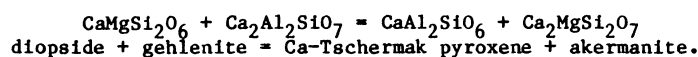


THERMOMETRY OF CA-AL-RICH INCLUSIONS. E. Stolper¹, G.J. MacPherson², J.R. Beckett³, and L. Grossman³. ¹Div. Geol. Planet. Sci., Caltech, Pasadena, CA 91125. ²Dept. Min. Sci., Smithsonian Inst., Washington, D.C. 20560. ³Dept. Geophysical Sci., U. Chicago, Chicago, IL 60637.

One of the most significant and elusive factors in the petrogenesis of Ca-Al-rich inclusions is temperature. The temperature of CAI formation is usually inferred by comparison with the calculated condensation sequence of the nebula¹ or the experimentally determined crystallization sequences of CAI-like compositions². If temperatures could be determined from the mineral assemblages of CAIs, independent of assumptions regarding the mechanism of their formation, it might be possible to distinguish between contrasting evolutionary histories and to resolve ambiguous textural interpretations^{3,4}. Aside from temperature limits provided by the stability fields of individual minerals⁵, few quantitative temperature estimates are available, although Haggerty⁶ suggested the potential of Ti^{3+}/Ti^{4+} in pyroxenes for thermometry.

We present here an approach to determining equilibration temperatures that should be widely applicable to Type B CAIs. Consider the coexistence of melilite and clinopyroxene in the system $CaMgSi_2O_6$ - $CaAl_2SiO_6$ - CaO . Equilibrium between these two phases is governed by the following exchange reaction:



The equilibrium constant for this reaction is: $K = (a_{CaTs}^{px} / a_{Di}^{px}) \cdot (a_{Ak}^{mel} / a_{Geh}^{mel})$,

where a_m^n refers to the activity of component m in phase n. Thermochemical data⁷ has been used to predict the dependence of K on temperature shown in Figure 1.

The temperature dependence of K shown in Figure 1 offers a straightforward approach to determining the temperature recorded by equilibration between coexisting melilite and pyroxene. One simply determines the compositions of adjacent pyroxenes and melilites and then, providing that the relationships between composition and activity are known, calculates K and reads off a temperature from Figure 1. As a first approximation, we assume that activity (a) is equal to mole fraction (X) both in pyroxene and melilite solid solutions^{8,9}. We emphasize that this is only an approximation; both of these phases are manifestly non-ideal. As a check on the validity of this approximation in applications of the thermometer to CAI assemblages, we show in Figure 1 values of K calculated for several pyroxene-melilite pairs from experiments on CAI-like compositions^{2,10}. Most of the pyroxenes from these experiments are similar in composition to the fassaites found in natural CAIs, including their Ti^{3+}/Ti^{4+} ratios. The close correspondence between the values of K calculated from thermochemical data and from experimental pyroxene-melilite pairs assuming $a=X$ suggests that thermometric information may be obtainable without having to take detailed account of the complexities of these solid solutions. We note, however, that this approximation will probably break down as endmember compositions are approached and at low temperatures.

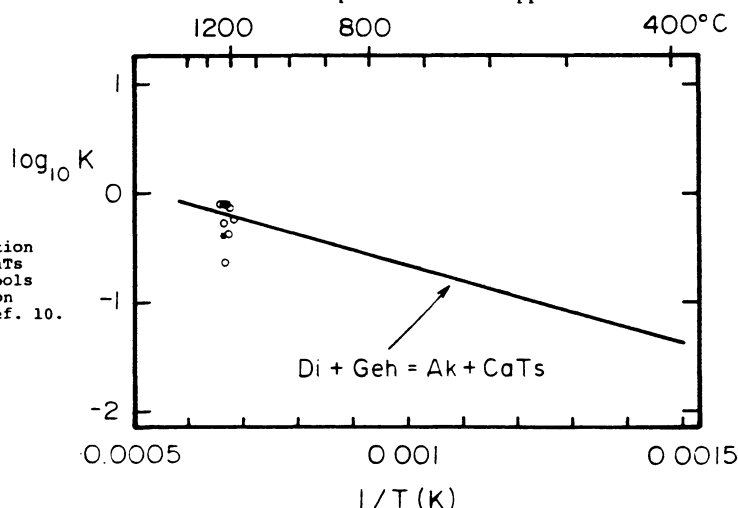


Figure 1. Solid line is calculated variation in $\log_{10} K$ of the reaction $Di + Geh = Ak + CaTs$ vs. $1/T$ based on compilation in (7). Symbols are based on px-mel pairs in experiments on CAI-like compositions. * - ref. 2. O - ref. 10.

Very little of the voluminous data on pyroxene and melilite chemistry in CAIs can be used for thermometry since rarely are analyses of adjacent phases reported. Since most phases in CAIs are strongly zoned, meaningless results will be obtained unless only phases in contact and only analyses at the contact are utilized.

