post-fractionation residual liquids. It was recognised that modifications would be required to the structure of the haplogranitic model to accommodate this range (section 2.3.4). In particular, the free energy of mixing arising from the regular solution model is a function of no higher order compositional terms than x_i^2, as opposed for example to the model of Hudon et al. (2005), which includes term up to x_i^7. While the simpler mathematical form is preferred for its parsimony, it was acknowledged from the outset that some equivalent of terms in $x^{n>2}$ might be needed, and this has to some degree proved to be the case.

2.2.4 Summary

The ultimate goal of the new mafic melt model is to simulate the behaviour of natural melts derived from mantle peridotite, based on a fully thermodynamic formulation. It is being developed in small systems—this project describes its calibration in binary and ternary systems and the system CaO-MgO-Al_2O_3-SiO_2—and this characteristic will allow calculations with the completed model in simplified systems.

There is no intuitively obvious structure for a macroscopic mixing model describing a variously polymerised silicate liquid. The new model takes the form of a regular solution. Although this has no foundation in the microscopic behaviour of silicate liquids, it has proved effective both in the work of Ghiorso et al. (2002) and in the haplogranitic melt model of Holland and Powell (1998). Modifications were required to achieve a reasonable fit across a wide compositional range.

2.3 Approach to modelling

The formulation of the thermodynamic models developed in this project must now be documented.

Comprehensive models were calibrated for the solid solutions orthopyroxene, clinopyroxene and garnet, as well as the silicate liquid. Most are regular solution models, though the models for clinopyroxene and garnet are asymmetric. The regular solution used for the liquid model, being empirical with respect to the physicochemical behaviour of the liquid, contains a number of features that are designed to give the shape of the model more flexibility.

The models were developed to be compatible with THERMOCALC, the phase equilibrium calculation software of Powell and Holland (1988). THERMOCALC has two aspects, the code that calculates equilibria and an internally consistent dataset of thermodynamic properties

for pure phases and end-members of solid solutions. The use of THERMOCALC's thoroughly calibrated dataset end-members in the models is considered to be a major advantage of the modelling approach followed here.

2.3.1 Formulating chemical potentials

Free energies of pure phases and mixtures

The most basic aim of modelling is to reproduce the free energy surfaces of the various phases, as functions of $P, T, \vec{X}$, sufficiently well that calculated $P, T, \vec{X}$ of specified equilibria match those seen in experiments. For a pure end-member y the free energy is a function of pressure and temperature, $G_y(P,T)$. The project is mainly concerned with mixtures—solid solutions or liquids—which are described in terms of a set of chosen mixing units or compositional end-members that span the composition space of the mixture. For a mixture, a phase J with endmembers $J_1, J_2, \ldots, J_j$, the free energy at coordinates $\vec{X}_J$ in the composition space of J is the sum of two parts: the free energy of a mechanical mixture of $J_1, J_2, \ldots, J_j$, which is the average free energy of the end-members weighted by their proportions at composition $\vec{X}_J$, and the additional free energy $G_J^{mix}(P,T,\vec{X}_J)$ that is derived from the thermodynamics of mixing itself:

$$G_J(P,T,\vec{X}_J) = \sum_j p_j G_j(P,T) \quad + \quad G_J^{mix}(P,T,\vec{X}_J) \tag{2.1}$$

where the p_j are the proportions of the end-members of J.

Equilibria between phases

When considering equilibria among phases it is helpful to work in terms of chemical potentials, or partial molar free energies, μ_i, of the model end-members involved. For a pure solid end-member, e.g. pure spinel (sp), the chemical potential may be written simply as

$$\mu_{sp} = G_{sp}(P,T). \tag{2.2}$$

The expression is more complicated for an end-member in a mixture, e.g. the component diopside (di, $CaMgSi_2O_6$) in clinopyroxene solid solution:

$$\mu_{di}^{cpx} = G_{di_{C2/c}}(P,T) + \mathrm{R}T \ln a_{di}^{cpx}. \tag{2.3}$$

where a_{di}^{cpx} is the activity of the diopside end-member in the clinopyroxene mixture. The activity can be described as the thermodynamically effective concentration of diopside in clinopyroxene at P, T. $G_{di_{C2/c}}$ is specifically the free energy of diopside with the symmetry of the clinopyroxene solid solution, C2/c. Referring back to equation 2.1, it is apparent that $G_{di_{C2/c}}$ is the contribution of diopside to the mechanical mixing part of G_J, and $\mathrm{R}T \ln a_{di}^{cpx}$ is the partial free energy of mixing. R is the gas constant.

