

## Can $\text{Ti}^{4+}$ replace $\text{Si}^{4+}$ in silicates?

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**SUMMARY.** It is argued on crystal-chemical grounds that Si deficiency is compensated by the entering of Al,  $\text{Fe}^{3+}$ , or  $\text{Ti}^{4+}$ , in this order of preference, into tetrahedral sites. It is pointed out that  $\text{Ti}^{4+}$  occurs in tetrahedral coordination in exceptional circumstances only, while  $\text{Fe}^{3+}$  relatively easily takes a tetrahedral coordination.

SEVERAL silicates, notably garnets, pyroxenes, amphiboles, and micas, contain small, and sometimes substantial amounts of titanium. Usually the Ti is assumed to be in octahedral coordination. Deficiency of silicon in tetrahedral coordination is in most cases compensated by putting Al in its place. However, in several cases the amount of Al present is insufficient to compensate completely the Si deficiency. Other ions to fill up the tetrahedral voids are  $\text{Ti}^{4+}$  and  $\text{Fe}^{3+}$ . When it comes to decide which of the two is most likely to replace Si, the various authors do not show agreement. Thus, for example, Deer, Howie, and Zussman (1962, 1963) prefer Ti rather than  $\text{Fe}^{3+}$  in tetrahedral coordination. In 63 cases of garnets, pyroxenes, amphiboles, and micas sufficient  $\text{Fe}^{3+}$  is present to compensate the tetrahedral deficiency. In eleven cases even the amount of  $\text{Fe}^{3+}$  is not enough and so  $\text{Ti}^{4+}$  has to be placed in the tetrahedral voids in order to leave no vacancies.

Recently, however, Howie and Woolley (1968) even preferred Ti instead of Al in tetrahedral coordination in titanium garnets. This led the present author to the following review of crystal-chemical arguments.

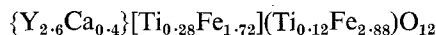
Arguments in favour of  $\text{Ti}^{4+}$  in tetrahedral coordination:  $\text{Ti}^{4+}$  has the smaller Goldschmidt radius ( $\text{Ti}^{4+}$ : 0.64 Å and  $\text{Fe}^{3+}$ : 0.67 Å); it must be remarked here that the inverse is true for the Ahrens radii. And  $\text{Ti}^{4+}$  has the same charge as  $\text{Si}^{4+}$ , so no problems of charge balance arise when Ti substitutes directly for Si.

In favour of  $\text{Fe}^{3+}$  in tetrahedral coordination: No titanium minerals are known with tetrahedral Ti; it is true that compounds in which the coordination of Ti is less than six are known—5-coordinated Ti is found in the mineral fresnoite  $\text{Ba}_2\text{TiO}[\text{Si}_2\text{O}_7]$  (Moore and Louisnathan, 1967), and in the compounds  $\text{K}_2\text{Ti}_2\text{O}_5$  (Andersson and Wadsley, 1961) and  $\text{Y}_2\text{TiO}_5$  (Mumme and Wadsley, 1968); 4-coordinated Ti has so far been found in one compound only, namely  $\text{Ba}_2\text{TiO}_4$  (Tarte, 1961; Bland, 1961), which has a  $\beta$ - $\text{K}_2\text{SO}_4$  structure and is related to  $\beta$ - $\text{Ca}_2\text{SiO}_4$  (the structure is a rather loose packing of Ba and O with Ti in distorted tetrahedral interstices; Ti–O distances are 1.63, 1.64, 1.75, and 1.82 Å. The compound  $\text{Sr}_2\text{TiO}_4$  has a  $\text{K}_2\text{NiF}_4$  structure (Ruddlesden and Popper, 1957), where Ti is octahedrally coordinated).

