

COMPOSITIONAL DEVIATIONS IN LUNAR PYROXENES: ANALYTICAL ERROR OR NON-STOICHIOMETRY? D. J. Andersen and D. H. Lindsley, Dept. of Earth and Space Sciences, State Univ. of New York, Stony Brook, N. Y. 11794

Pyroxenes are potentially useful indicators of the temperature, pressure, and fO_2 at which the rocks containing them have formed. Detailed application of available experimental data is hampered by the largely unknown effects of minor elements such as Al, Ti, Cr, Na, and Fe^{3+} . Na and Fe^{3+} are very low in lunar pyroxenes, but some Ti may occur as Ti^{3+} (e.g., [1]) or Cr as Cr^{2+} (e.g., [2]), owing to the reduced nature of many lunar rocks. To determine the most appropriate compositions for phase equilibrium experiments, we have collected 239 analyses of non-basaltic lunar pyroxenes, so as to discover any substitutional couples present. Similar statistical treatments have been done for pyroxenes from deep-sea basalts [3] and from planetary basalts [4,5].

The pyroxenes are from lunar anorthosites, norites, troctolites, dunites, and gabbros; all were analyzed by electron microprobe [6-49]. Only 51% of the analyses as published passed criteria for superior analyses [3]; most of those rejected failed the constraint of 1 ± 0.02 cations/6 oxygens in the M2 site. Estimation of Ti^{3+} by a charge-balance equation $IVAl + Na = VIAI + 2Ti^{4+} + Ti^{3+} + Cr^{3+}$ enabled another 6% of the analyses to pass the criteria; even so, the 57% judged superior compares unfavorably with the 72% of terrestrial non-basaltic pyroxenes that passed the same tests [50]. It appears either that the published analyses of lunar pyroxenes are of lower quality or that many lunar pyroxenes are non-stoichiometric, in which case the criteria of [3] would not all be applicable. The apparent non-stoichiometry is evident on a plot of Si + Al vs. all other elements (per 6 oxygens; Fig. 1). Analyses plotting on the 45° line have 4 cations/oxygens and are stoichiometric. But only in the vicinity of Si + Al = 2 do the analyses approach the 45° line; instead they scatter about a line having SiO_2 and olivine as its endpoints! Reckoning Ti as Ti^{3+} and Cr as Cr^{2+} does not improve the approach to stoichiometry; instead the trend in Fig. 1 is merely raised (to higher cation sums; Fig. 2), but it is not rotated towards the stoichiometric line.

A portion of the deviation can be explained as due to analytical errors. Counting statistics limit the inherent precision of individual microprobe analyses to $\pm 2\%$ of the amount present. Inasmuch as most pyroxenes contain approximately 50 wt. % SiO_2 , random fluctuations of up to ± 1 wt. % SiO_2 are to be expected. (Random fluctuations in the other oxides will tend to be self-cancelling.) If the true pyroxene composition plotted at (2,2) in Fig. 1, then fluctuations in SiO_2 would, in fact, produce a dispersion along the SiO_2 -Ol line, but the dispersion should be limited to the range $1.98 \leq Si + Al \leq 2.02$. Most of the points in Fig. 1 fall within those limits, but a number do not (see esp. Figs. 1a,c) and require further explanation. Minute inclusions of olivine or of silica phases could bias the analyses of pyroxenes towards those minerals, but there is no systematic correlation between the direction of deviation and the presence of olivine or of a SiO_2 phase in the rocks, so this

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explanation seems unlikely. Alternatively, the departures from stoichiometry may be real, with the pyroxenes actually containing SiO_2 or olivine components in solid solution. Experimental studies at high temperatures show that diopside can contain up to 8 wt.% Mg_2SiO_4 [51,52] or up to 2.5 wt.% SiO_2 [53], amounts that encompass most of the range observed (Fig. 1). Additional experiments are needed to determine whether similar degrees of solid solution are possible at lower temperatures and for compositions more like those of the lunar pyroxenes.

To the extent that the dispersion in Fig. 1 is due to analytical error, these non-basaltic pyroxenes contain little, if any, octahedral aluminum--a distinction from many mare-basalt pyroxenes [4]. The paucity of VIAl in the non-mare pyroxenes probably reflects a closer approach to equilibrium during their crystallization, as compared with pyroxenes from mare basalts.