The last term in equation 2.3 closely resembles the expression for the contribution to the configurational entropy of the clinopyroxene mixture from end-member diopside. That is, in a simple model in which 'molecules' of paired Ca and Mg cations from the diopside end-member mix randomly with 'molecules' of cation pairs from other end-members, the configurational entropy of mixing is derived purely from the number of ways of arranging the various types of 'molecule', and the partial molar entropy of mixing for diopside is -$\mathrm{R}T \ln X_{di}^{cpx}$, where X_{di} is the mole fraction of the CaMg 'molecules' in the clinopyroxene phase. With this in mind, equation 2.3 is well written as

$$\mu_{di}^{cpx} = G_{di_{C2/c}}(P,T) + \mathrm{R}T \ln \gamma_{di}^{cpx} + \mathrm{R}T \ln X_{di}^{cpx}, \tag{2.4}$$

in which a_{di}^{cpx} has been expressed as $\gamma_{di}^{cpx} X_{di}^{cpx}$. In the simplest type of model mixture, the ideal solution, in which the entropy is entirely configurational, $\gamma_k^{id\,sol} = 1$ for all end-members in a mixture, leaving only the $\mathrm{R}T \ln X_k^{id\,sol}$ terms. γ_j^J therefore describes the departure of the activity of a solution from ideality, and its model form is open to choice.

There are then two major aspects to modelling: (1) the determination of the $G_i(P,T)$ functions of all end-members, and (2) the generation of expressions for the $\gamma_j^J = a_j^J / X_j^J$ of solutions. Since the main aim of the current modelling is to produce expressions for the $G_J^{mix}(P,T,\vec{X_J})$, known as activity-composition models, the formulation of the γ_j^J will be considered in detail later in the section. Most of the end-member properties used in modelling were taken straight from the internally consistent dataset at the heart of THERMOCALC; the dataset and construction of $G_i(P,T)$ for the model end-members will be discussed in this context.

Firstly however the utility of the concept of end-member chemical potentials can be demonstrated by noting that:

- The free energy of a mixture J may be written as a summation of the mole fractions and chemical potentials of the end-members, as $G_J(P,T,\vec{X_J}) = \sum_j X_j \mu_j(P,T,X_j)$.
- At equilibrium, equations of the form $\sum_i \nu_i \mu_i(P,T,X_i) = 0$ can be written for all possible balanced reactions among the end-members, where ν_i is the reaction coefficient of phase i

in one of the reactions. Thus, for an equilibrium assemblage of orthopyroxene ($Mg_2Si_2O_6$-$MgAl_2SiO_6$, en-mgts), spinel ($MgAl_2O_4$, sp), forsterite (Mg_2SiO_4, fo) and pyrope garnet ($Mg_3Al_2Si_3O_{12}$, py) in the system MgO-Al_2O_3-SiO_2, an independent set of equations, with the balanced chemical reactions underneath, would be written simply as

$$\begin{aligned} \mu_{en}^{opx} + \mu_{mgts}^{opx} &= \mu_{py} \\ Mg_2Si_2O_6 + MgAl_2SiO_6 &= Mg_3Al_2Si_3O_{12} \end{aligned}$$

$$\begin{aligned} \mu_{en}^{opx} + \mu_{sp} &= \mu_{mgts}^{opx} + \mu_{fo} \\ Mg_2Si_2O_6 + MgAl_2O_4 &= MgAl_2SiO_6 + Mg_2SiO_4 \end{aligned}$$

with all of the reaction coefficients being unity.

2.3.2 Ideal activity and mixing on sites

Before contemplating the non-ideal activities of end-members in solid solutions, it is necessary to look again at the formulation of ideal activities.

