSC)
      IF (GSC.LT.GGG(L1)) THEN
      CALL ETC(IS,XXSC,GSC,AR001,GGG(L1))
      END IF
530  CONTINUE
      END IF
      CALL DISTAN(IS,AR001,XXEM)
      DXEND=DMAX1(DISTA,DXMIN)
      DO 531,I=1,NEND(IS)
531  XXEM(I)=AR001(I)
      GSOL=GGG(L1)
      IF (TEST.LT.0.0D0) THEN
      I001=STEP-1
      WRITE (UNIT=CH001,FMT=105) SOLNAM(IS),I001
105  FORMAT (1X,A16,2X,'STEP =',I4)
      DO 533,I001=1,NEND(IS),10
      DO 532,I=I001,MIN0(I001+9,NEND(IS))
      I002=34+MOD(I-1,10)*10
532  WRITE (UNIT=CH001(I002:),FMT='(F8.6)') XXEM(I)
      WRITE (UNIT=6,FMT='(A133)') CH001
      WRITE (UNIT=7,FMT='(A133)') CH001
533  CH001=' '
      WRITE (UNIT=6,FMT=106) DELTAX,DISTA,GNOM
      WRITE (UNIT=7,FMT=106) DELTAX,DISTA,GNOM
106  FORMAT (8X,'DELTAX = ',1PE12.5,4X,'DISTA = ',1PE12.5,
      *4X,'GALC = ',I4)
      END IF
      RETURN
      END
C-----
C*****
      SUBROUTINE STEEP(IS)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,

```

```

>MUE,VEKTOR,XXEM,DXEND,DXLAST
INTEGER*4 IS,I
REAL*8 DELMUE,SUMME
DELMUE=0.0D0
SUMME=0.0D0
DO 501,I=1,NEND(IS)
501 DELMUE=DELMUE+MUE(I)
DELMUE=DELMUE/NEND(IS)
DO 502,I=1,NEND(IS)
VEKTOR(I)=DELMUE-MUE(I)
502 SUMME=SUMME+VEKTOR(I)*VEKTOR(I)
SUMME=DSQRT(SUMME)
IF (SUMME.GT.0.0D0) THEN
DO 504,I=1,NEND(IS)
504 VEKTOR(I)=VEKTOR(I)/SUMME
END IF
RETURN
END

C-----
C*****
SUBROUTINE DISTAN(IS,X1,X2)
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
>STEM(SOMAX+1),TRY
REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
>MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
>DXEND,DXLAST(SOMAX+1,EMAX)
COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
>MUE,VEKTOR,XXEM,DXEND,DXLAST
INTEGER*4 IS,I
REAL*8 X1(EMAX),X2(EMAX),DIFF
DISTA=0.0D0
DO 501,I=1,NEND(IS)
DIFF=X2(I)-X1(I)
501 DISTA=DISTA+DIFF*DIFF
DISTA=DSQRT(DISTA)
RETURN
END

C-----
C*****
SUBROUTINE ETC(IS,XSTART,GSTART,XNEW,GNEW)
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,

```

```

>STEM(SOMAX+1),TRY
  REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
>MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
>DXEND,DXLAST(SOMAX+1,EMAX)
  COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
  COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
>MUE,VEKTOR,XXEM,DXEND,DXLAST
  INTEGER*4 IS,I,II,I001
  REAL*8 XSTART(EMAX),GSTART,XOLD(EMAX),GOLD,XNEW(EMAX),
*GNEW,DELX
  DELX=DELTAX
  GOLD=GSTART
  DO 500,I001=1,NEND(IS)
500 XOLD(I001)=XSTART(I001)
  CALL VECADD(IS,XSTART,DELX,XNEW)
  CALL GNONID(IS,XNEW,GNEW)
  DO 502,II=1,GCMAX
  IF (GNEW.GE.GOLD) GO TO 1
  DELX=DELX+DELTAX
  GOLD=GNEW
  DO 501,I001=1,NEND(IS)
501 XOLD(I001)=XNEW(I001)
  CALL VECADD(IS,XOLD,DELX,XNEW)
502 CALL GNONID(IS,XNEW,GNEW)
  1 GNEW=GOLD
  DO 503,I001=1,NEND(IS)
503 XNEW(I001)=XOLD(I001)
  DO 504,I=1,GCMAX
  IF (GNEW.LT.GSTART.OR.DELX.LE.DXMIN) GO TO 2
  DELX=DELX/2.0D0
  CALL VECADD(IS,XSTART,DELX,XNEW)
504 CALL GNONID(IS,XNEW,GNEW)
  2 IF (GNEW.GT.GSTART) THEN
  GNEW=GSTART
  DO 505,I001=1,NEND(IS)
505 XNEW(I001)=XSTART(I001)
  END IF
  RETURN
  END

C-----
C*****
  SUBROUTINE VECADD(IS,X1,DELX,X2)
  INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
  PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
  *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
  INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
>STEM(SOMAX+1),TRY
  REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
>MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
>DXEND,DXLAST(SOMAX+1,EMAX)
  COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY

```

```

COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
> MUE,VEKTOR,XXEM,DXEND,DXLAST
INTEGER*4 IS,I
REAL*8 X1(EMAX),X2(EMAX),DELX,SUMME
SUMME=0.0D0
DO 501,I=1,NEND(IS)
X2(I)=X1(I)+VEKTOR(I)*DELX
IF (X2(I).LT.0.0D0) X2(I)=0.0D0
501 SUMME=SUMME+X2(I)
IF (SUMME.GT.0.0D0) THEN
DO 502,I=1,NEND(IS)
502 X2(I)=X2(I)/SUMME
END IF
RETURN
END

C-----
C *****
SUBROUTINE GNONID(IS,XXX,GGG)
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
> STEM(SOMAX+1),TRY
REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
> MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
> DXEND,DXLAST(SOMAX+1,EMAX)
COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
> MUE,VEKTOR,XXEM,DXEND,DXLAST
INTEGER*4 IS,N,I,I001
REAL*8 XXX(EMAX),AAA(EMAX),XM,GGG,RTA
GNOM=GNOM+1
GGG=0.0D0
RTA=RT*ALPHA(IS)
IF (MODELL(IS).EQ.'I') THEN
DO 501,I001=1,NEND(IS)
501 AAA(I001)=XXX(I001)
ELSE
CALL ACTIVI(IS,XXX,AAA)
END IF
DO 502,I=1,NEND(IS)
IF (AAA(I).GT.0.0D0)
* GGG=GGG+XXX(I)*GG(EM(IS,I))+RTA*XXX(I)*DLOG(AAA(I))
502 CONTINUE
DO 504,N=1,NMARG(IS)
XM=1.0D0
DO 503,I=1,POLY(IS,N)
503 XM=XM*XXX(INDX(IS,N,I))
504 GGG=GGG+WG(IS,N)*XM
RETURN
END

```

```

C-----
C*****
      SUBROUTINE MUECAL(IS,XXX)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
      >MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 IS,IE,N,I,I001
      REAL*8 XXX(EMAX),AAA(EMAX),FF(MAMAX),RTA
      RTA=RT*ALPHA(IS)
      DO 501,N=1,NMARG(IS)
      FF(N)=WG(IS,N)
      DO 500,I=1,POLY(IS,N)
      IF (FF(N).EQ.0.0D0) GO TO 1
500 FF(N)=FF(N)*XXX(INDX(IS,N,I))
      1 CONTINUE
501 CONTINUE
      IF (MODELL(IS).EQ.'I') THEN
      DO 502,I001=1,NEND(IS)
502 AAA(I001)=XXX(I001)
      ELSE
      CALL ACTIVI(IS,XXX,AAA)
      END IF
      DO 504,IE=1,NEND(IS)
      IF (AAA(IE).LE.0.0D0) THEN
      MUE(IE)=-1D20
      ELSE
      MUE(IE)=GG(EM(IS,IE))+RTA*DLOG(AAA(IE))
      DO 503,N=1,NMARG(IS)
503 MUE(IE)=MUE(IE)+FF(N)*(QQ(IS,N,IE)/XXX(IE)+(1-POLY(IS,N)))
      END IF
504 CONTINUE
      RETURN
      END
C-----
C*****
      SUBROUTINE ACTIVI(IS,XXX,AAA)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,

```

```

> STEM(SOMAX+1),TRY
  REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
> MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
> DXEND,DXLAST(SOMAX+1,EMAX)
  COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
  COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
> MUE,VEKTOR,XXEM,DXEND,DXLAST
  INTEGER*4 IS,IE,I,II
  REAL*8 XXX(EMAX),AAA(EMAX),XBAS(10),ABAS(10),SUMM
  IF (MODELL(IS).EQ.'S') THEN
    DO 502,IE=1,NEND(IS)
      AAA(IE)=1.0D0
      DO 502,I=1,NSITE(IS)
        SUMM=0.0D0
        DO 501,II=1,NEQEM(IS,IE,I)
501  SUMM=SUMM+XXX(EQEM(IS,IE,I,II))
502  AAA(IE)=AAA(IE)*(SUMM**SITMUL(IS,I))
      RETURN
    ELSE
      DO 503,I=1,NEMBAS(IS)
        IF (EMBCCOD(IS,I).EQ.0) THEN
          XBAS(I)=0.0D0
        ELSE
          XBAS(I)=XXX(EMBCCOD(IS,I))
        END IF
503  CONTINUE
      CALL SOLCAL(SOLNAM(IS),P,T,NEMBAS(IS),XBAS,ABAS)
      DO 504,I=1,NEMBAS(IS)
        IF (EMBCCOD(IS,I).NE.0) AAA(EMBCCOD(IS,I))=ABAS(I)
504  CONTINUE
      RETURN
    END IF
    RETURN
  END
END
C-----
C *****
  SUBROUTINE REDUCE(K)
    INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
    PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
    INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
> STEM(SOMAX+1),TRY
    REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
> MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
> DXEND,DXLAST(SOMAX+1,EMAX)
    COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
    COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
> MUE,VEKTOR,XXEM,DXEND,DXLAST
    INTEGER*4 K,I,II
    REAL*8 F,AR(COMAX)
    F=X(K,K)

```

```

      IF (F.EQ.0.0D0) THEN
      DO 501,I=1,NMAX
501  X(I,K)=0.0D0
      ELSE
      DO 502,I=1,NMAX
      IF (X(I,K).NE.0.0D0) X(I,K)=X(I,K)/F
502  CONTINUE
      DO 503,I=1,NUN
503  AR(I)=X(K,I)
      DO 505,I=1,NUN
      IF (I.NE.K.AND.AR(I).NE.0.0D0) THEN
      DO 504,I=1,NMAX
      X(I,I)=X(I,I)-X(I,K)*AR(I)
      IF (DABS(X(I,I)).LT.1D-12) X(I,I)=0.0D0
504  CONTINUE
      END IF
505  CONTINUE
      END IF
      DO 506,I=1,NUN
506  X(K,I)=0.0D0
      X(K,K)=1.0D0
      RETURN
      END
C-----
C*****
      SUBROUTINE COLCHG(K,I)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
      >MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 K,I,I001
      DO 501,I001=1,COMAX
501  X(0,I001)=X(K,I001)
      NN(0)=NN(K)
      G(0)=G(K)
      NUMMER(0)=NUMMER(K)
      EMCODE(0)=EMCODE(K)
      SUGG(0)=SUGG(K)
      DELXXX(0)=DELXXX(K)
      DO 502,I001=1,EMAX
502  XEM(0,I001)=XEM(K,I001)
      DO 503,I001=1,COMAX
503  X(K,I001)=X(I,I001)
      NN(K)=NN(I)

```

```

      G(K)=G(I)
      NUMMER(K)=NUMMER(I)
      EMCODE(K)=EMCODE(I)
      SUGG(K)=SUGG(I)
      DELXXX(K)=DELXXX(I)
      DO 504,I001=1,EMAX
504  XEM(K,I001)=XEM(I,I001)
      DO 505,I001=1,COMAX
505  X(I,I001)=X(0,I001)
      NN(I)=NN(0)
      G(I)=G(0)
      NUMMER(I)=NUMMER(0)
      EMCODE(I)=EMCODE(0)
      SUGG(I)=SUGG(0)
      DELXXX(I)=DELXXX(0)
      DO 506,I001=1,EMAX
506  XEM(I,I001)=XEM(0,I001)
      RETURN
      END

C-----
C*****
      SUBROUTINE PRTCAL
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
      *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
      >STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
      >MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
      >DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
      >MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 I,II,I001,I002
      LOGICAL*4 SPACE
      CHARACTER*16 TEXT(COMAX)
      CHARACTER*133 CH001
      REAL*8 SUMM(COMAX),EXPO,ACT,XACT,SUMME,NNPC,AR001(EMAX),F001,
      *TOTAL
      I=1
1001 IF (I.GE.NUN) GOTO 1
      IF ((NUMMER(I+1).LT.NUMMER(I)).OR.(NUMMER(I).EQ.0.AND.
      *NUMMER(I+1).EQ.0.AND.EMCODE(I+1).LT.EMCODE(I))) THEN
      I001=I+1
      CALL COLCHG(I,I001)
      I=I-1
      ELSE
      I=I+1
      END IF
      IF (I.EQ.0) I=2
      GOTO 1001

```



```

1 CALL MULCHK
  IF (PRTLOG(6).OR.PRTLOG(7).OR.PRTLOG(8)) THEN
    TOTAL=0.0D0
    DO 491,I=1,NUN
      SUMME=0.0D0
      DO 490,II=1,NUN2
490 SUMME=SUMME+NN(II)*X(II,I)
491 TOTAL=TOTAL+SUMME*GG(I)
      TOTAL=-TOTAL
      SPACE=.TRUE.
      DO 502,I=1,NUN2
        IF (NUMMER(I).LE.0) THEN
          TEXT(I)=SOLNAM(EMCODE(I))
        ELSE
          TEXT(I)=NAME(NUMMER(I))
        END IF
        IF (NUMMER(I).LE.NUN.AND.NUMMER(I).NE.0) SPACE=.FALSE.
502 CONTINUE
      I001=LOO1-1
      WRITE (UNIT=6,FMT=100) P,PGAS,TC,T,NUN2,I001,GTOT,TOTAL,R
      WRITE (UNIT=7,FMT=100) P,PGAS,TC,T,NUN2,I001,GTOT,TOTAL,R
100 FORMAT ('1P =',F9.2,' bar',7X,'P(Gas) =',F9.2,' bar   T =',
  *F8.2,' C   =',F8.2,' K'/' STABLE PHASES:',I4,5X,'LOOP =',I4,
  */' G(-) =',1PE12.5,0P,5X,'G(System) =',F15.2,5X,'R =',F14.7)
      IF (.NOT.SPACE) WRITE (UNIT=6,FMT=101)
      IF (.NOT.SPACE) WRITE (UNIT=7,FMT=101)
101 FORMAT ('0COMPOSITION MAY BE OUTSIDE SPACE DEFINED BY PHASES')
      IF (NUN2.LE.0) RETURN
      END IF
      IF (PRTLOG(6)) THEN
        WRITE (UNIT=6,FMT=102)
        WRITE (UNIT=7,FMT=102)
102 FORMAT(/9X,'PHASE',19X,'N',9X,'MOL%',35X,'X',14X,'X',
  *9X,'ACTIVITY',7X,'ACT.(X)'/
  *9X,'-----',19X,'-',9X,'-----',35X,'-',14X,'-',
  *9X,'-----',7X,'-----')
      SUMME=0.0D0
      DO 503,I=1,NUN2
503 SUMME=SUMME+DABS(NN(I))
      DO 510,I=1,NUN2
        NNPC=(NN(I)/SUMME)*100.0D0
        WRITE (UNIT=CH001,FMT=103) NUMMER(I),EMCODE(I),TEXT(I),NN(I),
  *NNPC
103 FORMAT ('0',I3,I3,2X,A16,3X,F11.6,1X,F11.6)
        IF (EMCODE(I).GT.0) THEN
          DO 504,I001=1,EMAX
504 AR001(I001)=XEM(I,I001)
          CALL MUECAL(EMCODE(I),AR001)
          DO 505,II=1,NEND(EMCODE(I))
            EXPO=-GG(EM(EMCODE(I),II))/(RT)
            IF (EXPO.LT.-150) THEN
              ACT=0.0D0
            ELSE
              ACT=DEXP(EXPO)

```

```

END IF
EXPO=(MUE(II)-GG(EM(EMCODE(I),II)))/(RT)
IF (EXPO.LT.-150) THEN
XACT=0.0D0
ELSE
XACT=DEXP(EXPO)
END IF
WRITE (UNIT=CH001(61:),FMT=104) NAME(EM(EMCODE(I),II)),
*XEM(I,II),XEM(I,II),ACT,XACT
104 FORMAT (A16,2X,F9.6,2X,3(2X,1PE12.5))
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
505 CH001=' '
ELSE
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
CH001=' '
END IF
510 CONTINUE
END IF
IF (PRTLOG(7)) THEN
WRITE (UNIT=6,FMT=105)
WRITE (UNIT=7,FMT=105)
105 FORMAT (/ COMPOSITIONS OF STABLE PHASES [ MOL% ] :)
WRITE (UNIT=6,FMT='('' ''')')
WRITE (UNIT=7,FMT='('' ''')')
DO 512,I001=1,NUN,10
DO 511,I=I001,MIN0(I001+9,NUN)
I002=23+MOD(I-1,10)*11
WRITE (UNIT=CH001(I002:),FMT='(A5)') CHNAME(I)
511 CONTINUE
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
512 CH001=' '
DO 513,I001=1,COMAX
513 SUMM(I001)=0.0D0
DO 520,I=1,NUN2
WRITE (UNIT=CH001,FMT='(''0'',A16)') TEXT(I)
SUMME=0.0D0
DO 514,II=1,NUN
SUMME=SUMME+DABS(X(I,II))
514 SUMM(II)=SUMM(II)+X(I,II)*NN(I)
DO 516,I001=1,NUN,10
DO 515,II=I001,MIN0(I001+9,NUN)
I002=19+MOD(II-1,10)*11
F001=X(I,II)/SUMME*100.0D0
WRITE (UNIT=CH001(I002:),FMT='(F11.6)') F001
515 CONTINUE
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
516 CH001=' '
520 CONTINUE
WRITE (UNIT=CH001,FMT=106)
106 FORMAT ('0TOTAL:')

