

*Acknowledgements.* The authors wish to thank Mr. A. G. Cross for drawing the diagrams. This work was undertaken as part of the N.E.R.C. project 'The role of volatiles in alkaline magmatism' (GR/3/1982).

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## REFERENCES

- Chamberlin (R. T.), 1908. *Publs. Carnegie Instn.* 106.  
Cornu (A.) and Massot (R.), 1966. *Compilations of mass spectral data.* London (Heyden and Son).  
Harmand (C.) and Zimmermann (J.-L.), 1976. *C.R. Acad. Sci. Paris*, **282**, 1391-4.  
Huntingdon (A. T.), 1973. *Phil. Trans. R. Soc.* **A274**, 119-28.  
Jaggar (T. A.), 1940. *Am. J. Sci.* **238**, 313-53.  
Killingley (J. S.) and Muenow (D. W.), 1975. *Geochim. Cosmochim. Acta*, **39**, 1467-73.  
Muenow (D. W.), 1973. *Ibid.* **37**, 1551-61.  
Noble (D. C.), Smith (V. C.), and Peck (L. C.), 1967. *Ibid.* **31**, 215-23.  
Shepherd (E. S.), 1925. *J. Geol.* **33**, 289-370.  
— 1938. *Am. J. Sci.* **35A**, 311-52.

[Manuscript received 1 November 1976]

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MINERALOGICAL MAGAZINE, DECEMBER 1977, VOL. 41, PP. 553-4

## Titanium in aegirines—a comment on: Crystallization trends of pyroxenes from the alkaline volcanic rocks of Tenerife, Canary Islands, by P. W. Scott

IN a study of the clinopyroxenes from the volcanic rocks of Tenerife, Scott (1976) describes the occurrence of aegirine in the groundmass of phonolites and nepheline-syenite inclusions. Scott (1976) has commented on the following five points:

Many aegirines show enrichment of Ti as Na increases; Na often exceeds  $\text{Fe}^{3+}$  (total) in the structural formula; Al is insufficient to account for all Ti as  $\text{CaTiAl}_2\text{O}_6$  (Kushiro, 1962); many of the aegirines can be accounted for by the substitutions of the type:  $\text{Ti}_y^{4+} + \text{Fe}_z^{3+} \rightleftharpoons \text{Fe}_y^{3+} + \text{Si}_z$  and  $\text{Ti}_y^{4+} + \text{Al}_z^{3+} \rightleftharpoons \text{Fe}_y^{3+} + \text{Si}_z$  as proposed by Flower (1974) (however, the most Ti-rich aegirines still contain an excess of Ti); and substitution of Ti as  $\text{Ti}^{3+}$  can account for the excess Ti while maintaining charge balance.

Data collected by the author on titanian aegirines from a variety of alkaline rocks has been interpreted differently (Ferguson, 1977). The proposed neptunite end-component (Ferguson, 1977) also accounts for some unusual titanian sahlites in which  $\text{Al} < 2\text{Ti}$  (Cundari, 1973). However, the occurrence of  $\text{Ti}^{3+}$  in the titanian aegirines, as proposed by Scott (1976), was not discussed and thus requires comment.

$\text{Ti}^{3+}$  and  $\text{Fe}^{3+}$  are well known to be unstable together in aqueous solution,  $\text{Ti}^{3+}$  reducing the  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (see Helsop and Robinson, 1967). Consideration of the redox cell  $\text{Ti}^{3+} + \text{Fe}^{3+} \rightleftharpoons \text{Ti}^{4+} + \text{Fe}^{2+}$  with an E.M.F. of about 0.72 volt also indicates that the  $\text{Ti}^{4+} + \text{Fe}^{2+}$  pair is strongly favoured. There is no evidence to suggest that this should not apply also to silicate melts.

Manning and Nickel (1969) studied the absorption spectrum of a natural titanaugite and concluded that the colour was due to a combination of  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  and  $\text{Ti}^{3+}$  *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  $\text{Ti}^{3+}$ , not  $\text{Ti}^{4+}$ , in the titanaugite. 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  $\text{Ti}^{3+}$  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  $\text{Fe}^{3+}$  and the  $\text{Ti}^{4+}$  excess over Al. Additional discussions on the nature of Ti substitution in aegirines are presented elsewhere (Ferguson, 1977).

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#### REFERENCES

- Cundari (A.), 1973. *J. Geol. Soc. Australia*, **20**, 465-92.  
 Ferguson (A. K.), 1977. *Contrib. Mineral. Petrol.* **60**, 247-53.  
 Flower (M. F. J.), 1974. *Amer. Mineral.* **59**, 536-48.  
 Helsop (R. B.) and Robinson (P. L.), 1967. *Inorganic Chemistry*. Elsevier, Amsterdam.  
 Kushiro (I.), 1962. *Japan. Geol. Geography*, **33**, 213-20.  
 Manning (P. G.) and Nickel (E. H.), 1969. *Canad. Min.* **10**, 71-83.  
 Scott (P. W.), 1976. *Mineral. Mag.* **40**, 805-16.

[*Manuscript received 8 February 1977, revised 1 April 1977*]

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MINERALOGICAL MAGAZINE, DECEMBER 1977, VOL. 41, PP. 554-5

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