In the example given above, the clinopyroxene (cpx) solid solution was described using a molecular mixing model, envisaging 'molecules' of the cations CaMg of diopside mixing with those of other end-members over the M_1 and M_2 sites of the pyroxene lattice. A molecular-type model is used in this project for the liquid, in which complete mixing units of e.g. anorthite liquid and quartz liquid (anL and qL) are imagined in the mixture, such that the ideal activity of anL can be written $a_{anL}^{anL-qL} = X_{anL}^{anL-qL}$.

However for solid solutions the more complex approach of mixing on sites is taken. This concept treats the mixing of cations on the M_1 and M_2 sites in cpx separately, so that strictly $a_{di}^{cpx} = nX_{Ca}^{M_2}X_{Mg}^{M_1}$, where n is a normalisation constant ensuring that the activity of diopside is 1 in the pure end-member (n=1 in this case). The activity is given by $a_j^J = \prod_s (X_{c_s}^s)^{\nu^s}$, where s is a site type in the lattice of J, e.g. M_1, M_2 in pyroxenes or x in garnet, the $\vec{c_s}$ are the cations mixing on site s, and ν^s is the number of s sites in the formula unit.

A mixing on sites perspective acknowledges that complex microscopic interactions may be taking place in non-ideal solutions, both between cations on the same site and between cations on different sites.

2.3.3 Activity-composition models for non-ideal mixtures

The discussion will now turn back to the pursuit of activity-composition models to describe non-ideality in solutions. So far there has been little attempt made to express the free energy of a solution in terms of its constituent thermodynamic parts, enthalpy, entropy and volume, though it was noted in section 2.2.1 that it is not practical to do this in a naturalistic way. A more feasible approach to describing the thermodynamic properties of the mixture is embodied in the regular solution model (e.g. Anderson and Crerar, 1989).

Regular solution models

The regular solution model assumes that (1) entropy is wholly configurational; (2) non-ideal volume changes are negligible, beyond those of a mechanical mixture; (3) all non-ideality is expressed as an excess enthalpy of mixing, in addition to that of the mechanical mixture:

$$G_J(P,T,\vec{X}_J) = G_{mech\,mix} + H_{ex} + \mathrm{R}T\sum_j p_j \ln p_j \tag{2.5}$$

where $G_{mech\,mix}$ is the free energy of a mechanical mixture of end-members, H_{ex} is the excess enthalpy of mixing ('excess' because it exceeds the ideal enthalpy of mixing, $H^{id} = 0$), and p_j is the proportion of end-member j in phase J (incorporating any complex combinations of mole fractions that might arise from mixing on sites).

Symmetric and asymmetric formalism

Considering the chemical potential of end-member j in a phase J with k independent end-members,

$$\mu_j^J = G_j(P,T) + \mathrm{R}T\ln\gamma_j^J + \mathrm{R}T\ln p_j^J \tag{2.6}$$

in the context of a regular solution model, the term $G_j(P,T)$ is the contribution of j to the mechanical mixture and the term $\mathrm{R}T\ln p_j^J$ is the contribution to the configurational entropy, so the term contributing to the non-ideal, excess enthalpy of the regular solution is $\mathrm{R}T\ln\gamma_j^J$. Powell and Holland (1993) present a symmetric formalism for the $\mathrm{R}T\ln\gamma_j^J$:

$$\mathrm{R}T\ln\gamma_j^J = -\sum_{m=1}^{k-1}\sum_{n>m}^{k}(p'_m - p_m)(p'_n - p_n)\mathsf{W}_{m,n} \tag{2.7}$$

where p_o is the proportion of end-member o in phase J, p'_o is the value of p_o in the pure end-member j (i.e. $p'_o = 1$ where $o = j$; $p'_o = 0$ where $o \neq j$), and $W_{\mathrm{m,n}}$ is an interaction

energy parameter for the m, n binary. This very powerful expression allows all of the microscopic interactions that are envisaged between cations on the same or different sites to be represented by a single macroscopic interaction energy, $W_{m,n}$, between each pair of end-members. The expression is inherently normalised such that γ_j^J for the pure end-member is 1.