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SUMME=0.0D0
DO 521,I=1,NUN
521 SUMME=SUMME+DABS(SUMM(I))
DO 523,I001=1,NUN,10
DO 522,I=I001,MIN0(I001+9,NUN)
I002=19+MOD(I-1,10)*11
F001=SUMM(I)/SUMME*100.0D0
WRITE (UNIT=CH001(I002:),FMT='(F11.6)') F001
522 CONTINUE
WRITE (UNIT=6,FMT='(/,A133)') CH001
WRITE (UNIT=7,FMT='(/,A133)') CH001
523 CH001=' '
END IF
IF (PRTLOG(8)) THEN
WRITE (UNIT=6,FMT=107)
WRITE (UNIT=7,FMT=107)
107 FORMAT ('1',8X,'PHASE',19X,'N',13X,'G',9X,'ACTIVITY')
CALL PRSTR(1,NMAX)
END IF
999 RETURN
END

C-----
C*****
SUBROUTINE MULCHK
INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
*MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
>STEM(SOMAX+1),TRY
REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
>MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
>DXEND,DXLAST(SOMAX+1,EMAX)
COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
>MUE,VEKTOR,XXEM,DXEND,DXLAST
INTEGER*4 I,II,III,K,I001,I002
REAL*8 SUMME
NUN2=NUN
I=1
1001 IF (I.GT.NUN2) GO TO 11
IF (DABS(NN(I)).LT.1D-12) THEN
DO 501,K=I,(NUN2-1)
I001=K+1
501 CALL COLCHG(K,I001)
NUN2=NUN2-1
I=I-1
GO TO 999
END IF
IF (EMCODE(I).GT.0) THEN
DO 510,II=(I+1),NUN2
IF (EMCODE(II).EQ.EMCODE(I)) THEN

```

```

SUMME=0.0D0
DO 502,III=1,NEND(EMCODE(I))
502 SUMME=SUMME + DABS(XEM(I,III)-XEM(II,III))
   IF (SUMME.LT.EQUALX) THEN
     DO 503,III=1,NEND(EMCODE(I))
503  XEM(I,III)=(NN(I)*XEM(I,III) + NN(II)*XEM(II,III))/(NN(I) + NN(II))
     NN(I)=NN(I) + NN(II)
     NN(II)=0.0D0
     I001=I
     CALL XSOL(I001)
     DO 504,K=II,(NUN2-1)
     I001=K
     I002=K+1
504  CALL COLCHG(I001,I002)
     NUN2=NUN2-1
     I=I-1
     GO TO 999
     END IF
     END IF
510 CONTINUE
     END IF
999 I=I+1
     GO TO 1001
11  RETURN
    END
C-----
C *****
    SUBROUTINE PRTSTR(N1,N2)
      INTEGER*4 CALMAX,COMAX,EMAX,MAMAX,MPOMAX,PHMAX,SITMAX,SOMAX
      PARAMETER (COMAX=22,PHMAX=150,SOMAX=20,EMAX=10,SITMAX=5,
        *MAMAX=31,MPOMAX=4,CALMAX=200)
C-----GLOBAL COMMON BLOCK
C-----COMMON BLOCK FOR THERIAK
C-----END OF COMMON VARIABLES
      INTEGER*4 GNOM,LOCMIN(SOMAX+1),LOMIN1(SOMAX+1),NMAX,
>STEM(SOMAX+1),TRY
      REAL*8 DELTAX,DELXXX(0:CALMAX),DISTA,GSOL,GTEST,GTOT,
>MINCOM(SOMAX+1,EMAX,EMAX),MUE(EMAX),VEKTOR(EMAX),XXEM(EMAX),
>DXEND,DXLAST(SOMAX+1,EMAX)
      COMMON /TOIN/ GNOM,LOCMIN,LOMIN1,NMAX,STEM,TRY
      COMMON /TORE/ DELTAX,DELXXX,DISTA,GSOL,GTEST,GTOT,MINCOM,
>MUE,VEKTOR,XXEM,DXEND,DXLAST
      INTEGER*4 I,II,N1,N2,I001,I002
      REAL*8 EXPO,ACT
      CHARACTER*16 TEXT
      CHARACTER*133 CH001
      DO 510,I=N1,N2
      IF (SUGG(I).LE.NPHA) THEN
        CH001=' P'
      ELSE
        CH001=' S'
      END IF
      WRITE (UNIT=CH001(3:),FMT='(I5)') SUGG(I)
      IF (NUMMER(I).LE.0) THEN

```

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TEXT=SOLNAM(EMCODE(I))
ELSE
TEXT=NAME(NUMMER(I))
END IF
EXPO=-G(I)/(RT)
IF (EXPO.LT.-150.0D0) THEN
ACT=0.0D0
ELSE
ACT=DEXP(DMIN1(150.0D0,EXPO))
END IF
WRITE (UNIT=CH001(8:),FMT=101) TEXT,NN(I),G(I),ACT
101 FORMAT (2X,A16,2X,1PE12.5,2X,0P,F12.2,2X,1PE12.5)
IF (EMCODE(I).GT.0) THEN
DO 502,I001=1,NEND(EMCODE(I)),5
DO 501,II=I001,MIN0(I001+4,NEND(EMCODE(I)))
I002=70+MOD(II-1,5)*12
501 WRITE (UNIT=CH001(I002:),FMT='(1PE11.4)') XEM(I,II)
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
502 CH001=' '
ELSE
WRITE (UNIT=6,FMT='(A133)') CH001
WRITE (UNIT=7,FMT='(A133)') CH001
END IF
510 CONTINUE
RETURN
END

```

APPENDIX C: THE MOESSBAUER FURNACE

In order to separate the M1 and M2 absorption peaks in a Mössbauer spectrum for olivine, the sample has to be heated to approximately 300 °C. (Eibschütz and Ganiel (1967)). It is also important that the surrounding can be evacuated or filled with an inert gas, to prevent oxydation.

The vacuum furnace used in this investigation was built by Mr. Doug Polson following the design of Sudaram et al. (1971) with some major modifications. The design of the furnace is shown in Fig. 22 and 23 and the materials used are listed in table 16. The furnace is mounted on two rails which makes the supporting legs unnecessary. The inlet and outlet for vacuum pumping are drilled through the outer flanges.

Only one Chromel-Alumel thermocouple is used for measuring the temperature. It was found that a constant voltage of ca. 50 V provided by a variac, resulted in a temperature of ca. 300 °C with a maximum variation of $\pm 2^{\circ}\text{C}$, as long as the vacuum pump was operating constantly. If the valve is closed and the pump turned off, the temperature dropped approximately 10 °C in 8 hours. All measurements were done with the pump working.

Fig. 21: The Moessbauer furnace

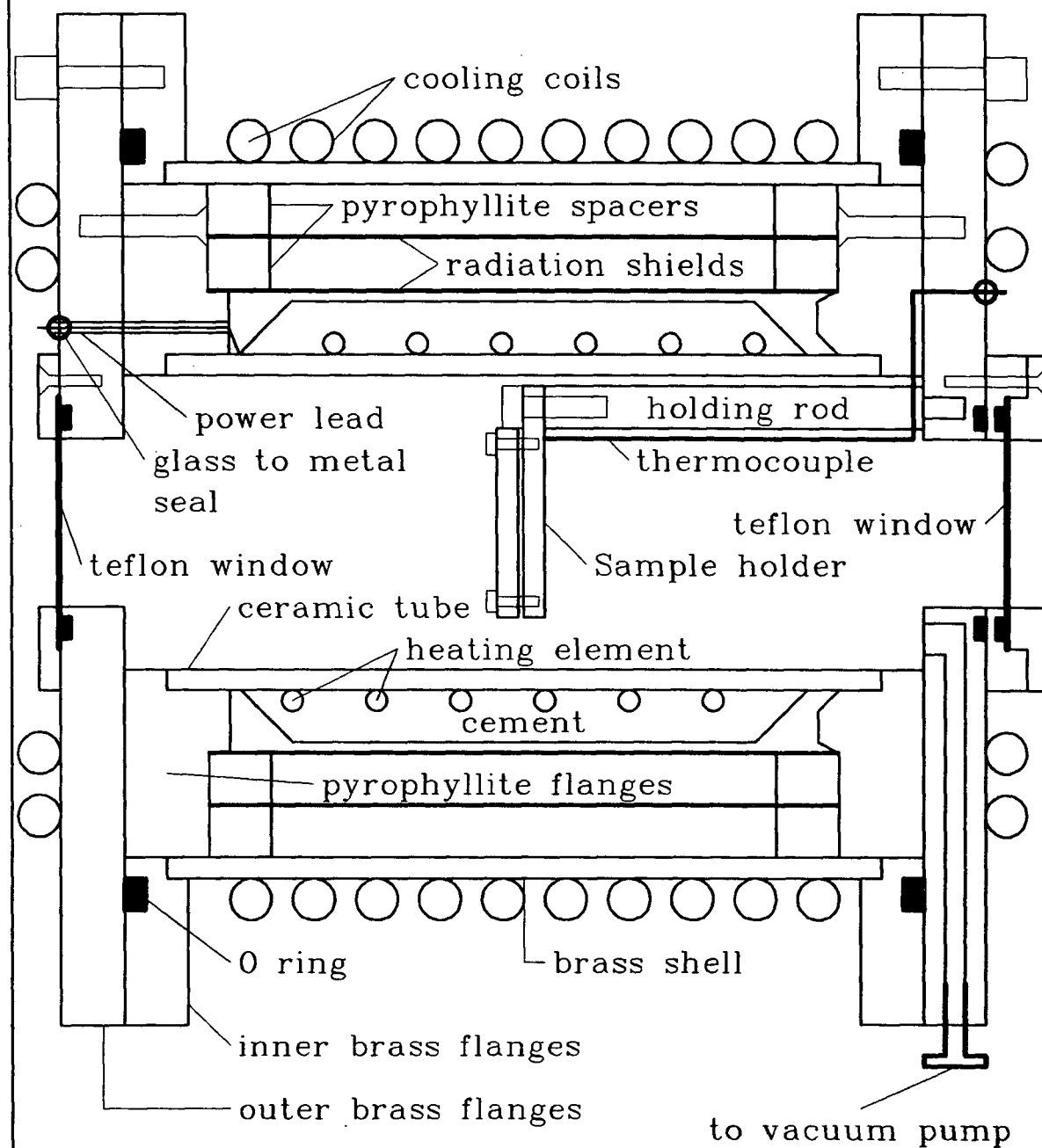


Fig. 22: The sample holder
for the Moessbauer furnace

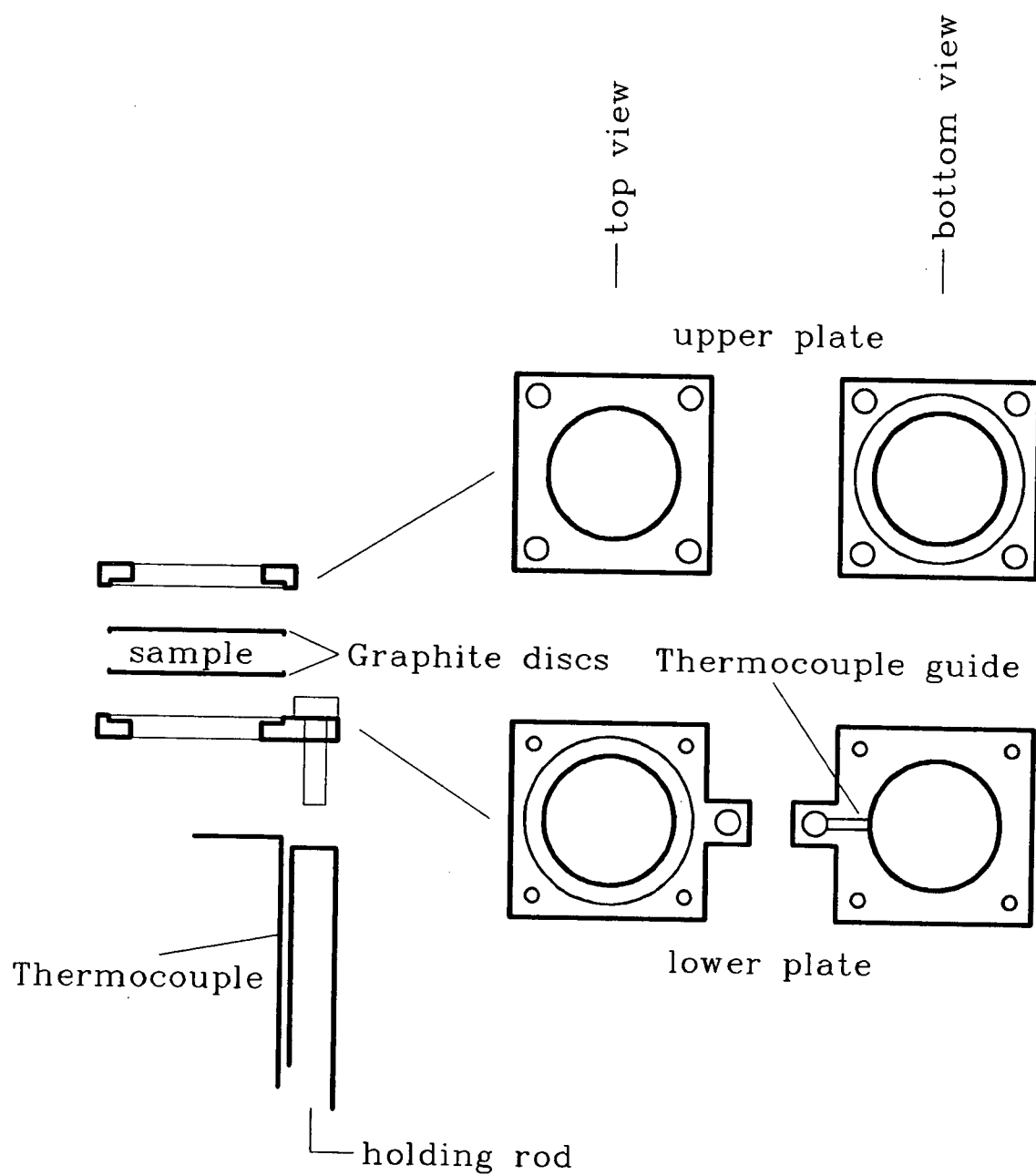


Table 16.: The materials used in the vacuum furnace

description	material,remarks
thermocouple	Chromel - Alumel, in 2-hole ceramic tube
ceramic tube	Alumina, for heating element
needle valves	Brass, to vacuum line
sample holder	stainless steel, type 316
holding rod	stainless steel, type 316
windows	teflon
glass to metal seal	for the thermocouple and the power leads
heating element	Nichrome
cement	Sauereisen
radiation shields	stainless steel, type 304
ceramic spacers	pyrophyllite, supporting the shields
ceramic flanges	pyrophyllite, supporting the furnace
O rings	Neoprene, different sizes
shell	brass
outer flanges	brass
inner flanges	brass
cooling coils	flexible copper tube

