Thermochemistry of pyroxenes on the join $Mg_2Si_2O_6$-$CaMgSi_2O_6$: A revision of the model for pressures up to 30 kbar

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Carlson and Lindsley (1988) presented a model for the thermodynamic properties of the $Mg_2Si_2O_6$-$CaMgSi_2O_6$ join that describes most of the known subsolidus phase relations up to 1600 °C and 60 kbar. They recognized that devising a model to cover this wide range required the adoption of a number of compromises, none of which violates the explicit data available for that join. The preferred values for their model parameters generate an extraordinarily complex *P-T* diagram, especially at pressures below 5 kbar (Fig. 1). Much of that complexity is illustrated by the 1-atm *T-X* diagram (Fig. 2a). The two coincidences of Pig and Opx compositions (one stable at 1387 °C, the other metastable at 1303 °C for 1 atm) result from complex intersections of the Opx and Cpx free-energy curves. Complexities involving PEn result from the choice to make it ideal, in contrast to the strong nonidealities of Opx and Cpx. The very wide field for Opx at high temperatures results from the relatively low temperature for the inversion of Di to "orthodiopside." Another effect of that low temperature is the predicted breakdown of Pig to Aug + Opx *with increasing temperature* at 1389 °C. They were aware of these complexities, but similar features arose in all variations on the model that satisfactorily replicated the experimental data over the entire range of pressures from 1 atm to 60 kbar. Because the goal of their modeling was to provide a thermodynamic framework encompassing the full range of experimental data on the Fe-free join, the complexities appearing at low pressure and high temperature were accepted as an unavoidable compromise. Those complexities were regarded as inconsequential to the principal goal of their model, inasmuch as the complexities occur predominantly above the solidus and therefore would not be stable.

Davidson and Lindsley (1989) attempted to remodel quadrilateral pyroxene phase relations, using the Di-En join of Carlson and Lindsley (1988) as a starting point. Davidson and Lindsley's model was quite successful in describing the known phase equilibria and calorimetric data for the quadrilateral, with one serious exception. That quadrilateral model was unable to duplicate the lower thermal stability of Pig in the range $0.1 < Fe/(Fe + Mg)$

< 0.3; the calculated diagram (Fig. 3) shows a hiatus in that range, with no stability for Pig at any temperature. However, pigeonites in that range *are* found in rocks and simple experimental systems (Lindsley, 1983, and references therein) and in experiments on naturally occurring compositions (e.g., Grove and Juster, 1987). Inspection of Figures 2a and 3 makes it clear that the pigeonite hiatus is an artifact of the high-temperature breakdown of Pig required for the Di-En join by the Carlson and Linds-
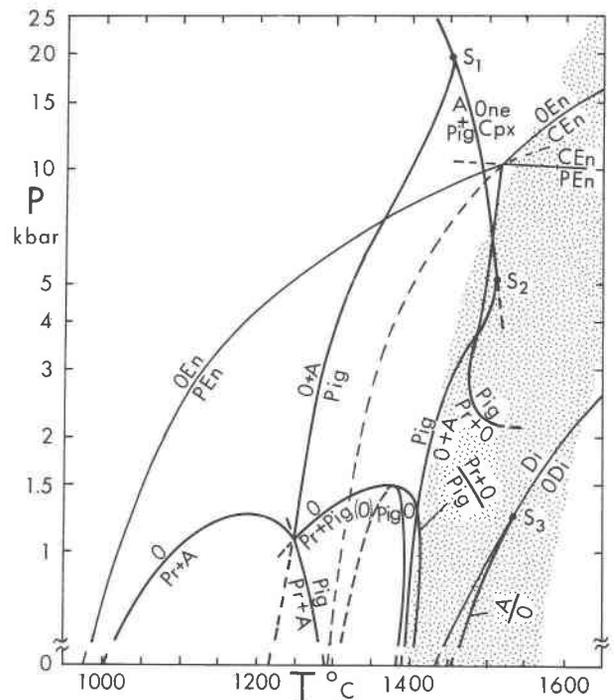
Fig. 1. *P-T* projection for the system $Mg_2Si_2O_6$-$CaMgSi_2O_6$ based on the Carlson and Lindsley (1988) model. This is an extension of Fig. 2 of Carlson and Lindsley. Melting relations are omitted, but the melting interval is approximated by the stippled area. Note log *P* scale. End-member phases are indicated as OEn, orthoenstatite; CEn, clinoenstatite; PEn, protoenstatite; Di, (clino)diopside; ODi, "orthodiopside." Solid solutions are abbreviated as O, orthopyroxene, some highly calcic; Pig, low-Ca clinopyroxene; A, high-Ca clinopyroxene; Pr, protopyroxene. Abbreviations in parentheses label metastable curves. S_1, S_2, and S_3 are singular points.

