

Lecture 8

A. More Examples of Experimental Approaches For Determination of TE Partition Coefficients

1) Partitioning of trace elements between two immiscible liquids:

Immiscible melts occur in petrologically relevant systems; for example, a well-known example is the system K_2O - FeO - Al_2O_3 - SiO_2 where at high temperature (1178 C) two immiscible melts are in equilibrium (Figure 23). The partitioning of trace elements between these two melts has two applications:

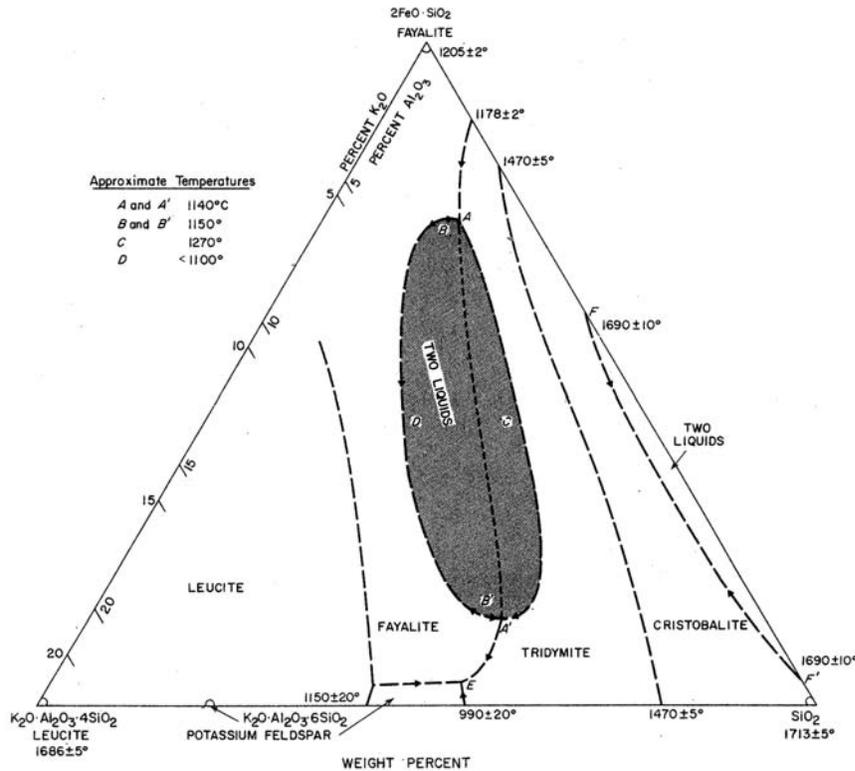


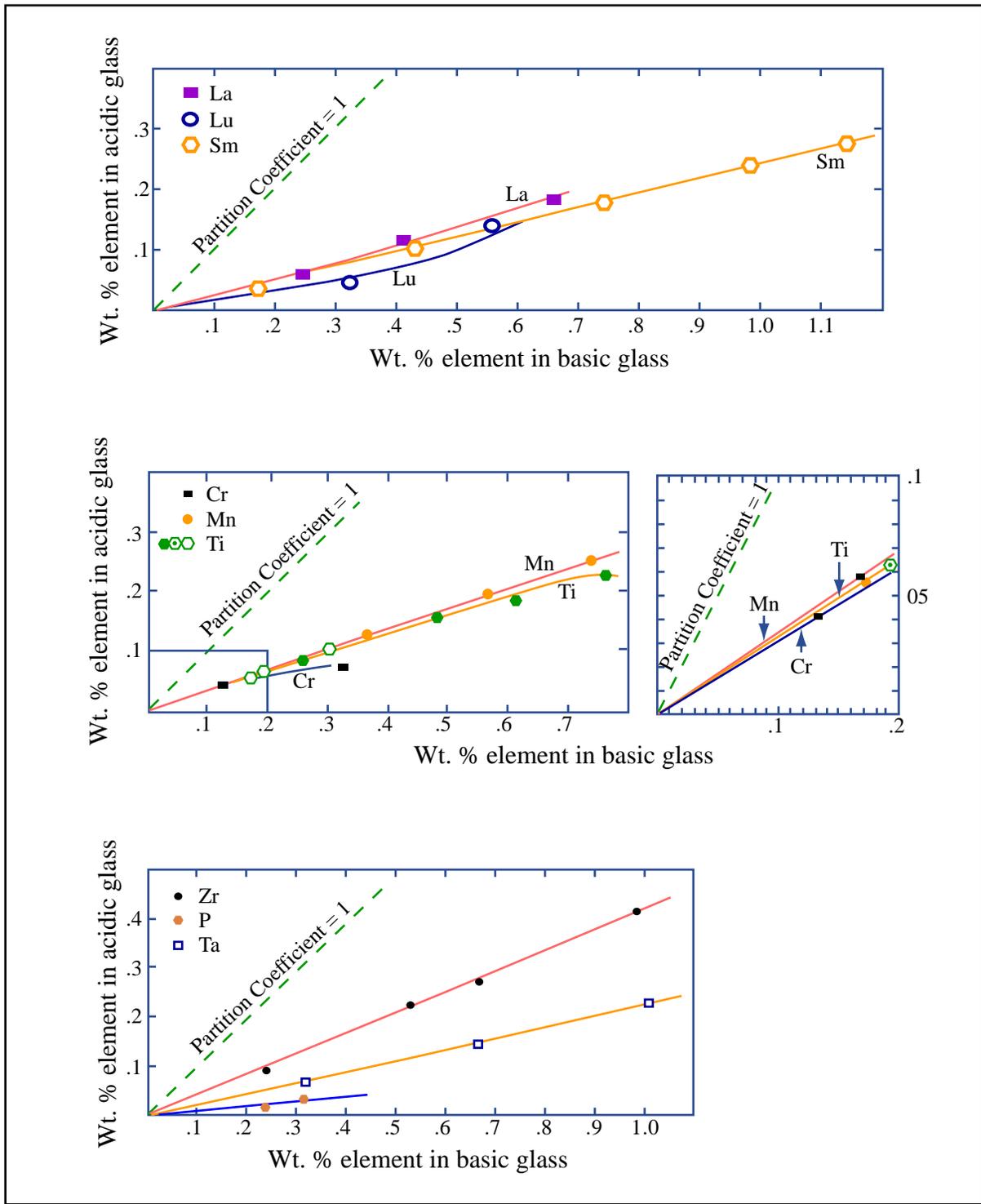
Figure courtesy of USGS.

Figure 23. Phase relations in the system K_2O - FeO - Al_2O_3 - SiO_2 showing the coexistence of two immiscible liquids along the line A-A'. Liquid A is relatively SiO_2 -poor and FeO -rich whereas liquid A' is SiO_2 and K_2O -rich.

(a) Liquid immiscibility is commonly observed in the groundmass of basalt; e.g., Roedder and Weiblen (1971) documented the coexistence of SiO₂ and K₂O-rich glasses and SiO₂-poor, FeO-rich glasses in the groundmasses of lunar basalts. However, an important question remains; is liquid immiscibility a major petrogenetic process that creates compositionally distinctive magma (e.g., Freestone and Hamilton, 1980)? In particular, is there a distinctive trace element signature associated with this process?

(b) Determination of partition coefficients between two coexisting melts of different composition provides direct information on the importance of melt compositions; such information is useful in understanding variations in mineral/melt partition coefficients as melt composition changes (e.g., Figure 19 and 21).

Watson (1976) studied the partitioning of several trace elements, Cs, Sr, Ba, La, Sm, Lu, Ti, Mn, Cr, Zr, Ta and P, between immiscible melts in the system K₂O-FeO-Al₂O₃-SiO₂ at 1 atm pressure and 1186 C. The coexisting melts are a silicic melt (74% SiO₂) with 4% K₂O and a basic melt with 56% SiO₂ and 40% FeO.



