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Thermodynamics of multicomponent pyroxenes: III. Calibration of Fe$^{2+}$(Mg)$_{-1}$, TiAl$_2$(MgSi$_2$)$_{-1}$, TiFe$_3^+$(MgSi$_2$)$_{-1}$, AlFe$_3^+$(MgSi)$_{-1}$, NaAl(CaMg)$_{-1}$, Al$_2$(MgSi)$_{-1}$ and Ca(Mg)$_{-1}$ exchange reactions between pyroxenes and silicate melts

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Abstract A thermodynamic model for the Gibbs free energy of igneous pyroxenes with the general formula [Na, Ca, Fe$^{2+}$, Mg]$^{M2}$[Fe$^{2+}$, Mg, Ti, Al, Fe$^{3+}$]$^{M1}$[Al, Fe$^{3+}$, Si]$_{Tet}$SiO$_6$ is calibrated from experimentally determined compositions of coexisting pyroxene and silicate melt. The model is based upon the general formulation, and relies upon the calibration of the “quadrilateral” subsystem, previously published by the present authors. The calibration database of pyroxene-liquid equilibria spans a broad spectrum of temperature, pressure and oxygen fugacity conditions, ranging from 1000°-1600° C, 0.001-30 kbar and iron-wüstite to air. Chemical potentials of endmember pyroxene components as well as exchange potentials between pyroxenes and coexisting liquids are defined utilizing the present authors’ thermodynamic melt model. Model parameters are extracted from these relations by regression analysis. The resulting model and derivative endmember properties are internally consistent with an existing standard state thermodynamic database. The success of the model and its applicability to igneous petrogenesis are demonstrated by comparing calculated and experimentally determined liquidus compositions, temperatures and symmetry states for pyroxenes crystallizing from a variety of silicate melts, ranging in composition from tholeiites and angrites through rhyolites to potash ankaratrites.

Introduction

Pyroxenes typical of igneous rocks have major element compositions which can be described by the general formula [Na, Ca, Fe$^{2+}$, Mg]$^{M2}$[Fe$^{2+}$, Mg, Ti, Al, Fe$^{3+}$]$^{M1}$[Al, Fe$^{3+}$, Si]$_{Tet}$SiO$_6$. With perhaps the exception of the spinels, pyroxenes show more chemical variability than any other common igneous rock-forming mineral. Although pyroxene compositions are commonly expressed by projection into the “quadrilateral” (e.g. [Ca, Fe$^{2+}$, Mg]$^{M2}$[Fe$^{2+}$, Mg]$^{M1}$Si$_2$O$_6$), non-quadrilateral, or “supersystem” components may be of considerable importance and central to the petrogenetic interpretation of the phase. Coupled substitutions embodied by the exchange vectors TiAl$_2$(MgSi$_2$)$_{-1}$, TiFe$_3^+$(MgSi$_2$)$_{-1}$, AlFe$_3^+$(MgSi)$_{-1}$, NaAl(CaMg)$_{-1}$, Al$_2$(MgSi)$_{-1}$ are direct indicators of magmatic intensive parameters (e.g. T, P, fO$_2$, $\mu_{SiO_2}$, etc.) and through compositional zonation profiles preserved in pyroxene phenocrysts, document the chemical and dynamical evolution of magmatic systems. An ability to model the precipitation of pyroxene from magmatic liquids as a function of evolving T, P, oxygen fugacity and liquid bulk composition is, consequently, crucial to the quantitative prediction of the liquid line of descent. This ability is predicated, however, on the existence of an internally consistent thermodynamic model for the Gibbs free energy of the magmatic system. It is the purpose of this paper to describe the calibration of such a model for igneous pyroxenes.

