

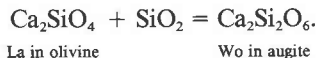
## Effect of Ca content and SiO<sub>2</sub> activity on augite + olivine equilibria

PAULA M. DAVIDSON,\* DONALD H. LINDSLEY

Center for High Pressure Research, Department of Earth and Space Sciences, State University of New York, Stony Brook, New York 11794, U.S.A.

### ABSTRACT

The Ca contents of coexisting augite and olivine are strongly correlated with the activity of silica through the equilibrium:



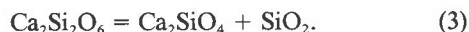
In turn, the Ca contents affect the distribution of Mg and Fe between augite (clinopyroxene, cpx) and olivine (ol). Thus any attempt to calibrate the Ca content of olivine for barometry or the Fe-Mg exchange for thermometry must take this relationship into account. For example, simple Fe-Mg exchange experiments between olivine and augite cannot give unique results if  $a_{\text{SiO}_2}$  is not fixed, either explicitly or implicitly, through fixing a sufficient number of intensive parameters (four of six from a set equivalent to  $X_{\text{Fe,cpx}}$ ,  $X_{\text{Ca,cpx}}$ ,  $X_{\text{Fe,ol}}$ ,  $X_{\text{Ca,ol}}$ ,  $P$ , and  $T$ ). Details of the relationship depend on the set of solution models chosen; we illustrate it for the Davidson and Lindsley (1989) model that has been incorporated into the QUILF program (Andersen et al., 1993; Lindsley and Frost, 1992; Frost and Lindsley, 1992).

### INTRODUCTION

Applying pyroxene + olivine exchange equilibria to geothermometry and geobarometry has a great potential for elucidating the thermal histories and pressures of both crustal and mantle-derived rocks. Thermodynamic models for exchange equilibria in the CMFS system are now available (Davidson and Lindsley, 1989; Sack and Ghiorso, 1994a, 1994b) that use the same formalism to describe experimentally studied phase relations for equilibria involving orthopyroxene, clinopyroxene, Ca-rich and Ca-poor olivine, and quartz; principal differences in the models arise from the adoption of different olivine models and different data bases for standard-state energy. It is tempting to use such models for ol + cpx exchange equilibria, for example, to determine equilibration temperatures. However, owing to the ternary nature of the exchange, we point out that knowing the Fe-Mg ratio of each phase in natural pairs is insufficient for determining temperatures; at least one more intensive parameter must be determined (in addition to pressure) to satisfy simultaneously a set of two exchange equilibrium relations, such as



Of the six intensive parameters obtained for coexisting CMFS cpx + ol (e.g.,  $X_{\text{Fe,cpx}}$ ,  $X_{\text{Ca,cpx}}$ ,  $X_{\text{Fe,ol}}$ ,  $X_{\text{Ca,ol}}$ ,  $P$ ,  $T$ ), four must be specified before Reactions 1 and 2 can be solved to yield the remaining two. The choice of which to specify is not limited to this group; more convenient choices may arise in specific situations. Alternatives include (but of course are not limited to) activities of silica, Fe +  $f_{\text{O}_2}$ , and iron oxides. For example, if we know the value for silica activity in the system (through other equilibria or trivially by the presence of quartz or another silica polymorph), then we may solve for three of the seven variables (adding  $a_{\text{SiO}_2}$  to the intensive variables) by incorporating a reaction between cpx and ol end-members of the type



The choice of which end-member is, of course, arbitrary; only one such reaction, in concert with Reactions 1 and 2, is independent. For many applications, the Fe or Mg end-member reaction is more convenient.

### DISCUSSION AND CONCLUSIONS

The mass transfer reaction (Reaction 3) involves a change in the relative proportions of cpx and ol, so its rate may be slower than those of the cation-exchange required for Reactions 1 and 2. Therefore, phase assemblages with apparent-equilibrium Mg-Fe ratios may simply reflect their current (disequilibrium) Ca contents, not true equilibrium.

Davidson and Lindsley (1989) discussed the interde-

\* Present address: Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, Washington, DC 20015-1305, U.S.A.

