

# Vitusite—an apatite derivative structure

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## Abstract

The uncommon sodium rare-earth phosphate mineral vitusite-(Ce) ( $\text{Na}_3\text{RE}(\text{PO}_4)_2$ ) can be considered as the extreme product of sodium and rare-earth substitution in the apatite structure. Lesser amounts of substitution provide sodium and rare-earth-bearing apatites up to about 80 mol.% exchange; beyond this point vitusite is the stable phase. The structure of vitusite, determined previously from a synthetic analogue, can also be considered as a derivative from apatite, but with cations exchanged on sites normally occupied by anions. Vitusite can therefore be considered as a sodium- and rare-earth-rich apatite end-member, with a distinct, but apatite-derived, structure, formed in highly perisodic and high rare-earth environments. From an examination of the literature on diffusion in apatite, vitusite in principle could be formed from apatite *sensu stricto* by subsolidus diffusion in response to late-stage Na- and RE-rich hydrothermal fluids.

KEYWORDS: vitusite, apatite, Ilímaussaq, Gardar, South Greenland.

## Introduction

THE understanding of the petrogenesis of peralkaline rocks is severely hampered by the plethora of unusual minerals, often unique to one locality, found in them. It has been suggested by Moore (1983) that some of these unusual minerals could be considered on the basis of their structures as rare element enriched analogues of more common minerals, thus providing a basis for analogy between extreme rocks and their more common counterparts.

This study considers the chemistry of apatite and apatite-derived minerals from alkaline and peralkaline rocks of the Gardar province, south Greenland (see Emelius and Upton, 1976, and Upton and Emelius, 1987, for a review). The Gardar apatites are unusual in that percentage-level substitution of silicon, rare-earths and sodium is known to occur, and other unusual phosphate minerals are also present. In the present short paper, the relationship between the chemistry and crystal structures of apatite and the mineral vitusite-(Ce) is discussed, and it will be demonstrated that vitusite can be considered as a missing end-member of sodium and rare-earth exchange in apatites.

## Previous work

Various phosphate minerals with alkaline earth, sodium and/or rare earth cations are known to occur in alkaline rocks. The most common of these is apatite, but in the perisodic and incompatible element enriched environments of alkaline rocks, apatites with significant substitutions of e.g. RE, Sr, Na, Si occur. In the past, a variety of phosphate minerals has been described, which, in addition to repeated renaming of the same mineral, has led to a confusing nomenclature. The conventions regarding these minerals have been reviewed by Nriagu (1984) who discredited several names which still appear in the literature.

In a recent communication, Kalsbeek *et al.* (1990) showed that britholite and lessingite possessed a derivative of the apatite crystal structure, related to apatite *sensu stricto* by the coupled exchange:



In addition to this exchange mechanism, Rønso (1989) demonstrated that natural apatites from the Ilímaussaq intrusion, south Greenland (see Larsen and Sørensen, 1987, for a review)

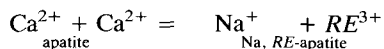
**Table 1:** Comparison of cell data between natural vitusite and synthetic

Na <sub>3</sub> Nd(PO <sub>4</sub> ) <sub>2</sub>			
	1	2	3
α	5.36	5.342	5.291 <sup>a</sup>
β	18.68	18.680	18.470 <sup>b</sup>
γ	13.96	14.062	13.952 <sup>b</sup>
SG	Pcmb or Pc2 <sub>1</sub> b		Pc2 <sub>1</sub> b <sup>b</sup>

1. Vitusite from the Lovozero alkaline Massif, Kola peninsula, USSR (Rønso et al., 1979).  
 2. Vitusite from the Ilímausaq complex, south Greenland (Rønso et al., 1979).  
 3. Synthetic Na<sub>3</sub>Nd(PO<sub>4</sub>)<sub>2</sub> (Salmon et al., 1978).

- a. α-dimension divided by 3 to allow direct comparison.  
 b. β and γ values interchanged to allow direct comparison between values. Published account describes the space group as Pbc2<sub>1</sub>.

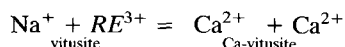
contained sodium, incorporated with rare earths by a second mechanism



to provide a hypothetical end-member Na<sub>5</sub>RE<sub>5</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>. This end-member composition has not been reported in the literature and was believed by Rønso (1989) not to exist naturally.