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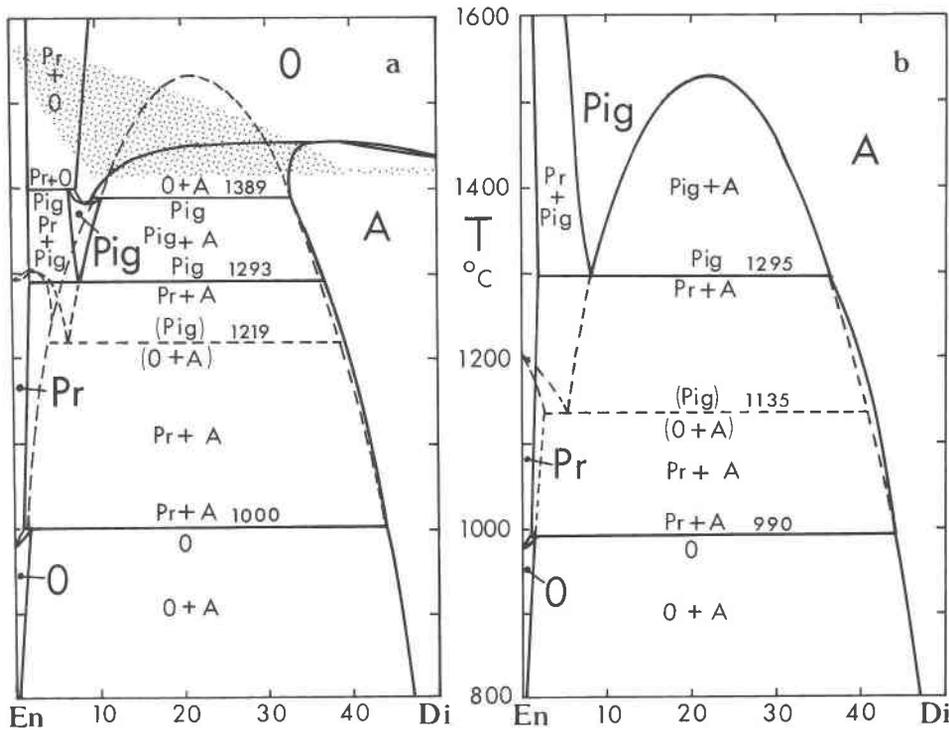
Fig. 2. Phase relations calculated at 1 atm from the Carlson and Lindsley (1988) model (**a**) and the revised solution model presented in this work (**b**). The melting interval is indicated by the stippled area in (a). Abbreviations as in Fig. 1. The Carlson and Lindsley model correctly predicts the re-appearance of orthopyroxene at near-solidus temperatures (Longhi and Boudreau, 1980; Carlson, 1988), but the relative compositions of O and Pig are not correct. Note that the predicted inversion of Di to "orthodiopside" lies just above the liquidus. The revised model (b) lacks any field for high-T orthopyroxene, but otherwise describes the available experimental data in a much simpler fashion than does the Carlson and Lindsley model. The revised model predicts that "orthodiopside" will not be stable below 1754 °C—comfortably above the liquidus.

ley (1988) model: with the addition of Fe, a peculiar feature that is "harmless" in the Fe-free system propagates into the subsolidus region with deleterious effect.

It is clear that the pigeonite hiatus stems from the low predicted temperature for the inversion of Di to "orthodiopside" in the Carlson and Lindsley (1988) model. Although their modeling had been structured to maximize this temperature, the high-pressure constraints required a barely supersolidus value for it in order to fit the experimental data at all pressures. It is therefore not possible to modify their model so as to eliminate the pigeonite hiatus in the quadrilateral *and* retain that model's ability to reproduce all the experimental data. We conclude that a different Di-En model—one that makes no attempt to fit a subset of the experimental data—must be used as a starting point for quadrilateral pyroxene models. This discussion presents that revised Di-En model.

For several reasons, we exclude the data at 40 kbar and above from the new modeling. Most data on quadrilateral pyroxenes have been obtained below 30 kbar, so it is important to use a Di-En model appropriate for lower pressures. In addition, most natural pyroxenes with Fe/(Fe + Mg) > 0.15 have crystallized at pressures well be-
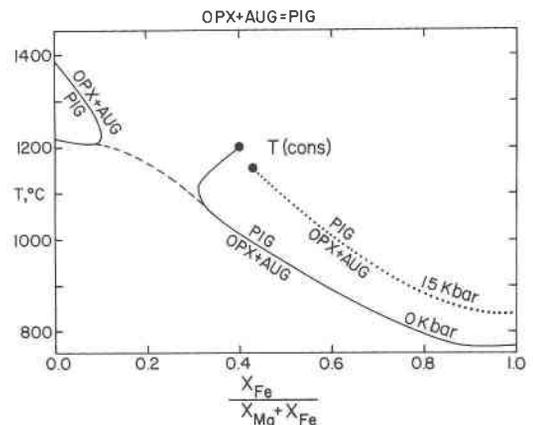
Fig. 3. Stability relations of Pig predicted by a quadrilateral solution model that incorporates the Carlson and Lindsley (1988) model for Di-En. Melting relations are not shown. The predicted gap in the stability of Pig at 0.10 < Fe/(Fe + Mg) < 0.30 is incompatible with a variety of experimental data and natural occurrences for which the minimum stability of Pig is indicated by the dashed line. T(cons) indicates the intersection of the calculated Pig = Opx + Aug reaction with the Pig–Aug consolute temperature.