APPENDIX D: LISTING OF PROGRAM LATEX

```

LATEX:PROCEDURE OPTIONS(MAIN);
DCL (BLAH,BAN,IDA,ABIN,MN1) FILE;
DCL (KODLP,ISYMCE,NS,NPOS,NCOMPO,NREF,NBED,BED(10,9),IDX(-3:3),
     I,II,III,K,N,M,I,J),CODE,CODE2,ANOCOD,HMAX,KMAX,LMAX)
     BIN FIXED(31);
DCL (A,B,C,ALPHA,BETA,GAMMA,WL,WWL4,ANO,PI2,TL,TH,SL,SH,FNEUT(8),
     SINA,SINB,SINC,COSA,COSB,COSC,SINABC,SINBC,SINAC,SINAB,
     VOL,AS,BS,CS,COAS,COBS,COCS,SX2,MAXINT,INT,THETA,DWERT,
     RELINT,QQ,SMA,SMB,XN,YN,ZN,SCAT,FBRA,DUM,ARG,INSUM(13),
     AE,BE,CE,AE2,BE2,CE2,BC2,AC2,AB2,HH2,KK2,LL2,FF)
     DECIMAL FLOAT(16);
DCL (XX(50),YY(50),ZZ(50)) DECIMAL FLOAT(16);
DCL 1 INP(0:1000),
     2 (HH,KK,LL) BIN FIXED(31),
     2 (MUL,Q) DECIMAL FLOAT(16),
     1 OUP(1000),
     2 (VINT,STRU,LOPO,SUMA,SUMB,SUMAX,SUMBX) DECIMAL FLOAT(16),
     1 ATOM(8),
     2 ELEM CHAR(4),
     2 NA BIN FIXED(31),
     2 (DELFR,DELFI,FA(4),FB(4),FC) DECIMAL FLOAT(16),
     2 POS(50),
     3 IDE CHAR(2),
     3 (X,Y,Z,MUP,OCC,BT,BII(6)) DECIMAL FLOAT(16),
     3 BTCODE BIN FIXED(31),
     1 EQUI(24),
     2 (TS(3),FS(3,3)) DECIMAL FLOAT(16);
DCL (TITEL) CHAR(200);
DCL (HKL(3),CH(3),AA) CHAR(1);
DCL (HKLCOD) CHAR(15) VARYING;
DCL STR(3) CHAR(20) VARYING;
DCL (WLCOD,SPGR,IDENT) CHAR(10);
DCL (ELE) CHAR(4);
OPEN FILE(SYSPRINT) LINESIZE(132);
AA="";
GET FILE(BLAH) LIST(TITEL,A,B,C,ALPHA,BETA,GAMMA,
                   AE,BE,CE,WLCOD,SPGR,TL,TH,ANO,KODLP);
PUT EDIT(TITEL,'SPACE GROUP : ',SPGR)(COL(1),A,SKIP(2),A,A);
ON ENDFILE(BLAH) GOTO AAFA;
NCOMPO=0;
DO WHILE('1'B);
  GET FILE(BLAH) EDIT(ELE)(COL(1),A(4)); CODE=0;
  DO I=1 TO NCOMPO WHILE(CODE=0);
    IF ELE=ELEMT(I) THEN DO; CODE=I; NA(I)=NA(I)+1; END;
  END;
  IF CODE=0
  THEN DO; NCOMPO=NCOMPO+1; I=NCOMPO; ELEMT(I)=ELE; NA(I)=1; END;
  ELSE I=CODE;
  GET FILE(BLAH) EDIT(IDE(I,NA(I)))(A(2));
  GET FILE(BLAH) LIST(X(I,NA(I)),Y(I,NA(I)),Z(I,NA(I)),
                     OCC(I,NA(I)),BT(I,NA(I)));
  IF BT(I,NA(I))=0

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THEN DO; DO II=1 TO 6;
      GET FILE(BLAH) LIST(BII(I,NA(I),II));
      END;
      BTCODE(I,NA(I))=1;
    END;
  ELSE BTCODE(I,NA(I))=0;
END;
AAFA:ON ENDFILE(BAN) GOTO NOSP; CODE=0;
DO WHILE(CODE=0);
  GET FILE(BAN) EDIT(IDENT)(COL(1),A(10));
  IF SPGR=IDENT THEN
    DO; CODE=1;
      GET FILE(BAN) LIST(NS,ISYMCE,FBRA,NBED);
      DO II=1 TO NS; GET FILE(BAN) LIST(TS(II,*),FS(II,*)); END;
      PUT EDIT('Bravais multiplicity =',FBRA)(SKIP(2),A,F(4,1));
      PUT EDIT(NBED,'conditions for non-extinction :')
        (SKIP(2),COL(1),F(3,0),X(1),A);
      CH(1)='H'; CH(2)='K'; CH(3)='L';
      DO I=1 TO NBED;
        GET FILE(BAN) LIST(HKLCOD);
        PUT EDIT(HKLCOD)(COL(38),A);
        BED(I,*)=0;
        DO J=1 TO 3; HKL(J)=SUBSTR(HKLCOD,J,1);
          IF HKL(J)='0' THEN BED(I,J)=;
        END;
        IF HKL(1)=HKL(2) THEN DO; BED(I,4)=1; BED(I,5)=2; END;
        IF HKL(1)=HKL(3) THEN DO; BED(I,4)=1; BED(I,5)=3; END;
        IF HKL(2)=HKL(3) THEN DO; BED(I,4)=2; BED(I,5)=3; END;
        DO J=1 TO 3;
          IF (INDEX(HKLCOD,'+'||CH(J))~0
            | INDEX(HKLCOD,'-'||CH(J))~0) THEN BED(I,5+J)=;
          IF (INDEX(HKLCOD,'+'||CH(J))~0) THEN BED(I,5+J)=-;
        END;
        BED(I,9)=FIXED(SUBSTR(HKLCOD,INDEX(HKLCOD,'')+1,1),6,0);
      END;
    END;
  END;
NOSP:IF CODE=0 THEN DO; PUT DATA(SPGR); STOP; END;
PUT EDIT(NS,'equivalent point positions :')
  (SKIP(2),F(3,0),X(1),A);
IF ISYMCE=1 THEN PUT EDIT('( + symmetry centre at the origin)')
  (X(5),A);
PUT SKIP(2) EDIT('')(A);
CH(1)='X'; CH(2)='Y'; CH(3)='Z';
DO I=1 TO NS;
  STR='';
  DO J=1 TO 3;
    STR(J)=STR(J)||CHAR(FIXED(TS(I,J),8,5));
    STR(J)=SUBSTR(STR(J),3);
    DO K=1 TO 3;
      IF FS(I,J,K)=1 THEN STR(J)=STR(J)||'+'||CH(K);
      IF FS(I,J,K)=-1 THEN STR(J)=STR(J)||'-'||CH(K);
    END;
    IF INDEX(STR(J),'0.00000+' )~0 THEN SUBSTR(STR(J),1,11)='';
  END;

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    IF INDEX(STR(J),'0.00000')~ = 0 THEN SUBSTR(STR(J),1,10)=' ';
END;
PUT EDIT(STR)(COL(3),3 A(15));
END;
ON ENDFILE(BAN) GOTO NOWL;
CODE=0;
DO WHILE(CODE=0);
    GET FILE(BAN) EDIT(IDENT)(COL(1),A(5));
    IF WLCOD=IDENT
    THEN DO; GET FILE(BAN) LIST(ANOCOD,WL); CODE=1; END;
END;
NOWL:IF CODE=0 THEN DO; PUT DATA(WLCOD); STOP; END;
DELFR=0; DELFI=0; FA=0; FB=0; FC=0;
ON ENDFILE(BAN) GOTO NOSC; CODE=-NCOMPO;
DO WHILE(CODE<0);
    GET FILE(BAN) EDIT(IDENT)(COL(1),A(4));
    CODE2=0;
    DO I=1 TO NCOMPO WHILE(CODE2=0);
        IF ELEMT(I)=IDENT
        THEN DO; CODE2=1; CODE=CODE+1;
            DO J=1 TO 4; GET FILE(BAN) LIST(FA(I,J),FB(I,J)); END;
            GET FILE(BAN) LIST(FC(I),FNEUT(I));
            DO J=1 TO ANOCOD;
                GET FILE(BAN) LIST(DELFR(I),DELFI(I));
            END;
        END;
    END;
END;
END;
END;
NOSC:IF CODE<0
THEN DO; DO I=1 TO NCOMPO;
    IF FA(I,1)=0 THEN PUT SKIP DATA(ELEMT(I));
    END; STOP;
END;
PUT EDIT('scattering factor coefficients :','a1','b1','a2','b2',
    'a3','b3','a4','b4','c','sum(ai)+c')
    (SKIP(2),A,COL(12),(4) (A,X(8),A,X(10)),A,X(12),A);
DO I=1 TO NCOMPO;
    PUT EDIT(ELEMT(I))(COL(1),A(4));
    DO J=1 TO 4; PUT EDIT(FA(I,J),FB(I,J))(F(12,5),F(10,5)); END;
    PUT EDIT(FC(I),SUM(FA(I,*))+FC(I))(F(12,5),X(5),F(12,5));
END;
PUT EDIT('radiation :',WLCOD,'landa =',WL)
    (SKIP(2),A,X(1),A,A,F(9,6));
PUT EDIT('anomalous dispersion correction terms :')(SKIP(2),A);
PUT EDIT('delfr','delfi')(X(9),A,X(5),A);
IF ANO=0 THEN PUT EDIT('(not used for calculations)')(X(4),A);
DO I=1 TO NCOMPO;
    IF (DELFR(I)~ = 0)&(DELFI(I)~ = 0) THEN
        PUT EDIT(ELEMT(I),DELFR(I),DELFI(I))(COL(40),A(4),2 F(10,4));
    IF ANO=0 THEN DO; DELFR(I)=0; DELFI(I)=0; END;
END;
DO M=1 TO NCOMPO;
    DO I=1 TO NA(M);
        DO J=1 TO NS;

```

```

XX(J)=TS(J,1)+FS(J,1,1)*X(M,I)+FS(J,1,2)*Y(M,I)+FS(J,1,3)*Z(M,I);
YY(J)=TS(J,2)+FS(J,2,1)*X(M,I)+FS(J,2,2)*Y(M,I)+FS(J,2,3)*Z(M,I);
ZZ(J)=TS(J,3)+FS(J,3,1)*X(M,I)+FS(J,3,2)*Y(M,I)+FS(J,3,3)*Z(M,I);
END;
IF ISYMCE=1
THEN DO; NPOS=2*NS;
      DO J=(NS+1) TO (2*NS);
        XX(J)=-XX(J-NS); YY(J)=-YY(J-NS); ZZ(J)=-ZZ(J-NS);
      END;
END;
ELSE NPOS=NS;
DO J=1 TO NPOS; XX(J)=MOD(XX(J),1); YY(J)=MOD(YY(J),1);
      ZZ(J)=MOD(ZZ(J),1);
END; MUP(M,I)=NPOS;
DO J=1 TO NPOS-1; CODE=1;
  DO JJ=(J+1) TO NPOS WHILE(CODE=1);
    IF (ABS(XX(J)-XX(JJ))<1E-9)&(ABS(YY(J)-YY(JJ))<1E-9)
      &(ABS(ZZ(J)-ZZ(JJ))<1E-9)
    THEN DO; MUP(M,I)=MUP(M,I)-1;
      CODE=0;
    END;
  END;
END;
MUP(M,I)=MUP(M,I)/NPOS;
END;
END;
PUT EDIT('atom positions')(SKIP(2),A);
PUT EDIT('x/a','y/b','z/c','Bt','mult','occ','N',
  'atoms / unit cell')
  (COL(12),A,COL(22),A,COL(32),A,COL(41),A,COL(48),A,
  COL(57),A,COL(65),A,COL(73),A);
DO I=1 TO NCOMPO;
  DO J=1 TO NA(I);
    PUT EDIT(ELEMT(I),IDE(I,J),X(I,J),Y(I,J),Z(I,J),BT(I,J),
      MUP(I,J),OCC(I,J),MUP(I,J)*NPOS,MUP(I,J)*NPOS*OCC(I,J))
      (COL(1),A,A,3 F(10,6),F(8,4),2 F(8,4),F(6,1),X(6),F(11,5));
  END;
END;
IF ISYMCE=0 THEN DUM=1; ELSE DUM=2;
PI2=8*ATAN(1); MAXINT=1;
SINA=SIND(ALPHA); SINB=SIND(BETA); SINC=SIND(GAMMA);
COSA=COSD(ALPHA); COSB=COSD(BETA); COSC=COSD(GAMMA);
SINABC=SIND((ALPHA+BETA+GAMMA)/2.0);
SINBC=SIND((-ALPHA+BETA+GAMMA)/2.0);
SINAC=SIND((ALPHA-BETA+GAMMA)/2.0);
SINAB=SIND((ALPHA+BETA-GAMMA)/2.0);
VOL=2*A*B*C*SQRT(SINABC*SINBC*SINAC*SINAB);
AS=B*C*SINA/VOL; BS=A*C*SINB/VOL; CS=A*B*SINC/VOL;
COAS=(COSB*COSC-COSA)/(SINB*SINC);
COBS=(COSC*COSA-COSB)/(SINC*SINA);
COCS=(COSA*COSB-COSC)/(SINA*SINB);
PUT EDIT('a =',A,'alpha =',ALPHA,'b =',B,'beta =',BETA,
  'c =',C,'gamma =',GAMMA,'vol =',VOL)(SKIP(2),
  (3) (COL(1),A,F(9,5),COL(18),A,F(10,5)),X(7),A,F(10,4));

```

```

AE2=AE*AE; BE2=BE*BE; CE2=CE*CE;
BC2=(B*C*BE*CE)**2; AC2=(A*C*AE*CE)**2; AB2=(A*B*AE*BE)**2;
PUT EDIT('anisotropy : ',AE,BE,CE)(X(5),A,(3) (F(9,5)));
ON ENDPAGE BEGIN;
PUT EDIT(WLCOD,WL,TITEL)(PAGE,A(6),F(8,5),X(4),A);
PUT EDIT('H','K','L','INT','ABS INT','2 TH','D','|F(hkl)|',
        'MULT','L.P.','sR*fr','sl*fr','sR*fl','sl*fl')
        (SKIP(2),COL(8),A,COL(12),A,COL(16),A,COL(22),A,COL(31),A,
        COL(43),A,COL(54),A,COL(61),A,COL(71),A,COL(79),A,COL(90),
        A,COL(102),A,COL(114),A,COL(126),A);
PUT EDIT(' ')(SKIP,A);
END;
SH=SIND(TH)**2; SL=SIND(TL)**2; NREF=0; WWL4=WL*WL/4.0;
HMAX=FLOOR(SQRT(SH/WWL4)/AS);
KMAX=FLOOR(SQRT(SH/WWL4)/BS);
LMAX=FLOOR(SQRT(SH/WWL4)/CS);
DO I=HMAX TO -HMAX BY -1;
DO II=KMAX TO -KMAX BY -1;
DO III=LMAX TO -LMAX BY -1;
QQ=(WWL4)*((I*AS)**2+(II*BS)**2+(III*CS)**2
+2*I*III*BS*CS*COAS
+2*I*III*AS*CS*COBS
+2*I*II*AS*BS*COCS);
IF QQ>SH THEN GOTO NEXT; IF QQ<SL THEN GOTO NEXT;
CODE=1; IDX(-3)=-III; IDX(-2)=-II; IDX(-1)=-I;
IDX(0)=0; IDX(1)=I; IDX(2)=II; IDX(3)=III;
DO J=1 TO NBED WHILE(CODE=1);
IF (IDX(BED(J,1))=0)&(IDX(BED(J,2))=0)&(IDX(BED(J,3))=0)
&(IDX(BED(J,4))=IDX(BED(J,5)))
&(MOD(IDX(BED(J,6))+IDX(BED(J,7))+IDX(BED(J,8)),BED(J,9))~0)
THEN CODE=0;
END;
IF CODE=0 THEN GOTO NEXT;
DO N=1 TO NREF WHILE(CODE=1);
IF ABS(Q(N)-QQ)<1E-9 THEN DO; MUL(N)=MUL(N)+1;
CODE=0;
END;
END;
IF CODE=0 THEN GOTO NEXT;
IF (I=0)&(II=0)&(III=0) THEN GOTO NEXT;
NREF=NREF+1; IF NREF>1000 THEN DO; NREF=1000;
GOTO ORD;
END;
Q(NREF)=QQ; MUL(NREF)=1;
HH(NREF)=I; KK(NREF)=II; LL(NREF)=III;
NEXT:END;
END;
END;
ORD:N=1;
DO WHILE(N<NREF);
IF Q(N)>Q(N+1) THEN DO; INP(0)=INP(N); INP(N)=INP(N+1);
INP(N+1)=INP(0);
N=N-1; IF N=0 THEN N=2;
END;