### Vitusite-(Ce)

Vitusite-(Ce) is a sodium, rare-earth phosphate, first described by Rønso *et al.* (1979) from alkaline rocks of the Ilímausaq intrusion, south Greenland, and of the Lovozero alkaline massif, Kola peninsula, U.S.S.R. Vitusite-(Ce) in thin section is a green mineral which commonly shows pseudo-hexagonal twinning (Rønso *et al.*, 1979). The formula proposed was Na<sub>3</sub>RE(PO<sub>4</sub>)<sub>2</sub>. The exact crystal structure of the new mineral was not determined, but Rønso *et al.* suggested that it was glaserite-derived and determined cell dimensions (Table 1). A hexagonal polymorph was observed at high temperatures, with the transformation occurring at 1083 °C. Rønso *et al.* (1979) also noted that some Ca was present in vitusite-(Ce) analyses, incorporated by the mechanism:



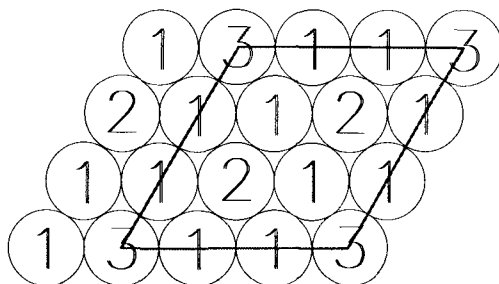
Very little information exists concerning vitusite-(Ce) in the geological literature, but a search of the solid-state chemistry literature has shown that a synthetic analogue of natural vitusite-(Nd) (Na<sub>3</sub>Nd(PO<sub>4</sub>)<sub>2</sub>) has been produced by materials scientists (Salmon *et al.*, 1978), and the crystal structure of this material was determined. A comparison of the X-ray diffraction data (JCPDS cards 33-1232 and 29-1250) and cell dimensions between vitusite-(Ce) and the synthetic analogue

shows close approximation (Table 1). In a subsequent, more detailed study, Chao *et al.* (1989) considered the structures of Na<sub>3</sub>RE(PO<sub>4</sub>)<sub>2</sub> phases as a function of the RE present and showed that the structure of Na<sub>3</sub>Nd(PO<sub>4</sub>)<sub>2</sub> is common to all the light RE isomorphs (RE = La–Sm). For the purposes of this discussion, we therefore draw on the description of the synthetic Na<sub>3</sub>Nd(PO<sub>4</sub>)<sub>2</sub> crystal structure (Salmon *et al.*, 1978) when considering the natural mineral.

### The crystal structures of apatite and vitusite

**Apatite.** The crystal structure of apatite has been well characterised in the literature following the studies of Náray-Szabó (1930) and Bragg (1937). Greater refinement of atomic positions is given by Sudarsanan and Young (1969). The structure of apatite can be considered in terms of the hexagonal close-packing of cylinders ('rods') (O'Keeffe and Andersson, 1977), with three different types of rod present (Moore, 1981). Rod 1 comprises alternate Ca atoms and PO<sub>4</sub> tetrahedra, Rod 2 consists of a chain of Ca atoms alone and Rod 3 comprises a chain of F atoms (Fig. 1).

**Vitusite.** The crystal structure of vitusite is orthorhombic, but it is glaserite-derived (Moore, 1981), and can also be approximated to a hexagonal structure and considered in the same manner as described above for apatite in terms of hexagonally-packed rods. In this case, there are two types of rods; Rod 1 comprises alternate Na atoms and PO<sub>4</sub> tetrahedra and Rod 2 comprises alternate Na and RE atoms, and the structure can be considered as comprising glaserite-type hexagonal pseudocells (Fig. 2). If the structures of vitusite and apatite are compared using the rod model (Fig. 3), it is observed that the Rod 1 in vitusite and Rod 1 in apatite are equivalent, with Na in vitusite taking the place of Ca in apatite. The structures differ in that Rod 2 in vitusite (Na, RE) is equivalent to both Rod 2 (Ca, Ca) and



**Fig. 1.** The structure of apatite using the rod notation. The apatite unit cell is outlined.

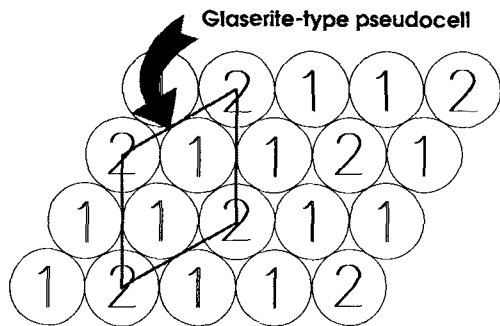


FIG. 2. The vitusite structure described using the rod notation. The glaserite pseudocell is outlined; the true unit cell for vitusite is orthorhombic.

Rod 3 (F,F) in apatite, the latter of which is the site of anions in the structure. Na and RE exchange for Ca has been observed in apatites from Ilímausaq (Rønsbo, 1989). The unusual difference between apatite and vitusite is that Na and RE cations occupy the anion sites of the apatite structure. Vitusite can therefore be considered as an apatite-derived structure of the type  $(Na_8RE_2)(PO_4)_6(NaRE)$ , cf.  $Ca_{10}(PO_4)_6F_2$ . Apatite-related structures with cations in sites previously thought only to have been occupied by anions have been reported in synthetic systems (e.g. Pliego-Cuervo and Glasser, 1978).