In the first paper of this series (Sack and Ghiorso 1994a, hereafter Part I) a model is formulated which broadly accounts for first order contributions to the Gibbs free energy of igneous pyroxenes. In the second contribution (Sack and Ghiorso 1994b, hereafter Part II), the model parameters applicable to the quadrilateral subsystem are calibrated from experimental data on cation ordering, enthalpy of solution, the extent of the miscibility gaps, and tie-line orientation between coexisting phases in the quadrilateral (senso stricto) and its constituent binaries. Ideally, we would have liked to continue in this paper to calibrate the “supersystem” by proceeding as in Part II, examining in order of sensitivity, data on: (1) cation-ordering of Fe$^{2+}$ and Mg between M2 and M1 sites and Fe$^{3+}$ and Al between M1 and tetrahedral sites as a function of temperature and com-
position, (2) tie-line orientation and the projection of the quadrilateral (Part II) and titanoo-luminate (Part I) miscibility gaps into the remainder of the supersystem, (3) solid-solid exchange reactions in the form of the compositions of coexisting pyroxenes and other thermodynamically well characterized solid phases at known $T_s$ and $P_s$, and (4) calorimetric constraints such as enthalpies of solution on solid solutions within the superset system. Unfortunately, outside of the pyroxene quadrilateral, only meager data exist along the lines indicated and these are woefully inadequate to effect a meaningful calibration. To proceed therefore, we are forced to adopt a somewhat unorthodox method of calibration.

It was first recognized by Sack and Carmichael (1984) that the thermochemistry of supersystem igneous pyroxenes could be elucidated by a systematic examination of exchange equilibria involving pyroxenes and co-existing silicate liquid. The underlying idea is quite simple. If the thermodynamic properties of the liquid are taken as "known", then compositions of coexisting pyroxene and liquid yield constraints on the exchange potentials of pyroxene components. We can see this by writing the pyroxene-liquid exchange reaction (after Sack and Carmichael 1984):

$$\text{CaMgSi}_2\text{O}_6(\text{pyx}) + \text{TiO}_2(\text{liq}) + \text{Al}_2\text{O}_3(\text{liq})$$

$$= \text{CaTiAl}_2\text{O}_6(\text{pyx}) + \frac{1}{2}\text{Mg}_2\text{Si}_4\text{O}_{10}(\text{liq}) + \frac{1}{2}\text{SiO}_2(\text{liq})$$ (1)

from which the exchange potential, $\mu_{\text{TiAl}_2\text{MgSi}_2}$, may be defined:

$$\mu_{\text{TiAl}_2\text{MgSi}_2} = \mu_{\text{TiO}_2} + \mu_{\text{Mg}_2\text{Si}_4\text{O}_{10}} - \frac{1}{2}\mu_{\text{SiO}_2} - \frac{1}{2}\mu_{\text{Al}_2\text{O}_3}.$$  

The difficulty, of course, is knowing the thermodynamic properties of the liquid. Sack and Carmichael (1984) utilized the calibration of Ghiorso et al. (1983) for liquid chemical potentials, but their analysis fell short of a useful calibration of the Gibbs free energy of the pyroxenes. The problem lay in inadequacies of the melt model, which were due in turn to the lack of an internally consistent database of standard state properties and a naive understanding of the energetics of the igneous rock forming minerals (e.g. olivines, feldspars, spinels) from which the melt properties were calibrated.

Since the work of Sack and Carmichael (1984), however, considerable effort has been aimed at improving our understanding of melt thermodynamics, to the point that a quantitative calibration of the energetics of supersystem pyroxenes is now possible. We will proceed along these lines by utilizing the thermodynamic model of Ghiorso and Sack (1994). This model is based upon the standard state thermodynamic database of Berman (1988) and upon revised and internally consistent solution theory for the major igneous solid phases, including our recent work on olivine and orthopyroxene (Sack and Ghiorso 1989), spinels (Sack and Ghiorso 1991a, b) and rhombohedral oxides (Ghiorso, 1990a; Ghiorso and Sack 1991a). The liquid model of Ghiorso and Sack (1994) is calibrated from over 2,000 experimental liquid-solid equilibria involving silicate melts and olivine, sphene, garnet, melilitc, feldspar, quartz, tridymite, leucite, corundum, spinel, rhombohedral oxides, whitlockite, apatite and water. Melt compositions range from komatite to potash ankaratrite to rhyolite, and experimental conditions vary between $1000^\circ$ and $1800^\circ$ C, 0.001 and 50 kbars, and relative oxygen fugacities defined by the iron-wüstite buffer up to air. The melt model of Ghiorso and Sack (1994) has overcome the shortcomings of the model of Ghiorso et al. (1983) and provides a firm foundation upon which to calibrate the pyroxene supersystem.

Before discussing the sources used in constructing the pyroxene-liquid database we extend the pyroxene thermodynamic model proposed in Part I to include Na.