```

```

ELSE N=N+1;
END;
DO N=1 TO NREF;
/* PUT EDIT(N,'Y',HH(N),KK(N),LL(N))
   (SKIP(2),COL(1),F(3,0),A,(3) (F(4,0))); */
THETA=ATAN(SQRT(Q(N)/(1-Q(N))));
LOPO(N)=(1+COS(2*THETA)**2)/(SIN(THETA)*SIN(2*THETA));
SX2=Q(N)/(WL*WL);
SUMA(N)=0; SUMB(N)=0; SUMAX(N)=0; SUMBX(N)=0;
DO M=1 TO NCOMPO;
SMA=0; SMB=0;
DO I=1 TO NA(M);
IF BTCODE(M,I)=1 THEN
BT(M,I)=BII(M,I,1)*HH(N)**2+BII(M,I,2)*KK(N)**2+BII(M,I,3)*
LL(N)**2+BII(M,I,4)*2*HH(N)*KK(N)+BII(M,I,5)*2*HH(N)*
LL(N)+BII(M,I,6)*2*KK(N)*LL(N);
DO J=1 TO NS;
XN=TS(J,1)+FS(J,1,1)*X(M,I)+FS(J,1,2)*Y(M,I)+FS(J,1,3)*Z(M,I);
YN=TS(J,2)+FS(J,2,1)*X(M,I)+FS(J,2,2)*Y(M,I)+FS(J,2,3)*Z(M,I);
ZN=TS(J,3)+FS(J,3,1)*X(M,I)+FS(J,3,2)*Y(M,I)+FS(J,3,3)*Z(M,I);
ARG=PI2*(HH(N)*XN+KK(N)*YN+LL(N)*ZN);
SMA=SMA+COS(ARG)*MUP(M,I)*OCC(M,I)*EXP(-BT(M,I)*SX2);
IF ISYMCE~ =1 THEN
SMB=SMB+SIN(ARG)*MUP(M,I)*OCC(M,I)*EXP(-BT(M,I)*SX2);
END;
END;
SCAT=0;
DO I=1 TO 4; SCAT=SCAT+FA(M,I)*EXP(-FB(M,I)*SX2); END;
SCAT=SCAT+DELFR(M)+FC(M);
SUMA(N)=SUMA(N)+SMA*SCAT;
SUMB(N)=SUMB(N)+SMB*SCAT;
SUMAX(N)=SUMAX(N)+SMA*DELFI(M)*FBRA*DUM;
SUMBX(N)=SUMBX(N)+SMB*DELFI(M)*FBRA;
END;
SUMA(N)=SUMA(N)*FBRA*DUM; SUMB(N)=SUMB(N)*FBRA;
STRU(N)=(SUMA(N)-SUMBX(N))**2+(SUMB(N)+SUMAX(N))**2;
VINT(N)=LOPO(N)*MUL(N)*STRU(N);
HH2=HH(N)*HH(N); KK2=KK(N)*KK(N); LL2=LL(N)*LL(N);
FF=(AE2*BC2*HH2+BE2*AC2*KK2+CE2*AB2*LL2)/(BC2*HH2+AC2*KK2+AB2*LL2);
FF=SQRT(FF); VINT(N)=VINT(N)*FF;
MAXINT=MAX(VINT(N),MAXINT);
END;
WEITER:N=N-1;
PUT FILE(ABIN) EDIT(AA,TITEL,AA,'')(COL(1),A,A(80),A,A);
PUT FILE(IDA) EDIT(AA,TITEL,AA,'')(COL(1),A,A(80),A,A);
INSUM=0;
DO I=1 TO N;
IF MOD(I,55)=1 THEN SIGNAL ENDPAGE;
DWERT=WL/(2*SQRT(Q(I)));
THETA=ATAND(SQRT(Q(I)/(1-Q(I))));
RELINT=VINT(I)*100/MAXINT;
IF HH(I)=0 & KK(I)=2 & LL(I)=0 THEN INSUM(1)=VINT(I);
IF HH(I)=1 & KK(I)=1 & LL(I)=0 THEN INSUM(2)=VINT(I);
IF HH(I)=1 & KK(I)=1 & LL(I)=1 THEN INSUM(3)=INSUM(3)+VINT(I);

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IF HH(I)=1 & KK(I)=2 & LL(I)=0 THEN INSUM(3)=INSUM(3)+VINT(I);
IF HH(I)=1 & KK(I)=2 & LL(I)=1 THEN INSUM(4)=INSUM(4)+VINT(I);
IF HH(I)=0 & KK(I)=0 & LL(I)=2 THEN INSUM(4)=INSUM(4)+VINT(I);
IF HH(I)=1 & KK(I)=3 & LL(I)=0 THEN INSUM(5)=VINT(I);
IF HH(I)=0 & KK(I)=2 & LL(I)=2 THEN INSUM(6)=INSUM(6)+VINT(I);
IF HH(I)=0 & KK(I)=4 & LL(I)=0 THEN INSUM(6)=INSUM(6)+VINT(I);
IF HH(I)=1 & KK(I)=3 & LL(I)=1 THEN INSUM(7)=VINT(I);
IF HH(I)=1 & KK(I)=1 & LL(I)=2 THEN INSUM(8)=VINT(I);
IF HH(I)=2 & KK(I)=0 & LL(I)=0 THEN INSUM(9)=INSUM(9)+VINT(I);
IF HH(I)=0 & KK(I)=4 & LL(I)=1 THEN INSUM(9)=INSUM(9)+VINT(I);
IF HH(I)=2 & KK(I)=1 & LL(I)=0 THEN INSUM(10)=VINT(I);
IF HH(I)=1 & KK(I)=2 & LL(I)=2 THEN INSUM(11)=INSUM(11)+VINT(I);
IF HH(I)=1 & KK(I)=4 & LL(I)=0 THEN INSUM(11)=INSUM(11)+VINT(I);
IF HH(I)=2 & KK(I)=2 & LL(I)=2 THEN INSUM(12)=INSUM(12)+VINT(I);
IF HH(I)=2 & KK(I)=4 & LL(I)=0 THEN INSUM(12)=INSUM(12)+VINT(I);
IF HH(I)=1 & KK(I)=2 & LL(I)=3 THEN INSUM(12)=INSUM(12)+VINT(I);
IF HH(I)=1 & KK(I)=5 & LL(I)=2 THEN INSUM(13)=VINT(I);
PUT EDIT(I,''),HH(I),KK(I),LL(I),RELINT,VINT(I),
    2*THETA,DWERT,SQRT(STRU(I)),MUL(I),LOPO(I),SUMA(I),SUMB(I),
    SUMAX(I),SUMBX(I))
    (COL(1),F(3,0),A,3 F(4,0),F(9,3),F(12,2),F(10,4),F(10,5),
    F(11,4),F(5,0),F(10,4),4 F(12,5));
PUT FILE(IDA) EDIT(HH(I),KK(I),LL(I),2*THETA,RELINT,' ')
    (COL(1),3 F(4,0),X(1),F(9,4),X(1),F(9,3),A);
PUT FILE(ABIN) EDIT(HH(I),KK(I),LL(I),VINT(I),' ')
    (COL(1),3 F(4,0),X(3),E(12,5,6),A);
END;
PUT EDIT(TITEL)(PAGE,SKIP(2),A);
PUT FILE(MN1) EDIT(AA,TITEL,AA,' ')(COL(1),A,A,A,A);
PUT EDIT('222')(SKIP(3),COL(115),A);
PUT EDIT('111','121','022','200','122','240')
    (COL(34),A,COL(43),A,COL(61),A,COL(88),A,COL(106),A,COL(115),A);
PUT EDIT('020','110','120','002','130','040','131','112','041',
    '210','140','123','152')
    (COL(16),(13) (A,X(6)));
PUT SKIP(2) EDIT('020')(COL(1),A);
PUT FILE(MN1) EDIT('020')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(1)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
    PUT FILE(MN1) EDIT(INSUM(1)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('110')(COL(1),A);
PUT FILE(MN1) EDIT('110')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(2)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
    PUT FILE(MN1) EDIT(INSUM(2)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('111+120')(COL(1),A);
PUT FILE(MN1) EDIT('111+120')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(3)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
    PUT FILE(MN1) EDIT(INSUM(3)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('121+002')(COL(1),A);
PUT FILE(MN1) EDIT('121+002')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(4)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
    PUT FILE(MN1) EDIT(INSUM(4)/INSUM(I))(COL(12+(I-1)*9),F(9,5));

```



```

END;
PUT SKIP(2) EDIT('130')(COL(1),A);
PUT FILE(MN1) EDIT('130')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(5)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(5)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('022+040')(COL(1),A);
PUT FILE(MN1) EDIT('022+040')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(6)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(6)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('131')(COL(1),A);
PUT FILE(MN1) EDIT('131')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(7)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(7)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('112')(COL(1),A);
PUT FILE(MN1) EDIT('112')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(8)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(8)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('200+041')(COL(1),A);
PUT FILE(MN1) EDIT('200+041')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(9)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(9)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('210')(COL(1),A);
PUT FILE(MN1) EDIT('210')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(10)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(10)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('122+140')(COL(1),A);
PUT FILE(MN1) EDIT('122+140')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(11)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(11)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('222+140+123')(COL(1),A);
PUT FILE(MN1) EDIT('222+140+123')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(12)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(12)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
PUT SKIP(2) EDIT('152')(COL(1),A);
PUT FILE(MN1) EDIT('152')(COL(1),A);
DO I=1 TO 13; PUT EDIT(INSUM(13)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
  PUT FILE(MN1) EDIT(INSUM(13)/INSUM(I))(COL(12+(I-1)*9),F(9,5));
END;
END LATEX;

```

Example of output

OLIVINE : M(1):FE(0.167)MN(0.333)MG(0.500) M(2):FE(0.167)MN(0.333)MG(0.500)

SPACE GROUP : P B N M

Bravais multiplicity = 1.0

2 conditions for non-extinction : HOL: H+L=2N
OKL: K=2N

4 equivalent point positions : (+ symmetry centre at the origin)

X	Y	Z
0.50000-X	0.50000+Y	0.50000-Z
-X	-Y	0.50000+Z
0.50000+X	0.50000-Y	-Z

scattering factor coefficients :

	a1	b1	a2	b2	a3	b3	a4	b4	c	sum(ai)+c
FE	11.76950	4.76110	7.35730	0.30720	3.52220	15.35350	2.30450	76.88049	1.03690	25.99040
MN	11.28190	5.34090	7.35730	0.34320	3.01930	17.86739	2.24410	83.75429	1.08960	24.99220
MG	5.42040	2.82750	2.17350	79.26110	1.22690	0.38080	2.30730	7.19370	0.85840	11.98650
SI	6.29150	2.43860	3.03530	32.33369	1.98910	0.67850	1.54100	81.69370	1.14070	13.99760
O	3.04850	13.27710	2.28680	5.70110	1.54630	0.32390	0.86700	32.90889	0.25080	7.99940

radiation : CUA1 landa = 1.540560

anomalous dispersion correction terms :

	delfr	delfi
FE	-1.1790	3.2040
MN	-0.5680	2.8080
MG	0.1650	0.1770
SI	0.2440	0.3300
O	0.0470	0.0320

atom positions

	x/a	y/b	z/c	Bt	mult	occ	N	atoms / unit cell
FE 1	0.000000	0.000000	0.000000	0.5031	0.5000	0.1667	4.0	0.66668
FE 2	0.988850	0.278870	0.250000	0.4702	0.5000	0.1667	4.0	0.66668
MN 1	0.000000	0.000000	0.000000	0.5031	0.5000	0.3333	4.0	1.33332
MN 2	0.988850	0.278870	0.250000	0.4702	0.5000	0.3333	4.0	1.33332
MG 1	0.000000	0.000000	0.000000	0.5031	0.5000	0.5000	4.0	2.00000
MG 2	0.988850	0.278870	0.250000	0.4702	0.5000	0.5000	4.0	2.00000
SI 1	0.425030	0.095400	0.250000	0.3463	0.5000	1.0000	4.0	4.00000
O 1	0.763510	0.092360	0.250000	0.4967	0.5000	1.0000	4.0	4.00000
O 2	0.215820	0.450440	0.250000	0.4950	0.5000	1.0000	4.0	4.00000
O 3	0.282480	0.163610	0.036750	0.5387	1.0000	1.0000	8.0	8.00000

a = 4.80630 alpha = 90.00000
b = 10.48500 beta = 90.00000
c = 6.09630 gamma = 90.00000 vol = 307.2173

CUA1 1.54056 OLIVINE : M(1):FE(O.167)MN(O.333)MG(O.500) M(2):FE(O.167)MN(O.333)MG(O.500)

H	K	L	INT	ABS	INT	2 TH	D	[F(hkl)]	MULT	L.P.	SR*FR	SI*FR	SR*FI	SI*FI
1)	0	2	0	13.657	83866.74	16.8981	5.24250	30.5769	2	44.8511	30.56316	0.00000	0.91593	0.00000
2)	1	1	0	1.445	8873.79	20.3087	4.36913	8.4984	4	30.7164	7.46161	0.00000	4.06791	0.00000
3)	0	2	1	28.053	172274.33	22.3477	3.97489	41.3562	4	25.1813	-41.34690	0.00000	0.87917	0.00000
4)	1	0	1	11.489	70555.55	23.5516	3.77436	27.9568	4	22.5681	-27.95599	0.00000	-0.21699	0.00000
5)	1	1	1	37.419	229785.65	25.0543	3.55127	38.0670	8	19.8215	-37.68133	0.00000	-5.40499	0.00000
6)	1	2	0	9.304	57133.25	25.1155	3.54276	26.9130	4	19.7200	-26.90281	0.00000	-0.73902	0.00000
7)	1	2	1	4.478	27499.35	29.1292	3.06309	15.4488	8	14.4026	-15.43549	0.00000	-0.64231	0.00000
8)	0	0	2	10.520	64599.98	29.2752	3.04815	47.6101	2	14.2496	-47.59129	0.00000	-1.33991	0.00000
9)	1	3	0	79.298	486966.21	31.6267	2.82667	100.4229	4	12.0718	99.96257	0.00000	9.60472	0.00000
10)	0	2	2	14.381	88312.18	33.9931	2.63511	46.2420	4	10.3249	44.88469	0.00000	11.12160	0.00000
11)	0	4	0	3.800	23333.75	34.1784	2.62125	33.8145	2	10.2035	32.43522	0.00000	9.55906	0.00000
12)	1	3	1	71.982	442039.67	34.9599	2.56442	75.4257	8	9.7125	75.15995	0.00000	6.32575	0.00000
13)	1	1	2	100.000	614093.41	35.8926	2.49989	91.4388	8	9.1688	91.13410	0.00000	8.16167	0.00000
14)	0	4	1	13.029	80009.63	37.3104	2.40808	48.7386	4	8.4205	-48.49572	0.00000	-4.85999	0.00000
15)	2	0	0	6.586	40446.54	37.3899	2.40315	49.1220	2	8.3811	47.51910	0.00000	12.44603	0.00000
16)	2	1	0	7.564	46448.71	38.3968	2.34241	38.3309	4	7.9034	38.30111	0.00000	1.51159	0.00000
17)	1	2	2	21.667	133053.35	38.9463	2.31062	46.6007	8	7.6586	-46.59961	0.00000	0.32147	0.00000
18)	1	4	0	17.488	107394.98	39.1112	2.30126	59.4867	4	7.5872	59.48598	0.00000	0.29266	0.00000
19)	2	1	1	11.518	70729.72	41.2536	2.18656	36.2232	8	6.7381	36.21458	0.00000	0.79116	0.00000
20)	2	2	0	0.160	980.76	41.2930	2.18457	6.0387	4	6.7238	5.99989	0.00000	0.68365	0.00000
21)	1	4	1	0.004	23.81	41.9273	2.15297	0.6767	8	6.4985	0.15466	0.00000	0.65882	0.00000
22)	1	3	2	5.472	33600.65	43.6339	2.07264	26.5866	8	5.9420	26.44664	0.00000	2.72403	0.00000
23)	2	2	1	1.113	6834.21	43.9938	2.05651	12.1017	8	5.8332	12.00654	0.00000	1.51458	0.00000
24)	0	4	2	2.429	14917.88	45.6072	1.98744	26.3338	4	5.3780	26.22587	0.00000	2.38168	0.00000
25)	2	3	0	1.370	8410.36	45.7833	1.98021	19.8591	4	5.3313	19.85714	0.00000	0.27930	0.00000
26)	1	5	0	4.314	26493.08	47.2520	1.92203	36.5296	4	4.9634	36.45160	0.00000	2.38635	0.00000
27)	0	2	3	0.009	54.83	47.9749	1.89474	1.6907	4	4.7953	1.33402	0.00000	-1.03869	0.00000
28)	2	0	2	0.744	4571.78	48.1792	1.88718	15.5131	4	4.7493	-15.49817	0.00000	-0.68072	0.00000
29)	2	3	1	0.031	188.93	48.2836	1.88334	2.2354	8	4.7260	-2.22590	0.00000	0.20583	0.00000
30)	1	0	3	0.307	1884.46	48.6037	1.87168	10.0595	4	4.6556	-10.05953	0.00000	0.00600	0.00000
31)	2	1	2	0.718	4408.80	49.0038	1.85733	10.9819	8	4.5696	-10.90031	0.00000	-1.33581	0.00000
32)	1	1	3	7.096	43573.47	49.4230	1.84256	34.8605	8	4.4819	34.45486	0.00000	5.30269	0.00000
33)	1	4	2	0.127	778.88	49.5936	1.83662	4.6791	8	4.4469	4.67822	0.00000	0.08951	0.00000
34)	1	5	1	5.195	31903.34	49.6958	1.83308	30.0165	8	4.4261	-29.80299	0.00000	-3.57388	0.00000
35)	2	2	2	68.656	421609.89	51.4186	1.77564	113.4350	8	4.0957	112.84963	0.00000	11.50889	0.00000
36)	2	4	0	21.141	129824.85	51.5512	1.77138	89.2812	4	4.0717	88.71310	0.00000	10.05579	0.00000
37)	1	2	3	3.258	20010.18	51.8235	1.76271	24.9343	8	4.0232	24.92375	0.00000	0.72482	0.00000
38)	0	6	0	0.058	357.82	52.3086	1.74750	6.7397	2	3.9387	6.39151	0.00000	2.13839	0.00000
39)	2	4	1	12.287	75453.70	53.8511	1.70103	50.5816	8	3.6864	-50.38080	0.00000	-4.50287	0.00000
40)	0	6	1	13.220	81184.34	54.5861	1.67985	75.3530	4	3.5745	75.11186	0.00000	6.02407	0.00000
41)	2	3	2	1.355	8319.67	55.2738	1.66056	17.3015	8	3.4742	-17.29937	0.00000	-0.26859	0.00000
42)	1	3	3	17.019	104515.02	55.6591	1.64998	61.8080	8	3.4198	-61.49901	0.00000	-6.17264	0.00000
43)	1	6	0	0.612	3757.61	55.9415	1.64232	16.6694	4	3.3807	16.66940	0.00000	-0.01424	0.00000
44)	1	5	2	10.113	62102.86	56.5605	1.62580	48.5203	8	3.2974	47.58214	0.00000	9.49504	0.00000
45)	0	4	3	8.332	51163.71	57.3214	1.60602	63.2313	4	3.1992	63.03969	0.00000	4.91840	0.00000

