

Manning and Nickel (1969) studied the absorption spectrum of a natural titanite and concluded that the colour was due to a combination of Fe^{2+} , and Fe^{3+} and Ti^{3+} *d-d* electron transitions and the pleochroism due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ charge transfer. On the basis of the spectrum they conclude that Ti is more likely to be present as Ti^{3+} , not Ti^{4+} , in the titanite. However, the natural titanian aegirines are green to blue-green or more rarely rellow-green in colour. Thus the absence of a purplish colour to these aegirines indicates that a significant amount of Ti^{3+} is unlikely to be present.

The data on titanian aegirines presented by Scott (1976) can be accounted for by the neptunite end-component, thus explaining the observed Na excess over Fe^{3+} and the Ti^{4+} excess over Al. Additional discussions on the nature of Ti substitution in aegirines are presented elsewhere (Ferguson, 1977).

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Titanium in aegirines—a reply

FERGUSON (1977a) has suggested that the data of Scott (1976) for the observed enrichment of Ti in aegirines from Tenerife can be accounted for by the presence of the neptunite end-member ($\text{Na}_2\text{Fe}^{2+}\text{Ti}^{4+}\text{Si}_4\text{O}_{12}$) as discussed for other Ti-rich aegirines by Ferguson (1977b). Scott (1976) suggested that, for charge balance to be maintained in the Ti-rich aegirines, Ti^{3+} may be present. The alternative explanation of Ferguson (1977a) is acceptable, but the use of electrochemical data in support of the stability of $\text{Ti}^{4+} + \text{Fe}^{2+}$ in silicate melts requires some comment. Standard redox potentials, referring to a closed system, measured at 25 °C and with ions at unit activity in water, may not be appropriate for silicate melts. The system is no longer simple and closed. The position of equilibrium in $\text{Ti}^{4+} + \text{Fe}^{2+} \rightleftharpoons \text{Ti}^{3+} + \text{Fe}^{3+}$ will be altered not only by deviations from the standard conditions (effects of change of temperature alone, however, are small), but also by the activity of other ionic species and the fugacity of gas phases.

Support for the presence of Ti^{3+} in pyroxenes is given by Strens (1967) and Manning and Nickel (1969), who report octahedrally co-ordinated Fe^{2+} , Fe^{3+} , and Ti^{3+} coexisting in titanite. Strens (1967), on a consideration of ΔG for crystal/liquid equilibria, also suggests that incorporation of Ti^{3+} in minerals does not necessarily depend on Ti^{3+} being available in

large amounts in the liquid. The availability of ions with a correct size is also important and, in this respect, Ti^{4+} and Ti^{3+} are almost equally suitable.

The data of Ferguson (1977a) support the conclusion of Scott (1976) that end-components of the type $NaTi(AlSi)O_6$ and $NaTi(Fe^{3+}Si)O_6$, shown experimentally to substitute in aegirines at high fugacities (Flower, 1974), cannot account for the high Ti content in some natural aegirines.

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Some disadvantages of $Pt_{95}Au_5$ as a container for molten silicates

OVER the last two years an alloy $Pt_{95}Au_5$ has become a fashionable container material for experimental melting studies of iron-bearing silicates without, apparently, quantitative data on iron losses to the alloy. In several literature citations the authors state, or imply, that the alloy was used (in preference to pure Pt) in order to reduce the extent of iron (and sometimes nickel) losses. From only one publication is it possible to estimate the extent of iron losses.

Duke (1976) loaded a starting material with 6.6 wt % FeO into $Pt_{95}Au_5$ capsules (1250 °C, $\log f_{O_2} = -9.7$, 30 hr) and recovered a liquid with 2.4 wt % FeO, olivine with 3.9 wt % FeO, and augite. At best, if his product had been all olivine his recovery of FeO would be 58 % but assuming realistically an equal mixture of crystals and liquid then the iron recovery was about 45 %. His other experiments at lower temperatures appear to be less iron-depleted but in one experiment at 1150 °C the recovery of NiO was at best 68 % and realistically probably 34 %; some cobalt may also have been lost. Mysen and Kushiro (1976) mention 20 % iron loss and Irvine and Kushiro (1976) report some loss of Ni.

The performance of $Pt_{95}Au_5$ alloy capsules was investigated. In each experiment four capsules were used side by side, one of $Pt_{95}Au_5$, one of pure Pt, one of $Ag_{40}Pd_{60}$ and one of $Pt_{90}Fe_{10}$ and the chosen conditions (1250 °C or 1200 °C, $\log f_{O_2} = -9$, 20 hr) are such that both Pt and AgPd alloys were known to be beyond their useful range and known to give recoveries of less than 60 % (Biggar, 1970, fig. 1).