In some binary systems the measurable thermodynamic properties, such as the enthalpy of mixing, are asymmetric in composition space. The asymmetric formalism (Holland and Powell, 2003) is a modification of the symmetric formalism—a reformulated van Laar model (van Laar, 1906)—in which the non-ideal activity term is made asymmetric by application of a van Laar parameter α to each of the end-members, such that the asymmetry of excess enthalpy in a binary system is a function of $\alpha_{\mathrm{m}}/(\alpha_{\mathrm{m}}+\alpha_{\mathrm{n}})$:

$$\mathrm{R}T \ln \gamma_j^J = -\sum_{m}^{k-1} \sum_{n>m}^{k} (\phi'_m - \phi_m)(\phi'_n - \phi_n)\mathsf{W}^*_{m,n} \tag{2.8}$$

Notation is as for equation 2.7, except that the new proportion terms ϕ_o are given by

$$\phi_o = \frac{p_o \alpha_o}{\sum_{j=1}^{k} p_j \alpha_j} \tag{2.9}$$

and $\mathsf{W}^*_{m,n}$ is also a function of the α parameters, taking the form

$$\mathsf{W}^*_{m,n} = W_{m,n} \frac{2\alpha_j}{\alpha_m + \alpha_n}. \tag{2.10}$$

Pressure and temperature dependence of $W_{m,n}$

The regular solution model *sensu stricto* neglects any variation in volume or non-configurational entropy with composition that arises from mixing alone. However it is sometimes necessary to introduce pressure dependence or additional temperature dependence into the model in order to satisfy experimental data. A linear pressure and temperature dependence can be added to the pairwise interaction energies $\mathsf{W}_{m,n}$: $\mathsf{W}_{m,n} = W_{\mathrm{m,n}} + W^t_{\mathrm{m,n}}\, T + W^p_{\mathrm{m,n}}\, P$. $W^t_{\mathrm{m,n}}$ and $W^p_{\mathrm{m,n}}$ have the units of entropy and volume respectively. When finite $W^t_{\mathrm{m,n}}$ and $W^p_{\mathrm{m,n}}$ terms are present, the $\mathrm{R}Tln\gamma_j^J$ terms of the symmetric and asymmetric formalisms represent excess free energies, rather than merely excess enthalpies.

Summary: activity-composition model structures and properties in this project

In summary, all of the models developed in this project are regular solution models, according to a broad definition that endows the model solutions with excess free energy terms. With respect to individual end-members, the partial molar excess free energy of mixing is given by $\mathrm{R}Tln\gamma_j^J$, and can be expressed in terms of a set of P,T-dependent interaction energy parameters operating between pairs of end-members in phase J (generating compositional terms in p_j^2), using the symmetric or asymmetric formalisms of Powell and Holland (1993) and Holland and Powell (2003).

Mixing of cations in solids is generally treated as though mixing on one type of site is independent of mixing on other types of site. Conversely, liquids are treated (for practical rather than physical reasons) as if they mix as indivisible 'molecules'. Such decisions about mixing units and mixing sites affect the derivation of the configurational entropy.

By convention, solid solution models designed for use with THERMOCALC take the structure described above (e.g. Green et al., 2007), as did the haplogranitic model of Holland and Powell (2001). However the conventional liquid model structure required modification in order to represent the behaviour of mafic liquids, and these modifications will be discussed in the next subsection.

Full details of all models used in this work may be found in appendix A.

2.3.4 Formulating the liquid model

The molecule-like end-members used in the liquid model are given names of the form xL, where x is the abbreviation used for the equivalent solid in the internally consistent dataset, e.g. foL (forsterite liquid), diL (diopside liquid).

Before modelling could begin several decisions had to be made about how to apply the regular solution approach to a liquid. Thereafter, other and subtler possibilities existed for refining the model. Some possible modifications are described in this section, and the following chapter will discuss the solutions adopted.

Fundamental decisions

The fundamental decisions to be made were:

1. What should be the limits of the liquid compositional space?