CUA1	1.54056	OLIVINE : M(1):FE(O.167)MN(O.333)MG(O.500)	M(2):FE(O.167)MN(O.333)MG(O.500)	SR*fr	SI*fr	SR*fi	SI*fi							
H	K	L	INT	ABS INT	2 TH	D	F(hk1)	MULT	L.P.	SR*fr	SI*fr	SR*fi	SI*fi	
46)	1	6	1	0.091	558.89	58.1222	1.58578	4.7468	8	3.1005	-4.74286	0.00000	0.19316	0.00000
47)	3	1	0	4.124	25327.53	58.2051	1.58372	45.2635	4	3.0906	45.00499	0.00000	4.83033	0.00000
48)	2	5	0	0.162	995.31	58.3542	1.58003	8.9988	4	3.0728	-8.98332	0.00000	0.52682	0.00000
49)	3	0	1	0.733	4500.72	59.6192	1.54949	19.6025	4	2.9282	-19.60247	0.00000	0.00591	0.00000
50)	2	1	3	2.158	13252.18	60.2405	1.53498	24.0622	8	2.8611	-24.05103	0.00000	-0.73391	0.00000
51)	3	1	1	4.867	29890.31	60.3335	1.53284	36.1998	8	2.8512	-35.76720	0.00000	-5.57956	0.00000
52)	3	2	0	1.770	10868.18	60.3634	1.53215	30.8869	4	2.8481	-30.84547	0.00000	-1.59891	0.00000
53)	2	4	2	3.837	23563.82	60.3898	1.53154	32.1748	8	2.8453	-32.10405	0.00000	2.13265	0.00000
54)	2	5	1	3.560	21863.66	60.4793	1.52949	31.0436	8	2.8359	-30.99811	0.00000	-1.68035	0.00000
55)	0	0	4	23.612	144996.73	60.7169	1.52407	160.5900	2	2.8112	160.02220	0.00000	13.49185	0.00000
56)	1	4	3	0.496	3048.75	60.7543	1.52323	11.6511	8	2.8073	11.63910	0.00000	-0.52929	0.00000
57)	0	6	2	31.336	192431.80	61.0733	1.51603	131.6716	4	2.7748	131.27929	0.00000	10.15647	0.00000
58)	2	2	3	0.499	3061.94	62.3559	1.48790	12.0180	8	2.6500	11.94727	0.00000	-1.30221	0.00000
59)	3	2	1	1.102	6765.21	62.4471	1.48594	17.8927	8	2.6414	-17.82120	0.00000	-1.59763	0.00000
60)	0	2	4	0.847	5201.02	63.5160	1.46349	22.6039	4	2.5448	22.58597	0.00000	0.90098	0.00000
61)	3	3	0	4.396	26998.11	63.8625	1.45638	51.8067	4	2.5148	51.05091	0.00000	8.81666	0.00000
62)	1	6	2	0.264	1622.01	64.3851	1.44581	9.0590	8	2.4706	-9.05873	0.00000	0.06453	0.00000
63)	1	1	4	0.176	1083.51	64.7251	1.43904	7.4464	8	2.4426	6.37733	0.00000	3.84425	0.00000
64)	1	7	0	12.317	75637.83	65.1834	1.43002	88.6584	4	2.4057	87.84183	0.00000	12.00501	0.00000
65)	2	3	3	0.144	882.24	65.7947	1.41821	6.8388	8	2.3580	-6.83297	0.00000	-0.28150	0.00000
66)	3	3	1	6.789	41689.08	65.8833	1.41652	47.0783	8	2.3512	46.79036	0.00000	5.19885	0.00000
67)	2	6	0	0.024	148.49	66.0505	1.41333	3.9843	4	2.3385	-3.17174	0.00000	2.41138	0.00000
68)	3	1	2	8.165	50139.76	66.4742	1.40535	52.1232	8	2.3069	51.64153	0.00000	7.06963	0.00000
69)	2	5	2	0.320	1967.41	66.6125	1.40277	10.3477	8	2.2968	-10.32505	0.00000	-0.68452	0.00000
70)	1	2	4	0.188	1152.56	66.7603	1.40002	7.9387	8	2.2860	-7.91391	0.00000	-0.62637	0.00000
71)	1	5	3	1.205	7399.24	66.9578	1.39637	20.1774	8	2.2718	19.88110	0.00000	3.44520	0.00000
72)	1	7	1	0.446	2741.18	67.1832	1.39223	12.3248	8	2.2557	-12.30172	0.00000	0.75311	0.00000
73)	2	6	1	1.919	11785.78	68.0374	1.37682	25.8959	8	2.1969	25.34440	0.00000	5.31600	0.00000
74)	3	2	2	11.427	70170.54	68.4829	1.36894	63.6165	8	2.1673	63.58784	0.00000	1.90975	0.00000
75)	3	4	0	3.526	21654.13	68.5944	1.36699	50.0620	4	2.1601	-50.06062	0.00000	-0.36877	0.00000

APPENDIX E: THE POLYNOMIAL FUNCTION FOR THE LATTICE

PARAMETERS

In Fig 12 to 15, a polynomial function was used to approximate the values of the lattice parameters as a function of composition. Although this function is not used further, it is given here for the sake of completeness.

$$f = F_1 \cdot x_{Fe} + F_2 \cdot x_{Mn} + F_3 \cdot x_{Mg} + F_4 \cdot x_{Fe}^2 \cdot x_{Mn} + F_5 \cdot x_{Fe}^2 \cdot x_{Mg} \\ + F_6 \cdot x_{Mn}^2 \cdot x_{Fe} + F_7 \cdot x_{Mn}^2 \cdot x_{Mg} + F_8 \cdot x_{Mg}^2 \cdot x_{Fe} + F_9 \cdot x_{Mg}^2 \cdot x_{Mn}$$

The values for the F_i are given below:

	a_0	b_0	c_0	vol.
F_1	4.819677	10.487292	6.093562	307.99417
F_2	4.904755	10.605876	6.262027	325.74903
F_3	4.754401	10.201505	5.982884	290.17196
F_4	-0.03020371	0.126914	-0.01660544	0.39120356
F_5	0.01548309	-0.06422586	-0.03276860	-2.8579071
F_6	-0.02622405	0.1723197	-0.05150567	-2.8579071
F_7	-0.02482657	0.2651929	0.1090701	10.459802
F_8	-0.00301987	0.05959161	0.05274279	3.7445689
F_9	-0.1072226	0.08315177	-0.0537160	-8.8489109

APPENDIX F: TABLES USED FOR THE APPROXIMATION OF THE
POSITIONAL PRARMETERS AND THE RESULTING UNCERTAINTIES

The following tables were used in chapter 2.7.

The multiple linear regression of table 4, was fitted with the data in table 17 and 18. Table 19 to 21 are the estimated uncertainties in the calculation of integrated intensities due to approximate positional parameters and temperature correction factors.

Table 17: Fe-Mn-Mg Olivines from the literature with reported site occupancies and/or structure data

Ref.	Fe	Mn	Mg	Fe+Mn+Mg	a	b	c	Fe(M1)	Mn(M1)	Mg(M1)	Fe(M2)	Mn(M2)	Mg(M2)
(01)Fa	1.0000	0.0000	0.0000	1.0000	4.81950	10.47880	6.08730	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(02)Fa	1.0000	0.0000	0.0000	1.0000	4.81800	10.47000	6.08600	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(03)Fa	1.0000	0.0000	0.0000	1.0000	4.81800	10.47000	6.08600	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(00)Fa	1.0000	0.0000	0.0000	1.0000	4.81980	10.48390	6.09190	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(04)Fa	1.0000	0.0000	0.0000	1.0000	4.82110	10.47790	6.08890	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(05)Fa	1.0000	0.0000	0.0000	1.0000	4.81900	10.47000	6.08600	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(06)Fa	1.0000	0.0000	0.0000	1.0000	4.81860	10.48220	6.11080	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
(14)OL5	0.8900	0.1100	0.0000	1.0000	4.82600	10.51400	6.10500	0.9760	0.0240	0.0000	0.8050	0.1950	0.0000
(14)OL4	0.6900	0.3100	0.0000	1.0000	4.84000	10.55600	6.13500	0.8260	0.1740	0.0000	0.5560	0.4440	0.0000
(14)OL3	0.4700	0.5300	0.0000	1.0000	4.85600	10.58500	6.16800	0.6110	0.3890	0.0000	0.3310	0.6690	0.0000
(14)OL2	0.3000	0.7000	0.0000	1.0000	4.87100	10.59400	6.20000	0.4040	0.5960	0.0000	0.1970	0.8030	0.0000
(14)OL1	0.0900	0.9100	0.0000	1.0000	4.89600	10.60300	6.24100	0.1350	0.8650	0.0000	0.0450	0.9550	0.0000
(01)Teph	0.0000	1.0000	0.0000	1.0000	4.90230	10.59640	6.25670	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000
(00)Teph	0.0000	1.0000	0.0000	1.0000	4.90330	10.60300	6.25790	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000
(12)Teph	0.0000	1.0000	0.0000	1.0000	4.90000	10.60500	6.26500	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000
(18)	0.5200	0.4600	0.0200	1.0000	4.84400	10.57700	6.14600	0.6600	0.2900	0.0400	0.3700	0.6300	0.0000
(17)Fa	0.9220	0.0370	0.0390	0.9980	4.81600	10.46900	6.09900	-	-	-	-	-	-
(16)	0.5500	0.0750	0.3750	1.0000	4.79800	10.38700	6.05500	-	-	0.3610	-	-	0.3890
(15)Fo51	0.0010	0.4820	0.5140	0.9970	4.79400	10.49100	6.12300	0.0000	0.0800	0.9200	0.0000	0.8900	0.1100
(17)Hya1	0.4560	0.0060	0.5350	0.9970	4.78500	10.32500	6.03800	-	-	-	-	-	-
(08)OG2B	0.2900	0.0000	0.7100	1.0000	4.77500	10.28000	6.01600	0.2920	0.0000	0.7080	0.2880	0.0000	0.7120
(09)3G17	0.1050	0.0000	0.8950	1.0000	4.76600	10.22500	5.97300	0.1050	0.0000	0.8950	0.1080	0.0000	0.8920
(17)Fo	0.1000	0.0000	0.9000	1.0000	4.76200	10.22500	5.99400	0.1000	0.0000	0.9000	0.1000	0.0000	0.9000

Table 17: (continued)

Ref.	Fe	Mn	Mg	Fe+Mn+Mg	a	b	c	Fe(M1)	Mn(M1)	Mg(M1)	Fe(M2)	Mn(M2)	Mg(M2)
(09)3G12	0.0950	0.0000	0.9050	1.0000	4.76400	10.22000	5.99200	0.0970	0.0000	0.9030	0.0950	0.0000	0.9050
(09)3G15	0.0950	0.0000	0.9050	1.0000	4.76900	10.22900	5.99400	0.1000	0.0000	0.9000	0.0880	0.0000	0.9120
(09)3G19	0.0900	0.0000	0.9100	1.0000	4.76400	10.22100	5.99200	0.0930	0.0000	0.9070	0.0930	0.0000	0.9070
(09)3G51	0.0900	0.0000	0.9100	1.0000	4.76200	10.22600	5.99200	0.0900	0.0000	0.9100	0.0860	0.0000	0.9140
(09)2500	0.0900	0.0000	0.9100	1.0000	4.76500	10.23800	6.00000	0.0900	0.0000	0.9100	0.0900	0.0000	0.9100
(09)2501	0.0900	0.0000	0.9100	1.0000	4.75400	10.20700	5.98700	0.0960	0.0000	0.9040	0.0860	0.0000	0.9140
(09)3G9	0.0850	0.0000	0.9150	1.0000	4.76900	10.22600	5.99000	0.0850	0.0000	0.9150	0.0850	0.0000	0.9150
(09)3G18	0.0750	0.0000	0.9250	1.0000	4.76500	10.22300	5.99200	0.0750	0.0000	0.9250	0.0740	0.0000	0.9260
(09)2488	0.0650	0.0000	0.9350	1.0000	4.77200	10.21700	5.99800	0.0700	0.0000	0.9300	0.0630	0.0000	0.9370
(10)-481	0.0120	0.0030	0.9850	1.0000	4.75330	10.19720	5.98210	0.0120	0.0000	0.9880	0.0180	0.0000	0.9820
(01)Fo	0.0000	0.0000	1.0000	1.0000	4.75340	10.19020	5.97830	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(11)Fo	0.0000	0.0000	1.0000	1.0000	4.75350	10.19430	5.98070	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(00)Fo	0.0000	0.0000	1.0000	1.0000	4.75480	10.20040	5.98230	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(04)Fo	0.0000	0.0000	1.0000	1.0000	4.75400	10.19710	5.98060	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(05)Fo	0.0000	0.0000	1.0000	1.0000	4.75100	10.19700	5.97900	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(05)Fo	0.0000	0.0000	1.0000	1.0000	4.75300	10.19600	5.97900	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(06)Fo	0.0000	0.0000	1.0000	1.0000	4.75450	10.20000	5.98140	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(07)Fo	0.0000	0.0000	1.0000	1.0000	4.75600	10.19500	5.98100	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
(00)Fo	0.0000	0.0000	1.0000	1.0000	4.75480	10.20040	5.98230	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000

(00):This work

(03):Smyth (1975)

(06):Louisnathan and Smith (1968)

(09):Basso et al. (1979)

(12):Peters et al. (1973)

(15):Francis and Ribbe (1980)

(18):Brown (1980)

(01):Fujino et al. (1981)

(04):Schwab und Kuestner (1977)

(07):Yoder and Sahama (1957)

(10):Wenk and Raymund (1973)

(13):Bradley et al. (1966)

(16):Smyth and Hazen (1973)

(02):Hazen (1977)

(05):Fisher and Medaris (1969)

(08):Brown and Prewitt (1973)

(11):Hazen (1976)

(14):Annersten et al. (1984)

(17):Birle et al. (1968)

Table 18: Positional parameters for Fe-Mn-Mg Olivines from the literature

Ref.	X(M2)	Y(M2)	X(Si)	Y(Si)	X(O1)	Y(O1)	X(O2)	Y(O2)	X(O3)	Y(O3)	Z(O3)
(01)Fa	0.98598	0.28026	0.43122	0.09765	0.76814	0.09217	0.20895	0.45365	0.28897	0.16563	0.03643
(02)Fa	0.98510	0.28030	0.42920	0.09730	0.76800	0.09070	0.20790	0.45510	0.28900	0.16500	0.04030
(03)Fa	0.98530	0.28000	0.42920	0.09750	0.76870	0.09280	0.20760	0.45290	0.28840	0.16370	0.03830
(01)Teph	0.98792	0.28041	0.42755	0.09643	0.75776	0.09363	0.21088	0.45369	0.28706	0.16384	0.04140
(18)	0.98880	0.27990	0.42770	0.09520	0.76180	0.09040	0.21410	0.45180	0.28810	0.16270	0.03880
(17)Fa	0.98608	0.28004	0.43070	0.09723	0.76683	0.09197	0.21027	0.45308	0.28806	0.16532	0.03626
(16)	0.98670	0.27920	0.42870	0.09570	0.76610	0.09180	0.21270	0.45140	0.28440	0.16330	0.03570
(15)Fo51	0.98700	0.27900	0.42260	0.09100	0.75850	0.08670	0.23010	0.44890	0.27820	0.15900	0.03740
(17)Hya1	0.98598	0.27880	0.42843	0.09587	0.76566	0.09430	0.21642	0.45084	0.28264	0.16370	0.03435
(08)OG2B	0.98800	0.27820	0.42750	0.09500	0.76660	0.09190	0.21790	0.44890	0.28060	0.16380	0.03400
(09)3G17	0.98980	0.27780	0.42670	0.09440	0.76610	0.09180	0.22050	0.44790	0.27880	0.16320	0.03370
(17)Fo	0.98975	0.27743	0.42693	0.09434	0.76580	0.09186	0.22012	0.44779	0.27810	0.16346	0.03431
(09)3G12	0.99010	0.27760	0.42670	0.09430	0.76590	0.09160	0.22060	0.44760	0.27820	0.16310	0.03370
(09)3G15	0.99000	0.27770	0.42690	0.09440	0.76620	0.09180	0.22010	0.44780	0.27840	0.16330	0.03370
(09)3G19	0.99010	0.27770	0.42670	0.09440	0.76590	0.09170	0.22050	0.44770	0.27850	0.16320	0.03360
(09)3G51	0.99010	0.27760	0.42660	0.09430	0.76600	0.09180	0.22040	0.44780	0.27830	0.16310	0.03360
(09)2500	0.99010	0.27770	0.42680	0.09440	0.76570	0.09180	0.22050	0.44750	0.27830	0.16320	0.03350
(09)2501	0.99010	0.27770	0.42670	0.09430	0.76590	0.09170	0.22030	0.44770	0.27850	0.16310	0.03360
(09)3G9	0.99010	0.27770	0.42670	0.09430	0.76580	0.09170	0.22050	0.44760	0.27840	0.16320	0.03360
(09)3G18	0.99010	0.27760	0.42680	0.09430	0.76610	0.09160	0.22040	0.44770	0.27840	0.16320	0.03350
(09)2488	0.99010	0.27760	0.42650	0.09440	0.76630	0.09160	0.22090	0.44760	0.27780	0.16330	0.03350

Table 18: (continued)

Ref.	X(M2)	Y(M2)	X(Si)	Y(Si)	X(O1)	Y(O1)	X(O2)	Y(O2)	X(O3)	Y(O3)	Z(O3)
(10)-481	0.99119	0.27744	0.42625	0.09409	0.76557	0.09144	0.22163	0.44721	0.27723	0.16311	0.03315
(01)Fo	0.99169	0.27739	0.42645	0.09403	0.76594	0.09156	0.22164	0.44705	0.27751	0.16310	0.03304
(11)Fo	0.99150	0.27740	0.42620	0.09400	0.76570	0.09130	0.22150	0.44740	0.27770	0.16280	0.03310