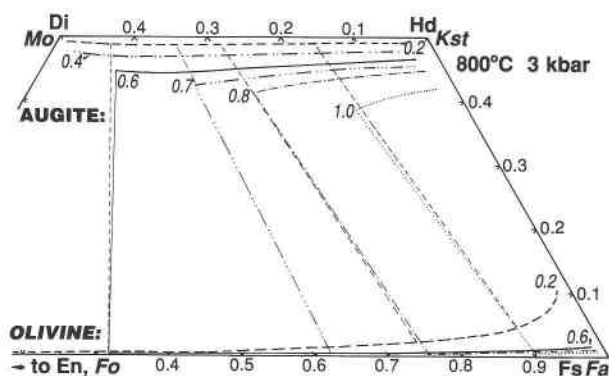


Fig. 1. Superimposed Ca-Mg-Fe quadrilaterals for cpx + ol, with contours showing compositions of cpx + ol coexisting for several different values of  $a_{\text{SiO}_2}$ ;  $P = 3$  kbar,  $T = 800$  °C. Note how strongly the Ca content depends on  $a_{\text{SiO}_2}$ . The contours for  $a_{\text{SiO}_2} = 1.0, 0.8, 0.7,$  and  $0.6$  terminate where the cpx + ol assemblage reaches equilibrium with opx at the given value of  $a_{\text{SiO}_2}$ ; tie lines at these terminations are shown, along with tie lines for similar olivines at  $a_{\text{SiO}_2} = 0.2$  for comparison. Olivine contours for  $a_{\text{SiO}_2} = 0.4$  and  $0.7$  have been omitted for clarity.

pendence of  $\text{SiO}_2$  activity,  $P$ , and Ca contents (see discussion of their Fig. 12); however, the effect of Ca content on Fe-Mg ratios of coexisting phases was not emphasized by them. This effect has tended to be overlooked (e.g., Perkins and Vielzeuf, 1992). We demonstrate this point with a plot of compositions of coexisting cpx and ol at several values of  $a_{\text{SiO}_2}$  (Fig. 1).

For geothermometry and geobarometry applications, it is therefore important to determine, as completely as possible, the compositions of pairs of cpx + ol. Variations of <1 mol% larnite component ( $\text{Ca}_2\text{SiO}_4$ ) have a significant effect on coexisting augite compositions and consequently the model-derived equilibrium temperature. If other means of specifying  $a_{\text{SiO}_2}$  are available, they provide a powerful test of equilibrium or, in some cases, the necessary information for estimating  $P$  and  $T$ .

Similarly, the ternary nature of the cpx + ol exchange must be considered when designing experiments for con-

straining exchange equilibria. If the Ca contents of both phases are allowed to vary without controlling a sufficient number of intensive parameters (such as  $P$ ,  $T$ , bulk composition, and one more, possibly  $X_{\text{Ca,ol}}$ ,  $a_{\text{SiO}_2}$ , or, equivalently,  $a_{\text{Fe}} + f_{\text{O}_2}$ ), then the exchange of Fe and Mg can, at best, reflect equilibrium with the current amount of Ca in the phases. Of course, these observations apply to olivine + orthopyroxene (opx) exchange equilibria as well; however, the magnitude of the effect of Ca content in ol on the exchange of Fe and Mg is greatly reduced (cf. Fig. 12 of Davidson and Lindsley, 1989) because the Ca content of opx changes but little.

#### ACKNOWLEDGMENTS

We thank David Andersen for developing the QUILF program that made Figure 1 a snap to calculate and Steve Bohlen and Mark Ghiorso for reviews. This work was supported by NSF grants EAR-9104024 and EAR-9304699 to D.H.L.; these are gratefully acknowledged. Stony Brook Mineral Physics Institute Publication no. 121.

#### REFERENCES CITED

- Andersen, D.J., Lindsley, D.H., and Davidson, P.M. (1993) QUILF: A PASCAL program to assess equilibria among Fe-Mg-Ti oxides, pyroxenes, olivine, and quartz. *Computers in Geosciences*, 19, 1333-1350.
- Davidson, P.M., and Lindsley, D.H. (1989) Thermodynamic analysis of pyroxene-olivine-quartz equilibria in the system CaO-MgO-FeO-SiO<sub>2</sub>. *American Mineralogist*, 74, 18-30.
- Frost, B.R., and Lindsley, D.H. (1992) Equilibria among Fe-Ti oxides, pyroxenes, olivine, and quartz: II. Applications. *American Mineralogist*, 77, 1004-1020.
- Lindsley, D.H., and Frost, B.R. (1992) Equilibria among Fe-Ti oxides, pyroxenes, olivine, and quartz: I. Theory. *American Mineralogist*, 77, 987-1003.
- Perkins, D., and Vielzeuf, D. (1992) Experimental investigation of Fe-Mg distribution between olivine and clinopyroxene: Implications for mixing properties of Fe-Mg in clinopyroxene and garnet-pyroxene thermometry. *American Mineralogist*, 77, 774-783.
- Sack, R.O., and Ghiorso, M. (1994a) Thermodynamics of multicomponent pyroxenes: I. Formulation of a general model. *Contributions to Mineralogy and Petrology*, 116, 277-286.
- (1994b) Thermodynamics of multicomponent pyroxenes: II. Phase relations in the quadrilateral. *Contributions to Mineralogy and Petrology*, 116, 287-300.

MANUSCRIPT RECEIVED APRIL 25, 1994

MANUSCRIPT ACCEPTED JULY 8, 1994