One problem that this thermometer is capable of addressing is whether the melilite in Type B CAIs is igneous^{2,3,11} or metamorphic⁴ in origin. In the case of an igneous origin, temperatures in the vicinity of the solidus should be expected (1100-1200°C)^{2,12}, whereas for a

metamorphic origin, a wide dispersion of temperatures extending well below the solidus would be expected. We have applied the pyroxene-melilite thermometer to five Type B CAIs to demonstrate its use and to shed some light on the igneous vs. metamorphic controversy. In each of the inclusions, several pyroxene-melilite pairs were analyzed using wavelength dispersive electron microprobe analysis. The phases in each pair were analyzed as close to their mutual boundary as possible without producing significant contamination, and several point analyses (70-100 sec. counting time each) were taken and averaged to arrive at the final coexisting compositions. Three types of melilite-pyroxene contacts were examined: (1) sharp contact between neighboring melilite and pyroxene crystals; (2) melilite crystals enclosed poikilitically within large pyroxene crystals, in one inclusion only (TS47F1); and (3) irregularly-shaped pyroxene grains enclosed within the outer edges of large, zoned melilite crystals. The third variety is the kind interpreted as metamorphic replacement of pyroxene by melilite⁴. Three of the inclusions are Type B1s and have been described in detail elsewhere (TS33F1³; TS34F1, TS23F1¹¹). Two of the melilite-pyroxene pairs from TS23F1 and one from TS34F1 that we have analysed here are illustrated in Figures 1, 2, and 10 of [11]. A fourth inclusion, TS47F1, is a Type B that is unusual in containing large poikilitic fassaites that enclose many small euhedral melilite crystals. The melilites are normally-zoned. A fifth inclusion, TS31F1, is a very Mg-rich Type B whose melilites are extremely δ kermanitic, typically $Ak > 80$. In this inclusion can be found all three types of the melilite-pyroxene relationships noted above.

Our data are plotted on Figure 2 along with temperature contours based on Figure 1 and the assumption of $a=X$. All of the pyroxene-melilite pairs indicate temperatures $> 1100^\circ\text{C}$. Most plot in the range 1200-1400 $^\circ\text{C}$. Data from TS31F1 plot away from the rest, at unrealistically high temperatures for such a composition. This could result from lack of equilibrium between the phases (perhaps an igneous feature) or from the fact that the assumption of $a=X$ breaks down as the diopside and δ kermanite endmembers are approached. We emphasize that quantitative applications of this thermometer must be considered preliminary at this stage and that further experimental work will be needed to rigorously calibrate it. Nevertheless, the narrow range of temperatures apparently recorded by the pyroxene-melilite pairs in four of the five inclusions that we have studied and the clustering of these temperatures around the solidus temperatures of CAIs are consistent with the bulk of such assemblages representing igneous features.

The thermometer described above is not the only one that has potential for resolving questions regarding the history of refractory inclusions. Others involving px-mel-plag-sp (e.g., $3An + 6Ak + Sp = 4Geh + 7Di$) and px-forsterite-sp (e.g., $Fo + CaTs = Sp + Di$) can also be readily formulated and applied to CAI assemblages (e.g. [13]). In general, however, careful experimental work will be required before quantitative conclusions can be reached with confidence.

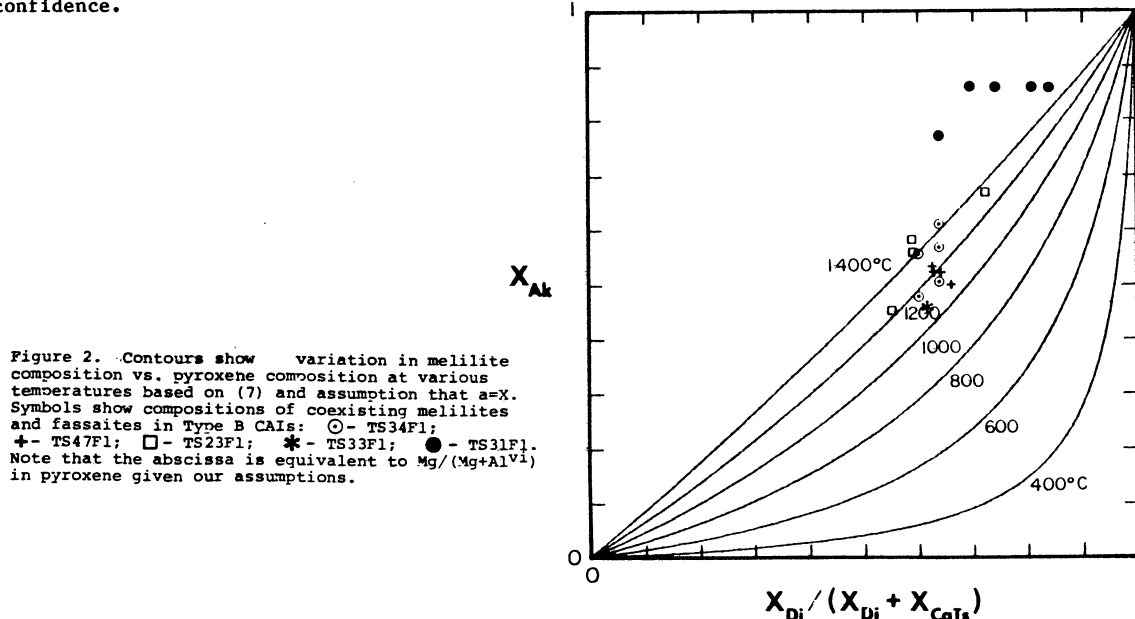


Figure 2. Contours show variation in melilite composition vs. pyroxene composition at various temperatures based on (7) and assumption that $a=X$. Symbols show compositions of coexisting melilites and fassaites in Type B CAIs: \odot - TS34F1; $+$ - TS47F1; \square - TS23F1; $*$ - TS33F1; \bullet - TS31F1. Note that the abscissa is equivalent to $Mg/(Mg+Al^{VI})$ in pyroxene given our assumptions.

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