(00):This work	(01):Fujino et al. (1981)	(02):Hazen (1977)
(03):Smyth (1975)	(04):Schwab und Kuestner (1977)	(05):Fisher and Medaris (1969)
(06):Louisnathan and Smith (1968)	(07):Yoder and Sahama (1957)	(08):Brown and Prewitt (1973)
(09):Basso et al. (1979)	(10):Wenk and Raymund (1973)	(11):Hazen (1976)
(12):Peters et al. (1973)	(13):Bradley et al. (1966)	(14):Annersten et al. (1984)
(15):Francis and Ribbe (1980)	(16):Smyth and Hazen (1973)	(17):Birle et al. (1968)
(18):Brown (1980)		

Table 19: Temperature correction factors for Fe-Mn-Mg Olivines from the literature

Ref.	Fe	Mn	Mg	B(M1)	B(M2)	B(Si)	B(O1)	B(O2)	B(O3)
(O1)Fa	1.0000	0.0000	0.0000	0.52000	0.47400	0.37200	0.51000	0.52600	0.58300
(O2)Fa	1.0000	0.0000	0.0000	0.48000	0.37000	0.35000	0.36000	0.33000	0.58000
(O3)Fa	1.0000	0.0000	0.0000	0.57000	0.50000	0.41000	0.53000	0.42000	0.49000
(O1)Teph	0.0000	1.0000	0.0000	0.62000	0.53100	0.38200	0.53700	0.54200	0.57900
(18)	0.5200	0.4600	0.0200	0.39000	0.41000	0.28000	0.54000	0.41000	0.54000
(17)Fa	0.9220	0.0370	0.0390	0.41000	0.36000	0.27000	0.43000	0.48000	0.52000
(16)	0.5500	0.0750	0.3750	0.44000	0.33000	0.33000	0.49000	0.50000	0.55000
(15)Fo51	0.0010	0.4820	0.5140	0.42000	0.54000	0.36000	0.50000	0.48000	0.50000
(17)Hya1	0.4560	0.0060	0.5350	0.32000	0.37000	0.19000	0.40000	0.56000	0.50000
(O8)OG2B	0.2900	0.0000	0.7100	0.37000	0.38000	0.29000	0.48000	0.46000	0.50000
(O9)3G17	0.1050	0.0000	0.8950	0.45000	0.49000	0.33000	0.48000	0.48000	0.52000
(17)Fo	0.1000	0.0000	0.9000	0.33000	0.36000	0.20000	0.35000	0.42000	0.41000
(O9)3G12	0.0950	0.0000	0.9050	0.42000	0.46000	0.30000	0.47000	0.47000	0.50000
(O9)3G15	0.0950	0.0000	0.9050	0.40000	0.41000	0.34000	0.48000	0.50000	0.53000
(O9)3G19	0.0900	0.0000	0.9100	0.50000	0.51000	0.36000	0.51000	0.53000	0.57000
(O9)3G51	0.0900	0.0000	0.9100	0.37000	0.37000	0.25000	0.44000	0.42000	0.45000
(O9)2500	0.0900	0.0000	0.9100	0.52000	0.54000	0.41000	0.59000	0.58000	0.62000
(O9)2501	0.0900	0.0000	0.9100	0.45000	0.45000	0.33000	0.50000	0.48000	0.52000
(O9)3G9	0.0850	0.0000	0.9150	0.49000	0.52000	0.40000	0.56000	0.57000	0.60000
(O9)3G18	0.0750	0.0000	0.9250	0.40000	0.41000	0.34000	0.50000	0.51000	0.54000
(O9)2488	0.0650	0.0000	0.9350	0.57000	0.56000	0.52000	0.70000	0.68000	0.70000

Table 19: (continued)

Ref.	Fe	Mn	Mg	B(M1)	B(M2)	B(Si)	B(O1)	B(O2)	B(O3)
(O1)Fo	0.0000	0.0000	1.0000	0.44700	0.44200	0.30400	0.40100	0.40300	0.43500
(11)Fo	0.0000	0.0000	1.0000	0.26000	0.22000	0.08000	0.26000	0.24000	0.28000
(00):This work				(01):Fujino et al. (1981)			(02):Hazen (1977)		
(03):Smyth (1975)				(04):Schwab und Kuestner (1977)			(05):Fisher and Medaris (1969)		
(06):Louisnathan and Smith (1968)				(07):Yoder and Sahama (1957)			(08):Brown and Prewitt (1973)		
(09):Basso et al. (1979)				(10):Wenk and Raymund (1973)			(11):Hazen (1976)		
(12):Peters et al. (1973)				(13):Bradley et al. (1966)			(14):Annersten et al. (1984)		
(15):Francis and Ribbe (1980)				(16):Smyth and Hazen (1973)			(17):Birle et al. (1968)		
(18):Brown (1980)									

Table 20.: Estimated errors in the calculation of integrated intensities: Example for Tephroite (Mn_2SiO_4)

hkl	xM2	yM2	xi	yi	x01	y01	x02	y02	x03	y03	z03	bM1	bM2	bi	b01	b02	b03	err. %	INT.
020	.	0.52	.	-0.73	.	-2.53	.	1.50	.	-4.38	.	-0.70	1.01	-0.22	-0.14	-0.34	0.35	5.52	9.21
110	-0.06	-0.86	-1.20	0.24	0.35	-0.05	1.04	-0.12	-0.56	0.61	.	-1.41	0.37	0.79	-0.02	0.16	0.15	2.64	7.15
021	.	-1.09	.	0.23	.	0.89	.	1.98	.	-0.53	3.37	0.00	0.59	-0.86	-0.48	0.33	-0.25	4.36	12.55
101	3.68	.	-2.30	.	0.02	.	0.23	.	-0.06	.	4.55	0.00	0.16	-0.59	0.70	-0.77	-0.37	6.42	7.44
111	0.13	-0.07	-0.34	-0.14	0.09	0.03	-0.13	-0.16	-0.10	-0.04	-0.43	0.00	-1.15	0.33	-0.01	-0.03	0.04	1.36	54.56
120	-1.30	0.10	-2.05	0.13	0.02	-1.02	-0.12	2.23	-0.19	-2.29	.	0.00	0.07	-0.61	0.71	0.46	1.37	4.49	6.82
002	.	.	.	.	.	.	.	.	.	.	2.60	1.29	-1.77	-1.01	-0.57	-0.64	1.03	3.79	7.17
121	-5.16	-0.06	-1.23	-0.55	0.01	4.02	0.29	2.28	0.04	-1.73	-3.13	0.00	-0.36	-0.48	0.62	-1.48	0.39	8.11	3.56
130	0.03	0.36	0.06	0.20	-0.01	-0.04	0.11	-0.15	0.17	0.01	.	-0.55	-0.41	-0.09	0.00	0.04	-0.11	0.86	86.70
022	.	-0.17	.	0.22	.	0.75	.	-0.44	.	-1.12	0.64	-0.97	-1.24	0.26	0.16	0.38	0.34	2.31	29.91
040	.	-0.78	.	-0.39	.	-1.40	.	1.85	.	3.11	.	-1.26	-1.25	0.72	0.37	-0.23	0.61	4.48	8.96
131	0.06	-0.33	0.33	-0.07	-0.09	0.01	0.19	0.18	0.00	-0.12	0.01	0.00	-1.10	-0.63	0.02	0.09	-0.00	1.39	64.32
112	0.01	0.16	0.22	-0.04	-0.06	0.01	-0.18	0.02	-0.08	0.09	0.12	-0.77	-0.20	-0.43	0.01	-0.09	0.07	0.99	100.00
200	0.31	.	1.21	.	0.02	.	-0.23	.	0.22	.	.	-1.11	-1.51	-0.45	0.45	0.45	0.84	2.55	12.53
041	.	0.85	.	-0.47	.	-1.51	.	0.87	.	-0.55	-1.40	0.00	-1.49	-0.79	-0.46	0.67	0.29	3.14	12.80
210	-3.94	-0.01	-0.89	0.15	0.21	0.06	0.25	0.34	0.76	0.31	.	0.00	-0.46	-0.84	-0.05	0.15	-0.76	4.33	6.12
122	0.75	-0.06	1.18	-0.07	-0.01	0.55	0.06	-1.19	-0.09	-1.08	-2.12	0.00	0.09	0.80	-0.88	-0.58	-1.48	3.65	11.98
140	-1.02	0.06	0.06	0.23	-0.00	-1.52	0.08	-0.85	-0.07	2.10	.	0.00	-0.12	0.42	-0.51	-0.72	-1.20	3.31	10.79
211	0.88	-0.07	-1.47	-0.12	0.34	-0.05	-0.94	0.11	0.13	-0.15	0.62	0.00	0.11	-1.59	-0.10	-0.62	-0.15	2.71	7.56
132	-0.10	-1.25	-0.20	-0.68	0.04	0.12	-0.36	0.48	0.48	0.04	-0.67	-3.50	2.65	0.58	-0.01	-0.25	-0.58	4.81	5.59
221	0.40	1.37	-4.00	-0.15	-0.06	0.96	-0.44	1.90	-0.17	-0.51	3.26	0.00	-2.69	2.09	-1.93	1.16	-0.89	7.16	2.47

Table 20. (continued)

hk1	xM2	yM2	xSi	ySi	x01	y01	x02	y02	x03	y03	z03	bM1	bM2	bSi	b01	b02	b03	err. %	INT.
042	.	1.43	.	0.73	.	2.46	.	-3.17	.	4.70	1.66	-3.91	3.97	-2.29	-1.09	0.70	1.58	9.17	2.29
150	-0.13	-1.24	0.73	0.11	-0.18	-0.03	0.05	-0.89	-0.20	-1.40	.	-3.58	4.11	-2.46	0.07	0.04	0.29	6.39	2.77
113	0.11	-0.06	-0.29	-0.12	0.07	0.02	-0.09	-0.12	0.20	0.09	0.70	0.00	-3.65	1.01	-0.03	-0.08	-0.30	3.89	9.95
151	0.08	-1.64	-0.08	0.96	0.03	-0.16	-0.43	-0.11	0.10	-0.16	0.45	0.00	-2.91	0.28	-0.01	-0.38	-0.16	3.58	5.47
222	0.15	-0.08	-0.23	0.06	-0.00	-0.33	0.09	0.17	-0.04	0.44	-0.25	-1.04	-1.31	0.16	-0.15	-0.33	-0.30	1.88	69.26
123	-2.52	-0.03	-0.61	-0.27	0.00	1.69	0.12	0.96	-0.05	2.02	2.91	0.00	-0.51	-0.71	0.78	-1.85	-1.35	5.45	2.64
240	0.14	-0.37	-0.60	-0.11	-0.01	0.62	-0.05	-0.71	-0.07	-1.20	.	-1.31	-1.29	0.42	-0.35	0.20	-0.51	2.61	21.67
241	0.25	0.71	0.98	-0.22	0.01	1.15	0.23	-0.58	-0.05	0.37	0.95	0.00	-2.45	-0.74	0.69	-0.89	-0.38	3.51	11.10
061	.	0.40	.	0.47	.	1.44	.	0.24	.	-0.73	0.09	0.00	-2.20	-0.66	-0.25	-0.73	-0.04	2.99	12.29
133	0.06	-0.33	0.33	-0.07	-0.08	0.01	0.16	0.15	-0.01	0.29	-0.03	0.00	-2.57	-1.51	0.04	0.17	0.01	3.05	15.24
152	0.06	0.55	-0.32	-0.05	0.07	0.01	-0.02	0.36	-0.07	-0.49	0.10	-2.20	-2.47	1.52	-0.04	-0.03	0.14	3.75	15.62
043	.	0.55	.	-0.32	.	-0.87	.	0.50	.	0.86	1.76	0.00	-2.13	-1.18	-0.58	0.85	-0.99	3.63	7.60
310	-0.14	-0.22	-2.05	0.01	-0.22	0.03	-0.52	0.07	0.29	-0.37	.	-2.77	0.71	0.14	0.12	-0.74	-0.69	3.75	4.92
004	.	.	.	.	.	.	.	.	.	.	-1.36	-0.96	-1.33	-0.78	-0.35	-0.39	-0.36	2.36	20.52
242	-0.41	1.08	1.82	0.31	0.02	-1.70	0.15	1.98	-0.18	-2.88	-1.03	-4.98	5.04	-1.67	1.28	-0.72	-1.63	8.88	2.99
062	.	-0.52	.	-0.15	.	-0.35	.	-0.88	.	0.12	-0.50	-1.26	-0.72	-0.91	-0.42	-0.09	-0.81	2.29	23.85
330	0.33	0.47	0.51	0.02	0.04	0.12	-0.27	0.43	-0.43	-0.04	.	-2.67	-1.96	-0.04	-0.03	-0.45	1.24	3.71	5.27
170	0.04	0.19	0.09	-0.37	-0.02	0.05	-0.05	-0.27	-0.07	0.42	.	-1.74	-2.34	-0.57	0.02	-0.07	0.17	3.05	12.43
331	0.67	-0.39	2.67	-0.01	0.27	-0.03	-0.42	-0.48	-0.01	0.33	-0.04	0.00	-4.14	-0.22	-0.18	-0.74	0.02	5.11	5.58
312	0.13	0.20	1.88	-0.01	0.19	-0.02	0.44	-0.06	0.21	-0.27	-0.34	-3.09	-0.80	-0.15	-0.13	0.78	-0.64	3.91	7.85
322	-1.09	0.08	-0.18	0.08	-0.03	0.23	0.22	-0.37	-0.30	-0.35	-0.69	0.00	-0.37	-2.51	-1.01	-0.51	-1.35	3.42	7.31
134	0.03	0.38	0.06	0.22	-0.01	-0.03	0.09	-0.12	0.07	0.01	-0.59	-2.47	-1.85	-0.44	0.01	0.15	-0.20	3.22	12.26

Table 21.: Estimated errors in the calculation of integrated intensities: Example for Fayalite (Fe_2SiO_4)

hkl	xM2	yM2	xSi	ySi	xO1	yO1	xO2	yO2	xO3	yO3	zO3	bM1	bM2	bSi	bO1	bO2	bO3	err. %	INT.
020	.	0.54	.	-0.75	.	-2.55	.	1.52	.	-4.43	.	-0.83	1.07	-0.22	-0.15	-0.35	0.37	5.61	8.98
110	-0.07	-0.81	-0.97	0.23	0.31	-0.10	0.94	-0.11	-0.50	0.58	.	-1.37	0.36	0.77	-0.06	0.16	0.15	2.43	8.46
021	.	-1.16	.	0.23	.	0.97	.	2.07	.	-0.52	3.50	0.00	0.64	-0.93	-0.52	0.35	-0.25	4.57	11.41
101	4.56	.	-2.86	.	0.05	.	0.30	.	-0.07	.	5.52	0.00	0.25	-0.67	0.88	-0.97	-0.43	7.87	4.98
111	0.15	-0.07	-0.29	-0.14	0.09	0.06	-0.12	-0.16	-0.09	-0.03	-0.43	0.00	-1.18	0.35	-0.02	-0.03	0.04	1.38	58.12
120	-1.39	0.13	-2.23	0.12	0.04	-1.13	-0.14	2.35	-0.20	-2.47	.	0.00	0.09	-0.59	0.76	0.50	1.47	4.82	6.10
121	-5.23	-0.08	-1.20	-0.48	0.02	3.91	0.31	2.24	0.04	-1.56	-3.16	0.00	-0.46	-0.42	0.66	-1.50	0.38	8.07	3.61
002	.	.	.	.	.	.	.	.	.	.	2.46	1.43	-1.95	-1.08	-0.61	-0.69	1.13	3.90	6.64
130	0.03	0.36	0.05	0.20	-0.01	-0.09	0.11	-0.15	0.17	0.01	.	-0.57	-0.42	-0.10	0.00	0.05	-0.12	0.88	91.75
022	.	-0.16	.	0.21	.	0.70	.	-0.41	.	-1.08	0.58	-1.00	-1.28	0.25	0.16	0.38	0.36	2.29	31.69
040	.	-0.74	.	-0.34	.	-1.35	.	1.70	.	2.90	.	-1.23	-1.23	0.69	0.33	-0.22	0.55	4.21	10.48
131	0.08	-0.34	0.29	-0.08	-0.09	0.02	0.18	0.19	0.00	-0.12	0.01	0.00	-1.16	-0.65	0.05	0.09	-0.00	1.44	64.86
112	0.01	0.16	0.19	-0.04	-0.06	0.02	-0.18	0.02	-0.08	0.10	0.11	-0.82	-0.21	-0.45	0.03	-0.09	0.08	1.03	100.00
200	0.35	.	1.00	.	0.04	.	-0.22	.	0.21	.	.	-1.07	-0.44	-0.50	0.41	0.41	0.77	1.93	15.07
041	.	0.86	.	-0.47	.	-1.41	.	0.86	.	-0.47	-1.39	0.00	-0.52	-0.76	-0.48	0.67	0.27	2.73	13.38
210	-3.75	-0.01	-0.98	0.13	0.18	0.13	0.23	0.33	0.69	0.30	.	0.00	-0.56	-0.75	-0.11	0.15	-0.76	4.16	6.98
122	0.75	-0.07	1.19	-0.06	-0.02	0.56	0.07	-1.16	-0.09	-1.09	-1.91	0.00	0.11	0.73	-0.88	-0.58	-1.52	3.53	12.20
140	-0.98	0.08	0.57	0.20	-0.01	-1.38	0.08	-0.81	-0.07	1.91	.	0.00	-0.15	0.35	-0.51	-0.70	-1.18	3.14	11.99
211	0.89	-0.09	-1.72	-0.11	0.34	-0.10	-0.92	0.12	0.12	-0.15	0.64	0.00	0.15	-1.50	-0.24	-0.68	-0.15	2.83	7.41
132	-0.12	-1.25	-0.19	-0.67	0.03	0.28	-0.34	0.49	0.47	0.02	-0.63	-3.62	2.72	0.65	-0.03	-0.27	-0.62	3.38	5.85
221	0.61	1.70	-4.42	-0.21	-0.16	1.18	-0.56	2.24	-0.20	-0.57	3.85	0.00	-3.43	3.08	-2.31	1.41	-1.00	8.62	1.65