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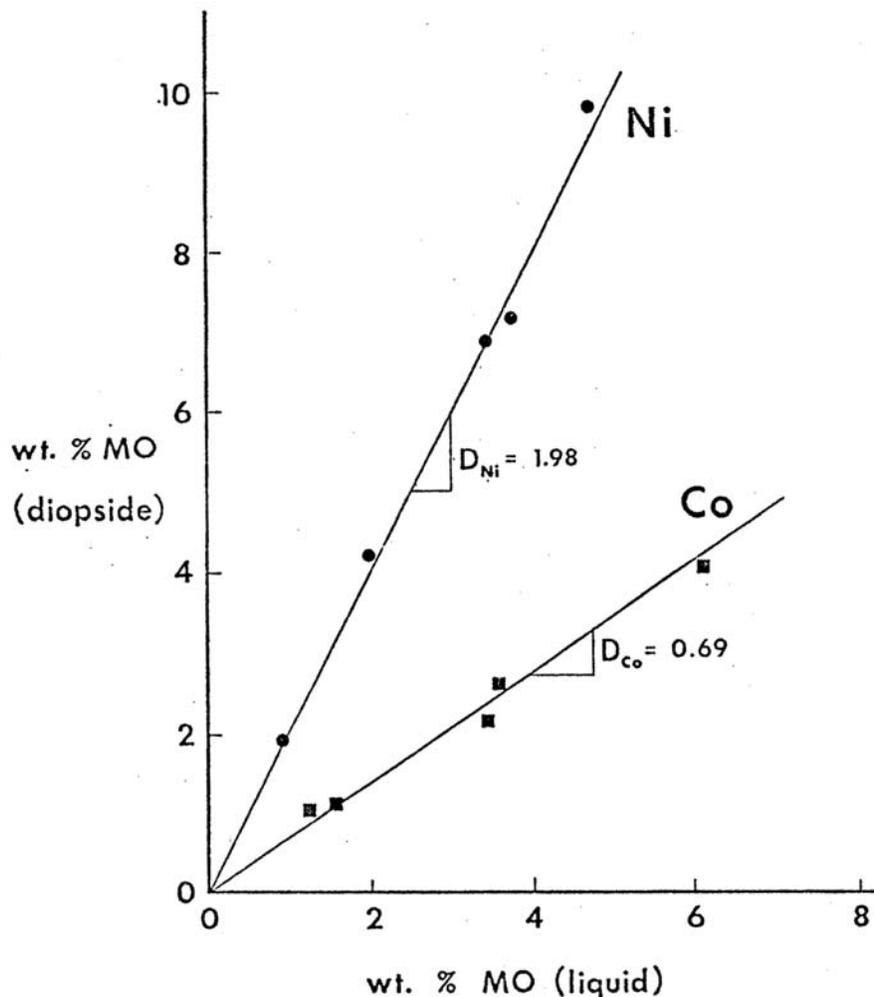
Figure 24. Wt% element in basic and acidic (SiO₂-rich glass) showing that REE (La, Sm, Lu), transition metals (Cr, Mn, Ti) and high field strength elements (Zr, P, Ta) are all preferentially partitioned into the basic glass, i.e., $D^{\text{basic/acidic}} > 1$. The generally linear trends for each element show that the D's are not sensitive to abundance of the element. Figure is adapted from Watson (1976).

The results show that except for Cs, all of these trace elements are preferentially incorporated into the basic melt (Figure 24 and Figure 3 of Watson, 1976, for Cs). The values of $D^{\text{basic/silicic}}$ range from ~ 0.3 for Cs to ~ 10 for P. A simple interpretation is that Cs, and K, are enriched in the SiO_2 -rich melt because they are coordinated with Al to create network formers such as KAlO_2 . In contrast, the smaller more highly charged cations act as network modifiers and prefer the SiO_2 -poor melt which has a higher abundance of O^{2-} ions. In fact, there is an approximate correlation of $D^{\text{basic/silicic}}$ with Z/r (Watson, 1976) indicating that the metal-oxygen bond is stronger as Z/r increases.