TABLE 1. Values of revised thermochemical parameters compared with those of Carlson and Lindsley (CL)

Parameter	CL	This work
ΔU_A^0	4.261	6.111
ΔV_A^0	0.05900	0.09754
ΔS_A^0	2.721	4.1323
ΔU_B^0	−35.92	−39.060
ΔV_B^0	−1.753	−0.1375
ΔS_B^0	−20.97	−17.295
ΔU_E^0	0.9814	1.1632
ΔV_E^0	−0.07954	−0.08199
ΔS_E^0	0.09328	0.16801
ΔU_F^0	−36.71	−6.129
ΔV_F^0	0.0	0.0
ΔS_F^0	2.444	10.2181
$W_{U1}(Cpx)$	26.23	26.125
$W_{U2}(Cpx)$	32.44	32.301
$W_{V1}(Cpx)$	−0.02229	−0.03843
$W_{V2}(Cpx)$	−0.08646	−0.00670
$W_U(Opx)$	28.60	20.0*
$W_V(Opx)$	−1.749	0.0*
$W_U(Proto)$	0.0*	20.0*

Note: Energy in kJ/mol; volume in kJ/(kbar·mol); entropy in J/(K·mol). Subscripts A, B, E, and F refer to relations given in Carlson and Lindsley (1988).
* Adopted values.

low 30 kbar. After exclusion of the high-pressure data (and a set at 1500 °C, 30 kbar), our approach to the modeling was virtually identical to that of Carlson and Lindsley (1988). We used linear programming and included in the objective function terms to maximize ΔH and minimize ΔS for the Di → ODi inversion. This combination makes the calculated temperature for that inversion as high as feasible. By omitting the 40 to 60-kbar data, we were also able to eliminate W_V^{Opx}, which has the implausibly large value of −1.749 J/(bar·mol) in the Carlson and Lindsley (1988) model. In preliminary fitting, we found that both W_H^{Opx} and W_H^{PEn} could vary from zero to more than 30 kJ. To minimize the complex interactions found in their model, we chose to make both values equal and reasonably close to the parameters for Aug. Because W_H^{Opx} varies antipathetically with ΔH for the Di → ODi inversion we adopted compromise values of 20 kJ for both W_H^{Opx} and W_H^{PEn}. Values for the fitted parameters are compared to those of Carlson and Lindsley in Table 1. The revised value for ΔU_A^0—6.111 kJ—is marginally closer to that extrapolated from calorimetric measurements (Newton et al., 1979). The value for ΔV_B^0 is very much smaller than that of Carlson and Lindsley (1988), probably because we were able to eliminate W_V^{OEn}, which is highly correlated with ΔV_B^0. More than three quarters of the parameters for the revised model lie outside the range of maximum and minimum values derived by Carlson and Lindsley, a striking expression of the influence of the high-pressure data used in that model and omitted in the revised model.

Elimination of the high-pressure constraints also permits several improvements in the fit to the low-pressure data. The revised Di-En model yields 1466 °C for the coexistence of Opx + Pig + Di at 15 kbar—much closer to the experimental value of 1465 ± 10 °C (Schweitzer, 1982) than the 1436 °C predicted by Carlson and Lindsley (1988). Except for the absence of a high-temperature field for orthopyroxene, this model fits the 1-atm data as well as does that of Carlson and Lindsley, and it avoids many of the complexities of their model at that pressure (Fig. 2b). Most important, the revised model avoids the second Pig = Opx + Aug reaction that led to the pigeonite hiatus in the quadrilateral model based on Carlson and Lindsley (1988). As a basis for fitting relations within the quadrilateral at pressures up to 30 kbar, the revised model is clearly superior.

What the revised Di-En model does *not* do nearly so well as that of Carlson and Lindsley (1988) is to predict the phase relations at simultaneous high pressures and temperatures—hardly a surprise since we were compelled to ignore the high-pressure data in deriving it. For compositions close to the Di-En join—especially for higher pressures—the Carlson and Lindsley 1988 model remains the model of choice.

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