Table 21. (continued)

hk1	xM2	yM2	xSi	ySi	x01	y01	x02	y02	x03	y03	z03	bM1	bM2	bS1	b01	b02	b03	err. %	INT.
042	.	1.43	.	0.69	.	2.51	.	-3.10	.	4.75	1.46	-4.09	4.18	-2.38	-1.05	0.71	1.57	9.33	2.33
150	-0.16	-1.28	0.64	0.08	-0.18	-0.10	0.06	-0.94	-0.21	-1.42	.	-3.76	4.29	-2.59	0.16	0.05	0.32	6.67	2.79
113	0.14	-0.06	-0.25	-0.12	0.07	0.05	-0.09	-0.12	0.18	0.07	0.74	0.00	-3.82	1.12	-0.06	-0.09	-0.30	4.08	10.11
151	0.10	-1.57	-0.04	0.92	0.03	-0.34	-0.40	-0.11	0.08	-0.15	0.43	0.00	-2.89	0.20	-0.04	-0.39	-0.14	3.52	6.25
222	0.18	-0.08	-0.20	0.07	-0.01	-0.31	0.10	0.16	-0.05	0.43	-0.23	-1.09	-1.37	0.18	-0.16	-0.33	-0.31	1.95	69.71
240	0.18	-0.38	-0.57	-0.12	-0.02	0.63	-0.06	-0.70	-0.07	-1.21	.	-1.41	-1.38	0.52	-0.33	0.20	-0.50	2.73	21.00
123	-2.64	-0.04	-0.62	-0.25	0.01	1.69	0.13	0.97	-0.05	1.90	3.18	0.00	-0.69	-0.65	0.87	-1.97	-1.37	5.69	2.42
241	0.31	0.71	0.85	-0.26	0.03	1.04	0.24	-0.56	-0.05	0.32	0.93	0.00	-2.51	-0.84	0.70	-0.88	-0.36	3.49	11.46
061	.	0.41	.	0.45	.	1.45	.	0.22	.	-0.66	0.06	0.00	-2.28	-0.72	-0.21	-0.73	-0.02	3.04	12.56
133	0.08	-0.33	0.29	-0.08	-0.08	0.02	0.16	0.16	-0.00	0.28	-0.02	0.00	-2.73	-1.59	0.09	0.19	0.01	3.22	15.08
152	0.07	0.55	-0.28	-0.03	0.07	0.04	-0.02	0.37	-0.07	-0.49	0.10	-2.25	-2.52	1.56	-0.09	-0.03	0.15	3.83	16.49
043	.	0.57	.	-0.33	.	-0.83	.	0.50	.	0.77	1.88	0.00	-2.28	-1.20	-0.63	0.89	-0.98	3.78	7.27
310	-0.19	-0.24	-2.13	0.02	-0.23	0.07	-0.53	0.08	0.29	-0.41	.	-3.18	0.81	0.50	0.32	-0.86	-0.79	4.21	4.13
242	-0.47	1.00	1.56	0.33	0.04	-1.57	0.15	1.77	-0.17	-2.67	-0.83	-4.85	4.90	-1.90	1.13	-0.67	-1.49	8.50	3.49
004	.	.	.	.	.	.	.	.	.	.	-1.25	-1.02	-1.41	-0.80	-0.35	-0.40	-0.42	2.39	20.32
062	.	-0.53	.	-0.16	.	-0.29	.	-0.86	.	0.07	-0.45	-1.31	-0.76	-0.90	-0.43	-0.09	-0.83	2.31	24.38
330	0.40	0.45	0.50	0.07	0.03	0.27	-0.25	0.43	-0.39	-0.02	.	-2.71	-1.94	-0.14	-0.05	-0.47	1.25	3.74	5.72
170	0.05	0.20	0.07	-0.38	-0.03	0.11	-0.05	-0.28	-0.06	0.44	.	-1.81	-2.42	-0.54	0.04	-0.08	0.17	3.15	12.82
331	0.73	-0.34	2.21	-0.02	0.22	-0.06	-0.34	-0.44	-0.00	0.27	-0.02	0.00	-3.75	-0.64	-0.38	-0.70	0.01	4.59	7.40
312	0.14	0.18	1.61	-0.01	0.16	-0.05	0.37	-0.05	0.18	-0.25	-0.29	-2.95	-0.74	-0.48	-0.28	0.76	-0.61	3.67	9.60
322	-1.11	0.11	-0.56	0.08	-0.07	0.23	0.24	-0.36	-0.31	-0.35	-0.62	0.00	-0.48	-2.58	-1.00	-0.51	-1.39	3.53	6.89

Table 22.: Estimated errors in the calculation of integrated intensities: Example for Forsterite (Mg_2SiO_4)

hkl	xM2	yM2	xS1	yS1	xO1	yO1	xO2	yO2	xO3	yO3	zO3	bM1	bM2	bS1	bO1	bO2	bO3	err. %	INT.
020	.	0.25	.	-0.79	.	-2.73	.	1.84	.	-4.80	.	-0.45	0.58	-0.28	-0.17	-0.38	0.40	5.96	22.34
110	-0.06	1.17	3.31	00.69	-1.01	0.26	-3.00	0.28	1.67	-1.30	.	2.04	-0.48	-2.50	0.16	-0.36	-0.35	6.19	2.76
021	.	-0.40	.	0.19	.	0.70	.	1.38	.	-0.31	2.54	0.00	0.21	-0.69	-0.38	0.29	-0.16	3.14	65.51
101	1.74	.	-2.31	.	0.04	.	0.16	.	-0.03	.	4.60	0.00	0.06	-0.59	0.74	-0.83	-0.32	5.59	22.00
111	0.15	-0.10	-1.03	-0.48	0.31	0.19	-0.49	-0.38	-0.27	-0.08	-1.09	0.00	-1.97	1.21	-0.07	-0.09	0.09	2.91	14.10
120	-0.65	0.04	-2.37	0.15	0.04	-1.25	-0.11	2.46	-0.16	-2.63	.	0.00	0.03	-0.69	0.86	0.65	1.72	5.02	14.78
121	-3.18	-0.03	-1.70	-0.64	0.03	5.02	0.25	3.29	0.03	-1.79	-3.97	0.00	-0.18	-0.66	0.89	-1.91	0.43	8.58	6.35
002	.	.	.	.	.	.	.	.	.	.	2.23	0.72	-0.98	-1.16	-0.65	-0.74	1.25	3.21	17.97
130	0.02	0.35	0.09	0.40	-0.02	-0.16	0.19	-0.24	0.35	0.03	.	-0.56	-0.38	-0.16	0.01	0.06	-0.18	1.03	62.83
131	0.04	-0.22	0.47	-0.09	-0.14	0.03	0.31	0.17	0.01	-0.11	0.02	0.00	-0.89	-1.05	0.06	0.11	-0.00	1.53	80.32
112	0.01	0.13	0.34	-0.07	-0.10	0.03	-0.30	0.03	-0.15	0.12	0.12	-0.67	-0.16	-0.81	0.05	-0.11	0.10	1.20	100.00
200	0.95	.	10.12	.	0.32	.	-1.46	.	1.45	.	.	-4.74	-6.43	-4.58	4.08	4.43	8.26	17.23	0.50
041	.	0.73	.	-0.75	.	-2.38	.	0.90	.	-0.75	-2.32	0.00	-1.18	-1.52	-0.86	1.28	0.41	4.45	12.98
210	-2.53	-0.01	-1.28	0.19	0.26	0.16	0.40	0.32	1.04	0.31	.	0.00	-0.24	-1.10	-0.14	0.17	-0.79	3.40	10.19
122	0.29	-0.02	1.05	-0.07	-0.02	0.51	0.05	-1.00	-0.06	-0.99	-1.56	0.00	0.03	0.71	-0.83	-0.63	-1.52	3.13	42.55
140	-0.46	0.03	0.67	0.21	-0.01	-1.45	0.06	-0.54	-0.05	2.21	.	0.00	-0.05	0.46	-0.57	-0.84	-1.30	3.31	29.48
211	0.40	-0.03	-1.72	-0.12	0.35	-0.09	-1.01	0.10	0.12	-0.09	0.49	0.00	0.04	-1.70	-0.22	-0.50	-0.10	2.79	19.89
132	-0.06	-1.17	-0.29	-1.31	0.06	0.47	-0.57	0.71	0.96	0.08	-0.75	-3.43	2.35	0.99	-0.04	-0.31	-0.91	4.99	4.53
230	2.96	0.06	-2.91	-0.18	0.57	-0.12	1.25	0.68	0.10	-2.17	.	0.00	0.40	-3.51	-0.44	0.75	-0.11	6.13	3.46
042	.	0.97	.	1.19	.	3.91	.	-5.04	.	7.42	2.12	-3.17	3.41	-3.60	-1.69	0.69	2.81	12.18	2.74
150	-0.05	-0.74	0.72	0.21	-0.19	-0.09	-0.05	-0.69	-0.20	-1.11	.	-2.05	2.15	-2.87	0.15	-0.03	0.23	4.48	6.77

Table 22. (continued)

hk1	xM2	yM2	xSi	ySi	x01	y01	x02	y02	x03	y03	z03	bM1	bM2	bSi	b01	b02	b03	err. %	INT.
113	0.12	-0.07	-0.77	-0.36	0.20	0.12	-0.31	-0.24	0.47	0.14	1.69	0.00	-5.52	3.34	-0.17	-0.21	-0.57	6.79	3.39
151	0.07	-1.55	-0.25	2.02	0.09	-0.66	-0.90	0.09	0.17	-0.18	0.70	0.00	-3.58	1.09	-0.08	-0.62	-0.21	4.78	3.58
222	0.10	-0.06	-0.40	0.11	-0.01	-0.54	0.11	0.35	-0.06	0.85	-0.36	-0.95	-1.21	0.35	-0.29	-0.60	-0.59	2.18	66.18
240	0.10	-0.30	-0.97	-0.22	-0.03	1.13	-0.04	-1.41	-0.10	-2.21	.	-1.24	-1.30	0.85	-0.61	0.24	-1.06	3.84	19.41
123	-0.59	-0.01	-0.84	-0.31	0.01	2.06	0.10	1.35	-0.03	2.10	4.10	0.00	-0.27	-0.97	1.10	-2.37	-1.49	6.21	4.62
241	0.13	0.56	1.49	-0.35	0.04	1.59	0.26	-0.56	-0.05	0.48	1.49	0.00	-1.78	-1.41	1.12	-1.58	-0.51	4.15	14.10
061	.	0.39	.	0.79	.	2.32	.	0.95	.	-0.91	0.18	0.00	-1.75	-0.95	-0.34	-1.13	-0.06	3.64	13.60
232	3.10	0.06	-3.09	-0.19	0.55	-0.11	1.21	0.66	-0.09	1.94	0.07	0.00	0.59	-5.27	-0.60	1.03	0.14	7.38	3.42
133	0.04	-0.22	0.47	-0.09	-0.11	0.02	0.26	0.14	-0.01	0.26	-0.04	0.00	-2.09	-2.49	0.13	0.22	0.02	3.33	19.62
152	0.07	1.10	-1.08	-0.31	0.26	0.13	0.06	0.95	-0.26	-1.40	0.20	-4.21	-4.36	6.15	-0.29	0.06	0.40	8.96	3.40
043	.	0.43	.	-0.45	.	-1.19	.	0.44	.	1.06	2.87	0.00	-1.54	-2.01	-0.95	1.41	-1.27	4.72	9.79
310	-0.10	-0.23	-4.25	0.03	-0.45	0.12	-1.22	0.12	0.68	-0.58	.	-3.05	0.71	0.76	0.54	-1.20	-1.18	5.84	3.26
242	-0.21	0.63	2.10	0.48	0.05	-2.19	0.08	2.80	-0.18	-3.95	-1.15	-3.44	3.68	-2.42	1.61	-0.62	-2.51	8.67	5.16
004	.	.	.	.	.	.	.	.	.	.	-1.60	-0.73	-1.00	-1.19	-0.51	-0.58	-0.72	2.57	29.20
062	.	-0.31	.	-0.16	.	-0.36	.	-1.01	.	0.21	-0.50	-0.87	-0.61	-1.30	-0.58	-0.28	-1.14	2.47	41.39
330	0.26	0.54	0.93	0.13	0.07	0.55	-0.59	0.81	-1.09	-0.10	.	-3.18	-2.12	-0.19	-0.10	-0.69	2.28	4.90	3.04
331	0.38	-0.26	3.90	-0.02	0.38	-0.08	-0.77	-0.45	-0.01	0.30	-0.06	0.00	-3.34	-0.85	-0.57	-0.95	0.03	5.44	7.57
170	0.03	0.26	0.19	-0.63	-0.05	0.17	-0.14	-0.29	-0.13	0.54	.	-1.68	-2.14	-1.36	0.07	-0.16	0.26	3.21	11.01
312	0.07	0.17	3.20	-0.02	0.31	-0.08	0.84	-0.08	0.42	-0.36	-0.36	-2.80	-0.65	-0.71	-0.47	1.05	-0.93	4.74	7.88
322	-0.50	0.03	-0.41	0.09	-0.06	0.23	0.18	-0.40	-0.24	-0.40	-0.63	0.00	-0.14	-2.62	-1.02	-0.70	-1.71	3.55	20.81
340	1.10	-0.06	-0.36	-0.38	-0.06	-0.89	0.34	-0.30	-0.28	1.24	.	0.00	0.31	-2.33	-0.97	-1.29	-2.01	4.03	7.57

APPENDIX G: THE PW1710 DIFFRACTOMETER

Because the diffractometer in the geological department was not operational for several months, about half of the measurements were done with a Phillips PW1710 automatic diffractometer in the oceanography department. Unfortunately the microprocessor was connected to a teletype terminal and so all data had to be typed into a computer for the analysis. The output of the PW1710 was formatted in a way that allows an easy check for typing errors. The measurements were done for 2 seconds at an interval of $0.01\ 2\theta$. The counts of five measurements, corresponding to an interval of $0.05\ 2\theta$ were added together and printed. Each line contains five accumulated counts and at the end the sum of all counts on that line.

Parameters and programs for the PW1710

Nr. of registers = 3.

lower level = 35%, upper level = 75 %

spinner ON, printing recorder OFF

Program 154

SCH a b	repeat from here to NXS for samples a to b.
HED	print heading.
LDC 4	load constant 4 into accumulator
STR 1	store content of accumulator in register 1.
CLR 2	clear register 2
CLR 3	clear register 3
SAN 15.000	set angle 2θ at 15.00 deg.
GAN	put current angle into accumulator
DEC 2	set number of decimals in output to 2.

BFR 0	store accumulator in output buffer
DEC 0	set number of decimals in output to 0.
REP 155 200	repeat program 155, 200 times.
REP 155 200	repeat program 155, 200 times.
REP 155 200	repeat program 155, 200 times.
REP 155 200	repeat program 155, 200 times.
REP 155 200	repeat program 155, 200 times.
REP 155 200	repeat program 155, 200 times.
NXS	load next sample.

Program 155

RCL 1	transfer register 1 to accumulator
CNE 156	if value in accumulator < 0, call program 156
REP 157 5	repeat program 157, 5 times
BFR	store register 2 in output buffer.
CLR 2	clear register 2
RCL 1	transfer register 1 to accumulator.
ADC -1	add -1 to accumulator
STR 1	store accumulator in register 1

Program 156

LDC 4	load constant 4 into accumulator
STR 1	store accumulator in register 1
PTR 3	store register 3 in output buffer and print buffer
CLR 3	clear register 3
GAN	put current angle into accumulator
DEC 2	set number of decimals in output to 2
BFR 0	store accumulator in output buffer.
DEC 0	set number of decimals in output to 0

Program 157

MES 2.00	measure the current angle for 2.00 seconds.
RCT	transfer number of counts to accumulator

ADD 2	add register 2 to accumulator
STR 2	store accumulator in register 2
RCT	transfer number of counts to accumulator
ADD 3	add register 3 to accumulator
STR 3	store accumulator in register 3
IAN 0.01	increment the angle with 0.01

The output on the teletype has the following format:

C=154							
CAPI	24	09-12-1986	10.08	PROGRAM	154		
15.00		45	41	44	31	33	194
15.25		31	43	46	37	43	200
15.50		29	33	42	46	44	194
.....							
.....				etc.			

APPENDIX H: SOME EXPERIMENTAL EQUILIBRIA BETWEEN OLIVINE AND GARNET IN THE SYSTEM FE-MN-MG-AL-SI-O

H.1 THE SYNTHESIS OF THE GARNETS

The starting materials for the garnets were the same as for the olivines (see chapter 2.4) plus:

Al₂O₃: From AlCl₃·6H₂O Baker Analyzed Reagent. LOT 429332. First the aluminium chloride is heated over a Bunsen burner (ca. 300 to 400 °C) under constant shaking in a beaker glass, until all Cl₂ and most H₂O is removed. The substance is then transferred into a Pt crucible and heated 1/2 hour at 800 °C and 12 hours at 700 °C. The resulting material is γ -Al₂O₃, and compares well with the description of Rooksby (1951).