There are two first order results arising from this experimental study.

- (a) As inferred from phenocryst/matrix studies (Figure 19), trace element partition coefficients are sensitive to melt composition; for example, in evaluating variations in trace element abundances in a sequence of lavas ranging from basalt to rhyolite in major element composition, it is evident that D values for a particular mineral will change as melt composition changes.
- (b) The abundance ratio K/P is likely to be a sensitive indicator of liquid immiscibility because in mafic mineral/melt partitioning the ratio K/P does not change significantly because both elements are highly incompatible. However, in a system with immiscible SiO_2 -rich and SiO_2 -poor melts, K is enriched in the former and P is enriched in the latter, thereby changing K/P by more than a factor of two.

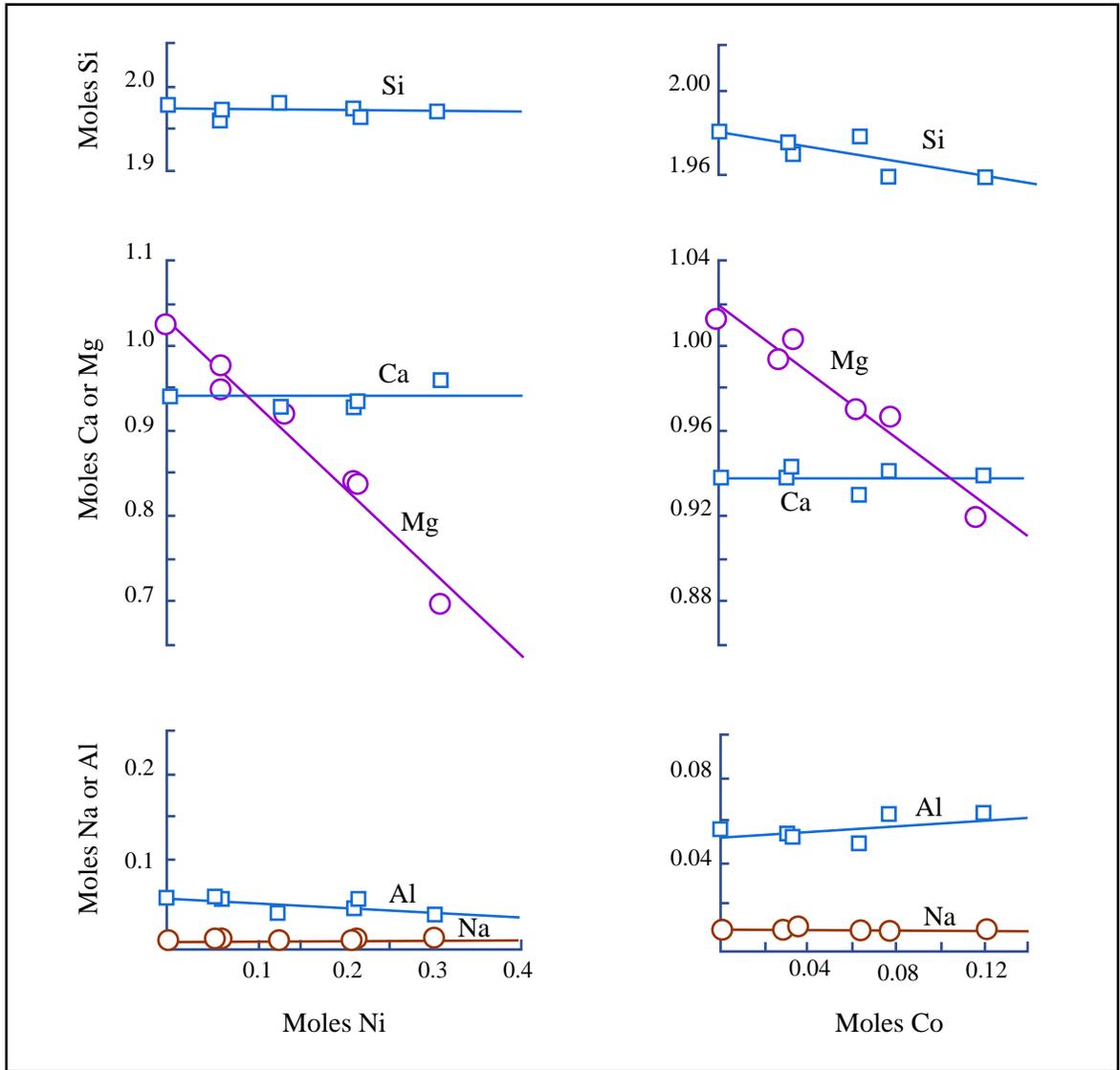
2) An experimental study of the first series transition elements, Ni, Co and Sc partitioning between diopside ($\text{CaMgSi}_2\text{O}_6$) and melt in the simple system Ab-An-Di at 1 atm and 1100 to 1360 C (Lindstrom and Weill, 1978). Figure 25 shows that $D_{\text{Ni}}^{\text{Di/melt}}$ and $D_{\text{Co}}^{\text{Di/melt}}$ are independent of Ni and Co contents even at concentration levels of 6 wt%; i.e. Henry's Law Behaviour is observed well beyond the natural abundance levels of these trace elements. Moreover, the compatibility of Ni and incompatibility of Co in diopside are consistent with clinopyroxene phenocryst/matrix estimates of these partition coefficients