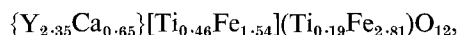
Tetrahedral  $\text{Fe}^{3+}$ , on the other hand, is known to occur in a number of compounds:

in the mineral cronstedtite  $\text{Fe}_4^{2+}\text{Fe}_2^{3+}(\text{Si}_2\text{Fe}_2^{3+})\text{O}_{10}(\text{OH})_8$  (Steadman and Nuttall, 1963); in synthetic iron biotite  $\text{K}_2\text{Fe}_6^{2+}(\text{Si}_6\text{Fe}_2^{3+})\text{O}_{20}(\text{OH})_4$  (Wones, 1958; Donnay *et al.*, 1964); in synthetic iron feldspar  $\text{KFe}^{3+}\text{Si}_3\text{O}_8$  (Faust, 1936; Wones and Appleman, 1961); and in synthetic rare earth garnets as  $\text{Y}_3\text{Fe}_5^{3+}\text{O}_{12}$  (Structure Reports **21** (1964)).

In synthetic garnets  $\text{Ti}^{4+}$  prefers octahedral sites, but also enters tetrahedral sites (cf. Geller, 1967); especially interesting are garnets with  $\text{Fe}^{3+}$ . Espinosa (1964) synthesized  $(\text{Y}_{3-x}\text{Ca}_x)\text{Ti}_x(\text{Fe}_{5-x})\text{O}_{12}$  and  $(\text{Y}_{3-x}\text{Ca}_x)\text{Ti}_x\text{Ga}_{5-x}\text{O}_{12}$ ; according to magnetic measurements (Geller *et al.*, 1965) for  $x = 0.40$  and  $0.65$  about 30 % of the Ti is in tetrahedral coordination leading to the formulae



and



where the atoms in square brackets have octahedral coordination.

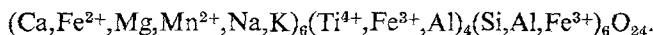
In synthetic spinels also  $\text{Ti}^{4+}$  prefers octahedral sites. This was shown to be the case for a number of spinels  $\text{Me}_2^{2+}\text{TiO}_4$  with  $\text{Me}^{2+} = \text{Mg, Mn, Fe, Co, and Zn}$  (see the review by Blasse, 1964*b*, p. 20, and Hardy *et al.*, 1964). For ulvöspinel,  $\text{Fe}_2^{2+}\text{TiO}_4$  Forster and Hall (1965) found that the ordering is incomplete, the degree of inversion being 0.92. Various substitutions of Ti in spinel have been studied. In the system  $\text{Mg}_2\text{TiO}_4\text{--MgFe}_2^{3+}\text{O}_4$  (Blasse, 1964*b*, Agranovskaya and Saksonov, 1966) Ti occupies octahedral sites. The same is true for the systems  $\text{Co}_2\text{TiO}_4\text{--CoFe}_2^{3+}\text{O}_4$  (Blasse, 1964*b*) and  $\text{Mg}_2\text{TiO}_4\text{--MgCr}_2\text{O}_4$  (Agranovskaya and Saksonov, 1966), whereas in  $\text{Ni}_2\text{TiO}_4\text{--NiFe}_2^{3+}\text{O}_4$  the Ti is divided between tetrahedral and octahedral sites and Ni occupies octahedral sites so that the tetrahedral sites are occupied mostly by  $\text{Fe}^{3+}$  (Gorter, 1954). Blasse studied several spinels containing Li. In spinels  $\text{LiMe}^{3+}\text{TiO}_4$  (Blasse, 1963*a*) the lithium atoms enter into the tetrahedral sites when  $\text{Me}^{3+} = \text{Al, V, Cr, Rh}$ ; with  $\text{Fe}^{3+}$ , however, the site occupancy becomes  $\text{Li}_{0.5}\text{Fe}_{0.5}[\text{Li}_{0.5}\text{Fe}_{0.5}\text{Ti}]\text{O}_4$  where the bracketed atoms are in octahedral coordination. In compounds  $\text{LiMe}_2^{2+}\text{Ti}_{1.5}\text{O}_4$  the titanium always occupies octahedral sites ( $\text{Me}^{2+} = \text{Mg, Co, Cu, Zn}$ ) (Blasse, 1964*b*). The same holds for the spinels  $\text{Li}_{1.25}\text{Me}_{0.25}^{3+}\text{Ti}_{1.50}\text{O}_4$  where  $\text{Me}^{3+} = \text{Al, Cr, Fe, Ga}$  (Blasse, 1964*a*), but Fe and Ga also enter the tetrahedral sites leading to the formulae  $\text{Li}_{0.75}\text{Fe}_{0.25}[\text{Li}_{0.50}\text{Ti}_{1.50}]\text{O}_4$  and  $\text{Li}_{0.75}\text{Ga}_{0.25}[\text{Li}_{0.50}\text{Ti}_{1.50}]\text{O}_4$ .