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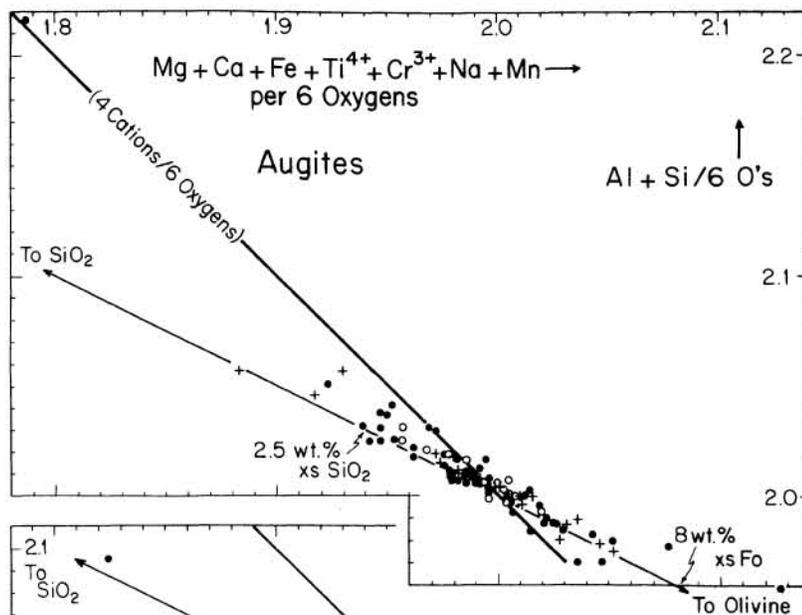


Figure 1a

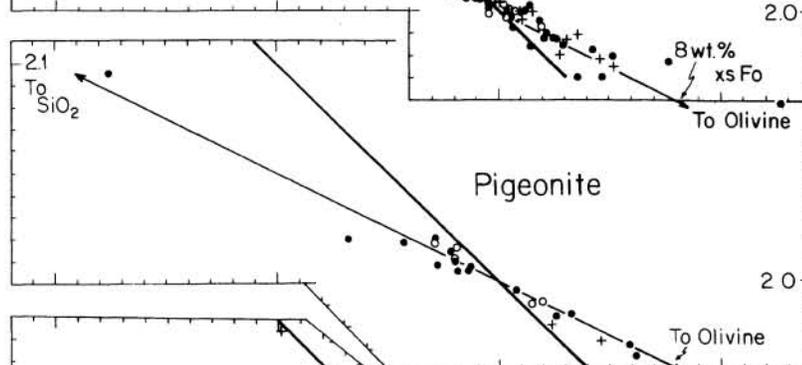


Figure 1b

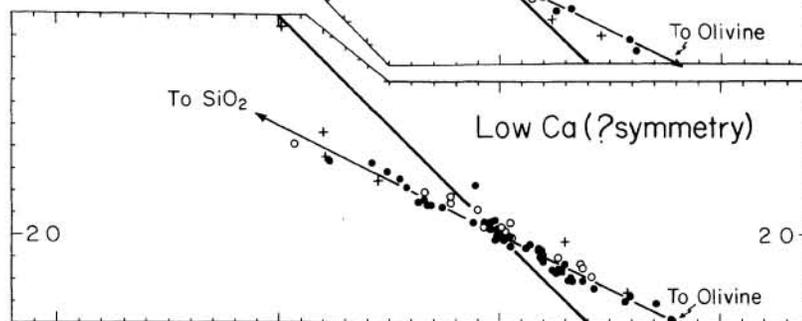


Figure 1c

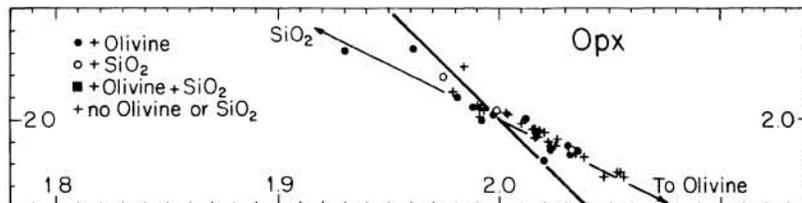


Figure 1d

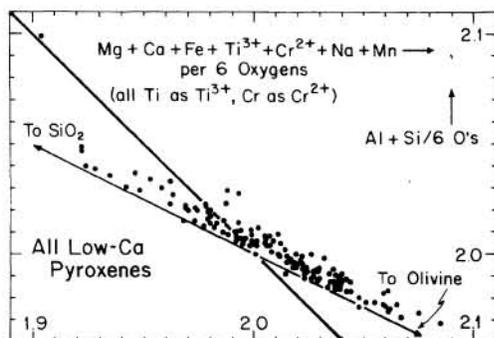


Figure 2