7ci fhYgmicZ9'gYj JYfZ' =bWZ' \Htd. ##k k k "gVYbVWXJFYWVtca "'l gYX'k Jh' dYfa Jgg]cb"

Figure 25. Wt% NiO and CoO in diopside versus wt% NiO and CoO in coexisting melt. The linearity of the data suggest Henry's Law Behaviour is followed; the slopes of the line are the diopside/melt partition coefficients. Figure is from Lindstrom and Weill (1978).

Addition of a trace element in such high concentrations provides information about which element (really which structural site) is replaced by Ni or Co.

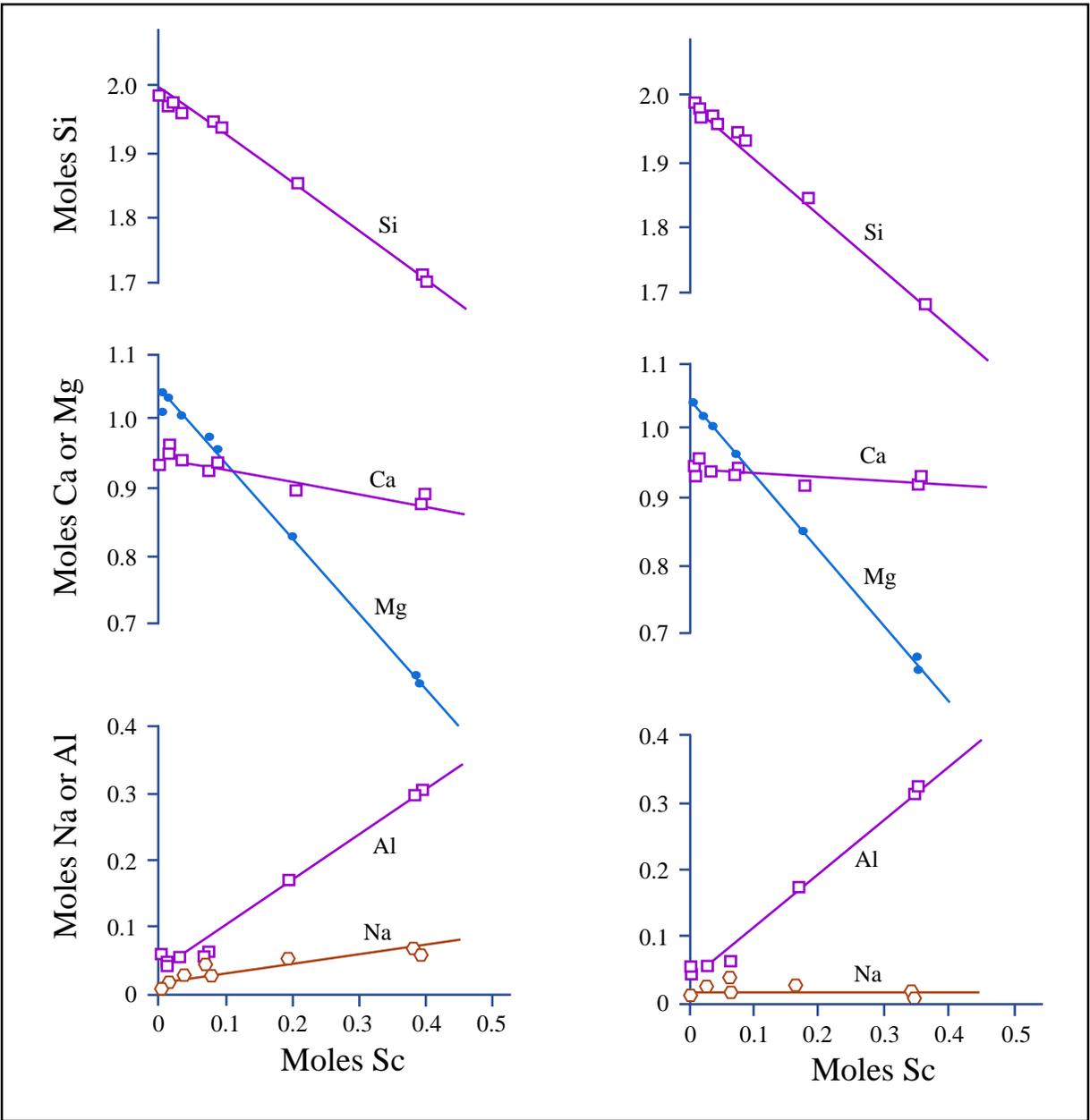


: [[i fY`VmA =H'CdYb7ci fgYK UFY"

Figure 26. Moles of Ni (left) and Co (right) in diopside versus moles of Si, Ca, Mg and Al and Na in diopside. The dominant trend is decreasing Mg content as Ni and Co content increases. Consequently Ni and Co are inferred to preferentially enter the M1 cation site in clinopyroxene. Figure is from Lindstrom and Weill (1978).

Figure 26 shows that as Ni and Co contents increase in diopside, the abundance of Mg decreases while Co content remains constant. Therefore, Ni and Co are substituting into the M1 site of clinopyroxene as predicted from crystal chemical considerations (see Figure 13A).

However the substitution for Sc^{+3} , which requires a charge balance mechanism is more complex because the decreasing Mg content with increasing Sc content is accompanied by increasing Na and Al and decreasing Si (Figure 27). These trends can be explained by Sc substituting into diopside as $\text{ScNaSi}_2\text{O}_6$ and ScCaAlSiO_6 .



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Figure 27. Moles of Sc in diopside versus moles of Si, Ca, Mg, Al and Na in diopside. The increase in Na content accompanying the Sc increase suggests that Sc^{+3} is charge balanced by Na^{+1} and formation of $\text{ScNaSi}_2\text{O}_6$ (left panel). The right panel shows the trends after subtraction of this $\text{ScNaSi}_2\text{O}_6$ component that charge balances 14.4% of the Sc. The decreasing Si and increasing Al can be explained if the remaining 85.6% of the Sc^{+3} is charge balanced by formation of a ScCaAlSiO_6 component. Figure is from Lindstrom (1976).

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