*Conclusions.* The following conclusions seem to be valid:  $\text{Ti}^{4+}$  takes on preferentially octahedral coordination; in a compound it takes tetrahedral coordination only when it is forced to do so by the presence of a large cation (Ba), otherwise it may obtain a 5-coordination in the presence of smaller ions (K, Y).  $\text{Fe}^{3+}$  easily takes on tetrahedral coordination when no Al is present. If there is competition between  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  the titanium prefers octahedral coordination as is evident from the structures of synthetic spinels and garnets.

In their paper on titanium garnets Howie and Woolley (1968) distribute the ions among the structural positions in such a way that their analyses can be written in the idealized form  $(\text{Ca, Fe}^{2+}, \text{Mg, Mn}^{2+}, \text{Na, K})_6(\text{Fe}^{3+}, \text{Al, Ti}^{4+})_4(\text{Si, Ti}^{4+}, \text{Al})_6\text{O}_{24}$ . Their preference for Ti in tetrahedral sites is based on two grounds: First, the infra-red spectra show a band at  $650\text{ cm}^{-1}$ , which might be ascribed to  $(\text{TiO}_4)$  tetrahedra, although the authors themselves express some doubt on this, as the absorption spectrum of sphene

shows similar features. Second, an electron microprobe traverse across a zoned garnet indicates that the amount of Fe remains fairly constant, while Si and Ti are strongly correlated in the negative sense, as is also evident from total chemical analyses. The reasoning is that while Ti increases as Si decreases, Ti should replace Si in its structural position. This, however, is not necessarily so. Two substitutions should be considered: (A)  $\text{Si}^{\text{iv}} \rightarrow \text{Ti}^{\text{iv}}$  and (B)  $\text{Si}^{\text{iv}} + \text{Fe}^{\text{vi}} \rightarrow \text{Fe}^{\text{iv}} + \text{Ti}^{\text{vi}}$  or  $\text{Si}^{\text{iv}} + \text{Al}^{\text{vi}} \rightarrow \text{Al}^{\text{iv}} + \text{Ti}^{\text{vi}}$ . In both cases the amount of Fe and Al is not changed. Considering the arguments given above that  $\text{Fe}^{3+}$  enters a tetrahedral void more easily than  $\text{Ti}^{4+}$  the substitution (B) is to be preferred. During the process of crystal growth an increase of  $\text{Ti}^{4+}$  in the fluid phase leads to more  $\text{Ti}^{4+}$  in octahedral coordination at the expense of  $\text{Al}^{\text{vi}}$  and  $\text{Fe}^{3+}$ . In order to keep the electrostatic balance an amount of Si, equal to the increase of Ti, does not enter the crystal, but is replaced by the Al or  $\text{Fe}^{3+}$  that could not fit into the octahedral sites.

In view of the conclusions reached earlier in this note, the author believes that it can be maintained that substitution of Si occurs in decreasing preference by Al,  $\text{Fe}^{3+}$ , and  $\text{Ti}^{4+}$ . The idealized formula of the titanium garnets is therefore:



In fact half of the garnets considered by Howie and Woolley can be described by Al substitution for Si only. The fact that in Y-Fe and in Y-Ga garnets Ti is also found in tetrahedral coordination does not imply that substitution in natural garnets goes as easily since the tetrahedral radii of  $\text{Fe}^{3+}$  and Ga are much larger than the radius of Si.

In the opinion of the author the answer to the question in title should be: sometimes, but not usually.

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