The garnet mixture was first treated the same way as the olivines, mixed with graphite and heated at 850 °C for 3 hours in vacuum. The garnets used in the exchange experiments were all synthesized dry in a salt-cell press at 15 - 20 KBars and 800 °C. (Table 23.) The Mn-rich products are optically not completely isotropic which means that their structure is not strictly cubic. This can however not be detected in the X-ray diffraction profiles.

H.2 THE EXCHANGE EXPERIMENTS

The exchange experiments were made hydrothermally in cold seal bombs at 2 KBars methane pressure and 800 °C, with H₂O present. The starting mixtures consist of approximately

70-90 % garnet and 10-30 % olivine. The exact amount of each phase cannot be determined because both have an unknown excess of graphite. The products were examined first by X-ray diffraction, in order to determine whether a reaction took place, by comparing the distance in 2θ between the peaks (112) of olivine and (420) of garnet. Because of the relatively small amount of olivine in some samples, this could not always be recognized. The minimum time for an exchange reaction was found to be around 30 days. This is also around the maximum time, as one experiment left for 62 days showed a completely different and (and also unstable) assemblage (garnet, quartz, oxides etc.). This also points to an additional fundamental problem: even after 30 days an unnoticeable amount of an undesired phase may be present and may influence the results. It is suggested that later work be concentrated on higher pressures (and maybe higher temperatures) to avoid unstable assemblages.

H.3 THE QUANTITATIVE ANALYSIS OF THE RUN PRODUCTS.

The sample preparation for the microprobe analysis was suggested by Jack M. Rice (pers. comm.) and also used by Wang (1986).

First the sample is placed in a glass vial with alcohol and put in the ultrasonic cleaner for 10 minutes. This insures that the individual grains, as long as they are not intergrown, become separated. A drop with suspended material is then taken and placed on a polished graphite or diamond

surface. On a good probe mount, the grains (ca. 2 - 5 μm diam.) are barely visible by eye and well separated. The advantage of using a diamond-mount is that if the sample looks not satisfactory under the binocular microscope, it can be wiped off easily and a new drop with suspended material can be used. The samples were coated with carbon. For the quantitative microprobe analysis on a CAMECA SX50 microprobe, synthetic and natural polished olivine and garnet standards were used. The composition was calculated without any corrections from $(I_{\text{sample}}/I_{\text{standard}}) \cdot x_{\text{standard}}$ and normalized to 100% (Fe+Mn+Mg). This method was chosen because the mass absorption correction produced by the CAMECA software could not correctly deal with analyses having totals of only 30 to 70 %. Several synthetic olivines and garnets with known composition were measured. Because the surface consists of varying grain shapes, the measured concentrations show a variation of 2-10 %, averaging around the correct composition. This allows an interpretation with an error of approximately 2 mol% for the compositions of interest. A summary of the analytical results is given in Table 25. Only those analysis which had Si and Al within 10% of the expected values for olivines and garnets were used. The relatively large analytical error limits any interpretation. Further improvement on the sample preparation may reduce this uncertainty. The results are presented in Table 24 and Fig. 23. The dashed distribution curves in Fig. 23 illustrate approximately the equilibrium

fractionations. The experiments are consistent but not sufficiently constraining to justify making a detailed thermodynamic model.

Table 23.: List of synthesized garnets.

Run	x(Fe)	x(Mn)	x(Mg)	T [°C]	p [KBars]	time	a ₀	comments
RCC2	0.000	1.000	0.000	700	3	13d	11.624	anisotropic, homogeneous, yellow
RCC19	0.000	1.000	0.000	550	4	20d	11.637	anisotropic, white
RCC13	0.000	0.500	0.500	600	2	22d	---	quartz, pyroxenes, unusable
RCC23	0.083	0.917	0.000	750	2	16d	11.542	quartz, pyroxenes, unusable
RCC24	0.083	0.917	0.000	780	2	10d	---	quartz, pyroxenes, unusable
PC4	0.083	0.917	0.000	800	15	24h	11.621	anisotropic
PC5	0.498	0.502	0.000	800	15	24h	11.577	isotropic
PC6	0.498	0.502	0.000	800	15	24h	11.569	isotropic
PC7	0.746	0.000	0.254	800	15	23h	11.511	isotropic
PC8	0.249	0.751	0.000	800	25	25h	11.591	anisotropic
PC9	0.497	0.003	0.500	800	15	27h	11.487	isotropic, few impurities, (pyroxene?)
PC12	0.248	0.752	0.000	800	20	46h	11.597	anisotropic, homogeneous
PC13	0.166	0.668	0.166	800	20	47h	11.570	anisotropic, homogeneous
PC14	0.000	0.667	0.333	800	20	49h	11.573	anisotropic, homogeneous
PC15	0.000	0.500	0.500	800	20	46h	11.540	anisotropic, homogeneous
PC16	0.166	0.668	0.166	800	20	42h	11.577	anisotropic, homogeneous
PC18	0.663	0.171	0.166	800	20	71h	11.529	anisotropic, homogeneous

Table 24.: List of usable exchange experiments

Run		----- garnet -----			----- olivine -----		
		x(Fe)	x(Mn)	x(Mg)	x(Fe)	x(Mn)	x(Mg)
RCC29/1	starting composition	0.4970	0.5030		0.9940	0.0060	
801° C, 2Kb, 31d	final composition	0.529±0.02	0.471±0.02		0.698±0.02	0.302±0.02	
RCC29/2	starting composition	0.4970	0.5030		0.0828	0.9172	
801° C, 2Kb, 31d	final composition	0.437±0.02	0.563±0.02		0.372±0.02	0.628±0.02	
RCC31/1	starting composition		0.5000	0.5000		0.5000	0.5000
805° C, 2Kb, 43d	final composition		0.553±0.02	0.447±0.02		0.266±0.02	0.734±0.02
RCC31/2	starting composition		0.5000	0.5000		0.6667	0.3333
805° C, 2Kb, 43d	final composition		0.557±0.04	0.443±0.04		0.315±0.02	0.685±0.02
RCC31/3	starting composition	0.4970	0.5030		0.4142	0.5858	
805° C, 2Kb, 43d	final composition	0.396±0.05	0.604±0.05		0.598±0.02	0.402±0.02	

Table 24. (continued)

Run		----- garnet -----			----- olivine -----		
		x(Fe)	x(Mn)	x(Mg)	x(Fe)	x(Mn)	x(Mg)
RCC32/1	starting composition	0.2485	0.7515		0.0000	1.0000	
797° C, 2Kb, 37d	final composition	0.191±0.02	0.809±0.02		0.074±0.02	0.926±0.02	
RCC32/2	starting composition	0.2485	0.7515		0.2485	0.7515	
797° C, 2Kb, 37d	final composition	0.160±0.03	0.840±0.03		0.405±0.02	0.595±0.02	
RCC32/3	starting composition	0.2485	0.7515		0.3313	0.6687	
797° C, 2Kb, 37d	final composition	0.176±0.04	0.824±0.04		0.417±0.02	0.583±0.02	

Fig. 23: Roozeboom diagrams for some exchange experiments in the binary Fe-Mn and Mn-Mg olivine - garnet systems

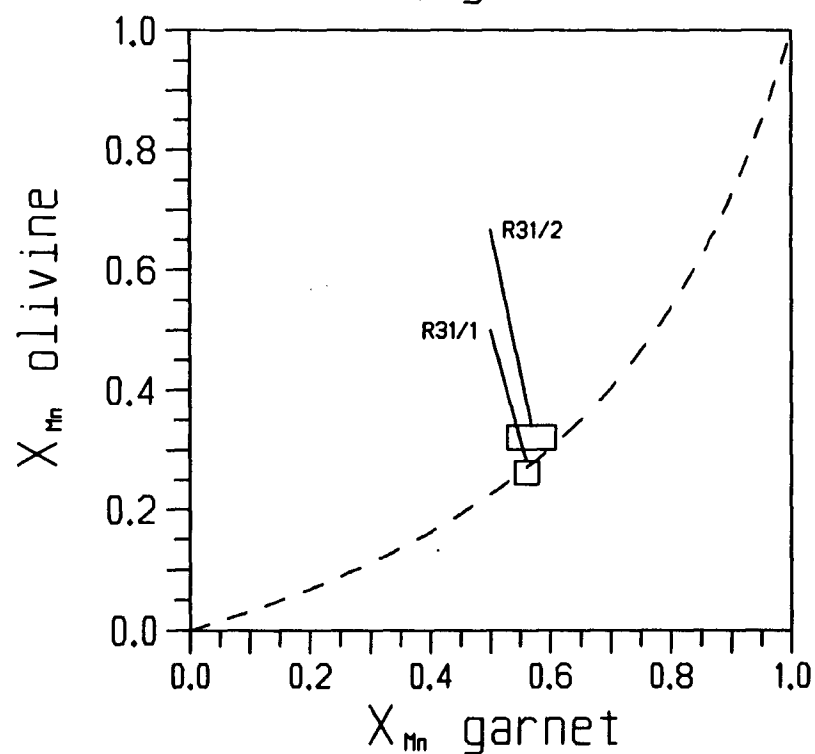
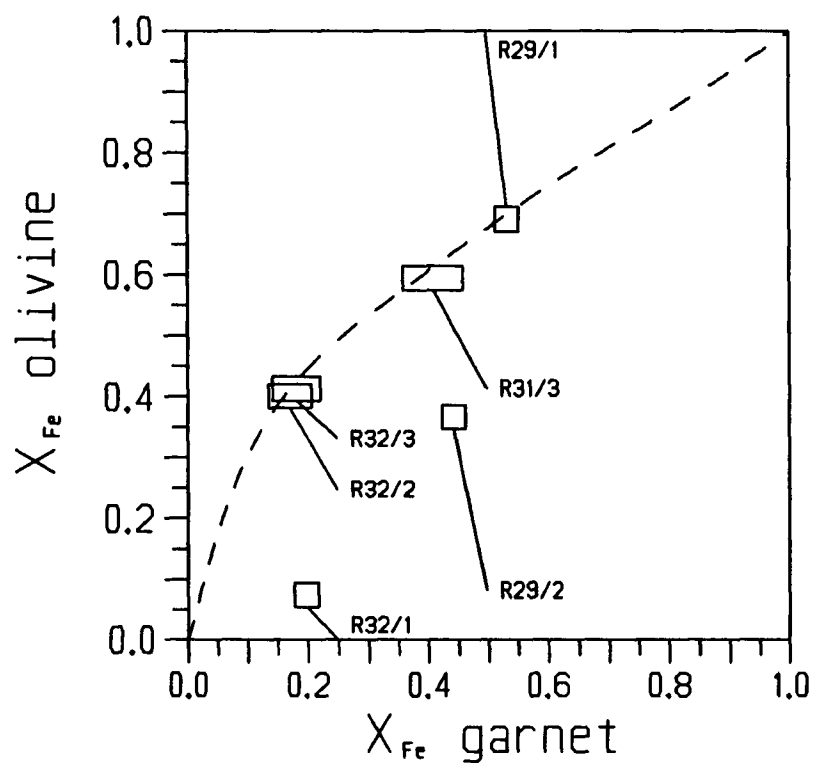


Table 25.: Summary of microprobe analyses (Fe+Mn+Mg = 100%)

		measured	expected
olivine 040800 n=11	Fe	33.2(1.7)	33.1
	Mn	66.8(1.7)	66.9
	Mg	0.0(0.0)	0.0
	Si	49.8(2.8)	50.0
	Al	0.0(0.0)	0.0
garnet PC05 n=15	Fe	50.2(1.2)	50.0
	Mn	49.8(1.2)	50.0
	Mg	0.0(0.0)	0.0
	Si	99.2(9.1)	100.0
	Al	65.9(4.8)	66.7
garnet PC06 n=14	Fe	50.5(3.4)	50.0
	Mn	49.5(3.4)	50.0
	Mg	0.0(0.0)	0.0
	Si	99.9(7.0)	100.0
	Al	68.1(4.6)	66.7
olivine 050700 n=13	Fe	41.2(2.3)	41.4
	Mn	58.8(2.3)	58.6
	Mg	0.0(0.0)	0.0
	Si	50.7(3.8)	50.0
	Al	00.0(0.0)	00.0

Table 25. (continued)

		measured	expected
olivine	Fe	07.7(0.5)	08.3
011100	Mn	92.3(0.5)	91.7
n=7	Mg	0.0(0.0)	0.0
	Si	49.4(3.2)	50.0
	Al	00.0(0.0)	00.0
garnet	Fe	24.9(1.2)	24.8
PC12	Mn	75.1(1.2)	75.2
n=13	Mg	0.0(0.0)	0.0
	Si	98.0(4.2)	100.0
	Al	66.8(3.6)	66.7
garnet	Fe	39.6(4.0)	
from R31/3	Mn	60.4(4.0)	
n=15	Mg	0.0(0.0)	
	Si	102.4(6.4)	
	Al	67.0(6.4)	
olivine	Fe	59.8(1.3)	
from R31/3	Mn	40.2(1.3)	
n=5	Mg	0.0(0.0)	
	Si	49.8(3.4)	
	Al	00.0(0.0)	

Table 25. (continued)

		measured	expected
garnet	Fe	52.9(1.7)	
from R29/1	Mn	47.1(1.7)	
n=11	Mg	0.0(0.0)	
	Si	99.3(4.2)	
	Al	67.3(5.9)	
olivine	Fe	69.8(1.4)	
from R29/1	Mn	40.2(1.4)	
n=4	Mg	0.0(0.0)	
	Si	46.9(5.6)	
	Al	00.0(0.0)	
olivine	Fe	00.0(0.0)	00.0
000606	Mn	48.6(4.4)	50.0
n=19	Mg	51.4(4.4)	50.0
	Si	49.8(4.0)	50.0
	Al	00.0(0.0)	00.0
olivine	Fe	00.0(0.0)	00.0
000804	Mn	65.8(4.5)	66.7
n=10	Mg	34.2(4.5)	33.3
	Si	47.6(3.5)	50.0
	Al	00.0(0.0)	00.0

Table 25. (continued)

		measured	expected
garnet	Fe	47.9(4.9)	50.0
PC15	Mn	52.1(4.9)	50.0
n=11	Mg	0.0(0.0)	00.0
	Si	101.3(5.2)	100.0
	Al	66.6(4.2)	66.7
olivine	Fe	99.4(0.2)	
120000	Mn	00.6(0.2)	
n=6	Mg	0.0(0.0)	
	Si	48.0(5.5)	
	Al	00.0(0.0)	
garnet	Fe	00.0(0.0)	
from R31/1	Mn	55.3(1.5)	
n=12	Mg	44.7(1.5)	
	Si	100.3(5.5)	
	Al	66.6(3.3)	
olivine	Fe	00.0(0.0)	
from R31/1	Mn	26.6(1.3)	
n=5	Mg	73.4(1.3)	
	Si	51.8(2.8)	
	Al	00.0(0.0)	

Table 25. (continued)

		measured	expected
garnet	Fe	00.0(0.0)	
from R31/2	Mn	55.7(3.6)	
n=8	Mg	44.3(3.6)	
	Si	101.9(9.6)	
	Al	68.0(6.5)	
olivine	Fe	00.0(0.0)	
from R31/2	Mn	31.5(1.8)	
n=8	Mg	68.5(1.8)	
	Si	48.6(4.2)	
	Al	00.0(0.0)	
olivine	Fe	65.8(1.6)	66.3
080400	Mn	34.2(1.6)	33.7
n=15	Mg	00.0(0.0)	00.0
	Si	50.2(3.6)	50.0
	Al	00.0(0.0)	00.0
garnet	Fe	43.7(1.7)	
from R29/2	Mn	56.3(1.7)	
n=13	Mg	00.0(0.0)	
	Si	100.1(6.8)	
	Al	67.3(3.3)	

Table 25. (continued)

		measured	expected
olivine	Fe	37.2(1.4)	
from R29/2	Mn	62.8(1.4)	
n=4	Mg	00.0(0.0)	
	Si	49.8(4.7)	
	Al	00.0(0.0)	
garnet	Fe	19.1(1.7)	
from R32/1	Mn	80.9(1.7)	
n=9	Mg	00.0(0.0)	
	Si	101.6(6.6)	
	Al	66.4(3.5)	
olivine	Fe	7.4(1.6)	
from R32/1	Mn	92.6(1.6)	
n=6	Mg	00.0(0.0)	
	Si	51.5(5.8)	
	Al	00.0(0.0)	
garnet	Fe	16.0(2.5)	
from R32/2	Mn	88.0(2.5)	
n=12	Mg	00.0(0.0)	
	Si	100.9(5.3)	
	Al	69.5(4.3)	

Table 25. (continued)

		measured	expected
olivine	Fe	40.5(1.3)	
from R32/2	Mn	59.5(1.3)	
n=5	Mg	00.0(0.0)	
	Si	47.9(1.2)	
	Al	00.0(0.0)	
garnet	Fe	17.6(3.5)	
from R32/3	Mn	82.4(3.5)	
n=11	Mg	00.0(0.0)	
	Si	98.1(5.5)	
	Al	66.4(5.3)	
olivine	Fe	41.7(1.3)	
from R32/3	Mn	58.3(1.3)	
n=5	Mg	00.0(0.0)	
	Si	52.3(3.3)	
	Al	00.0(0.0)	

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