Thermodynamics: extension to Na-bearing pyroxenes

To extend the thermodynamic formulation given in Part I to Na pyroxenes, it is convenient to select a reference Na-endmember other than that which corresponds to unit value of the Na composition variable ($X_N$, see Eqs. 3-4, Part I). $Na(Mg_{1/2}Si_{1/2})_{Na}Si_{1}O_{6}$

More sensible alternatives to this physically inaccessible component include NaTiAlSiO$_5$, NaTiFeSiO$_5$, NaFeSiO$_3$ (amendite) and NaAlSi$_2$O$_6$ (jasperite). The first two choices warrant consideration, but mutually high concentrations of Na and Ti in pyroxenes render the phase metastable with respect to aegirinate (Na$_2$Fe$_2$Ti$_2$Si$_6$O$_{20}$) under igneous conditions (Nicholls and Carmichael 1969). Amidite is a suitable alternative and is an abundant component in igneous pyroxenes crystallized at low pressure, but its standard state thermodynamic properties are not as well known as those of jadeite. Consequently, we adopt jadeite as the Na-vertex of composition space for the supersystem.

We seek to extend our equation for $\overline{G}$ to include both standard state contributions of $C/a$ ("hcp") jadeite (Jd) and its $P_{21/c}$ ("pbg") and $P_{bca}$ ("opx") equivalents and regular solution-type interaction parameters between Jd and the other vertices of composition ordering space. Eleven new parameters are required, and these include $\overline{G}_{Jd}, W_{Jd}, \overline{G}_{Ja}, W_{Ja}$, $W_{3Jd}, W_{5Jd}, W_{7Jd}, W_{9Jd}, W_{11Jd}, W_{13Jd}$, $T_{Jd}$, $T_{Ja}$, $T_{3Jd}$, $T_{5Jd}$, $T_{7Jd}$, $T_{9Jd}$, $T_{11Jd}$, $T_{13Jd}$, $\Delta T_{Jd}$, $\Delta T_{Ja}$, $\Delta T_{3Jd}$, $\Delta T_{5Jd}$, $\Delta T_{7Jd}$, $\Delta T_{9Jd}$, $\Delta T_{11Jd}$, $\Delta T_{13Jd}$. $\Delta \overline{G}_{Jd}$, $\Delta \overline{G}_{Ja}$ (see Table 2, Part I for a summary of additional supersystem parameters and notation conventions). The extension is tedious, but straightforward. First we recognize that the expression for $\overline{G}$ defined in Part I must be modified to include second (stage 1) and third (stage 2 and 3) order Taylor expansion coefficients in $X_N$.

1 In Part I only the configurational part of the molar Gibbs energy is defined for Na-bearing pyroxenes. The components corresponding to the following vertices of composition-ordering space ($X_1, X_2, X_3, X_4, X_5, X_6, X_7, X_8, X_9$) were chosen as endmember reference components for Na-free pyroxenes: CaMgSi$_2$O$_6$ ($0, 0, 0, 0, 0, 0, 0, 0, 0$), CaFeSiO$_3$ ($1, 0, 0, 0, 0, 0, 0, 0, 0$), CaTiAlSiO$_5$ ($0, 0, 0, 0, 0, 0, 0, 0, 0$), Na$_2$Fe$_2$Ti$_2$Si$_6$O$_{20}$, NaFeSiO$_3$ ($0, 0, 0, 1, 0, 0, 0, 0, 0$), CaMgAlSiO$_5$ ($0, 0, 0, 1, 0, 0, 0, 0, 0$), and Mg$_2$Si$_2$O$_6$ ($0, 0, 0, 0, 0, 0, 0, 0, 0$). For brevity, we will refer to these components as diopside (Di), hedenbergite (Hd), aluminoo-buffonite (Abb), buffonite (Bf), esseneite (Es), and enstatite (En), choosing the designator "buffonite" for the Fe$^{3+}$, Ti-bearing high calcium pyroxene in honor of the great French naturalist Georges Louis Leclerc Comte de Buffon (Sept. 7, 1707– Apr. 16, 1788). Buffon's experimental investigations of the cooling rates of heated iron balls led to the first estimate of the age of the earth not based upon biblical or stratigraphic interpretations. He is arguably the founder of modern experimental petrology.