### Discussion

Having considered the stoichiometry of vitusite, Na, RE exchange in apatites, the description of the mineral vitusite and the synthetic studies of  $Na_3Nd(PO_4)_2$ , we suggest that vitusite represents the extreme product of Na, RE exchange for Ca in apatites. Rønsbo *et al.* (1979) suggested that the substitution of Ca for Na and RE in vitusite, directly analogous to the mechanism observed in apatites (see above), represents solid-solution

with the mineral buchwaldite ( $NaCaPO_4$ ). We suggest rather that this substitution mechanism represents solid-solution towards apatite *sensu stricto*. The positioning of phosphate tetrahedra in both structures is essentially the same; differences lie in the nature of cations in the 4f and 6h sites and the occupancy of Rod 3. A study of synthetic apatites along the  $Ca_{10-2x}Na_xRE_x(PO_4)_6F_2$  solid-solution by Mayer *et al.* (1973) showed that significant exchange of Na and RE up to  $Ca_2Na_4RE_4(PO_4)_6F_2$  could take place without loss of the apatite-type structure. The crystal structure of  $Ca_6Na_2Eu_2(PO_4)_6F_2$  (Mayer and Cohen, 1983) showed that sodium exchange for calcium in apatite positioned sodium exclusively on Rod 2. Without forcing Na to exchange for Ca on the Rod 1 sites, and given that there are only four cation sites per unit cell in Rod 2, this suggests that the maximum sodium, rare-earth exchange possible in apatite is 80 mol.%, i.e. a composition of formula  $Ca_2Na_4RE_4(PO_4)_6F_2$ . This is consistent with experimental observations (Mayer *et al.*, 1973). The ordering of Na to Rod 1 may be a result of unfavourable coordination polyhedra in the Rod 2 cation sites.

The structure of  $Ca_6Na_2RE_2(PO_4)_6F_2$  apatite and vitusite, however, differ from each other in one important respect. The exchange of Na for Ca on Rod 1 in apatite is in contrast to the position of sodium in vitusite, where Na is present on Rod 2 as well. We suggest that placing Na on the unfavourable Rod 2 cation sites during continued exchange in apatite brings about a transformation of the structure from apatite to vitusite. This transformation would involve the diffusion of some Na from Rod 1 to Rod 2, and the replacement of the F in Rod 3 by Na and RE. We suggest that such a transformation serves to stabilise the structure since all the cation sites in the structure become more closely equivalent.

### Interconversion of apatite and vitusite in the subsolidus

There is an increasing amount of petrological (e.g. using CL) and experimental evidence to suggest that subsolidus exchange of elements in the apatite structure occurs. Cathodoluminescence studies of Gardar apatites (Finch, 1990) have shown that subsolidus diffusion of Na, RE and Si into apatites does occur. Diffusion of elements (O, Sr) into apatite in the subsolidus has been confirmed by Farver and Gilletti (1989) in experimental charges at 650°C. Exchange of elements in the apatite Rod 3 sites in the subsolidus is also implied by the work of Tacker and Stormer (1989) and by the everyday use of

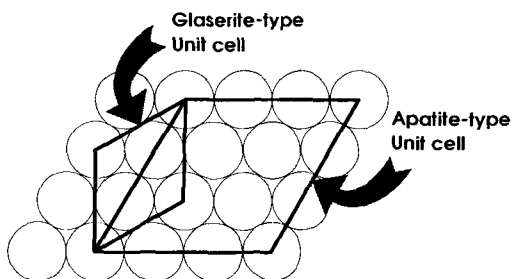


FIG. 3. Comparison of glaserite and apatite-type unit cells according to the rod model.

fluoride toothpaste! It is clear therefore sodium and rare-earth-rich late-stage fluids in contact with apatites can bring about exchange of Ca in apatite for Na and RE in the fluid. We propose that exchange of Na and RE for Ca in apatites continues after the 80 mol.% exchange limit (after which apatite structures become untenable) giving rise to vitusite *topotactically* according to the transformation mechanism described above. Such a topotactic transformation between structures of these types has been described during the oxidation of  $\text{Eu}_2\text{SiO}_4$  by Felsche and Kaldis (1972). Furthermore, cyclic twinning in glaserite-type structures has in the past without exception been attributed to transformation from a fully hexagonal polymorph (Fletcher, 1991) and we know of no case of cyclic growth twinning in this structure type. Hence the observation of pseudo-hexagonal twinning in vitusite-(Ce) suggests that the mineral once exhibited full hexagonal symmetry. Indeed a hexagonal polymorph of vitusite-(Ce) at high temperatures was demonstrated using a natural vitusite-(Ce) by Rønsbo *et al.* (1979) and in the synthetic analogues by Chao *et al.* (1989). However, the transformation temperatures observed by these authors were around 1050°C, in excess of the maximum liquidus temperatures of apatitic melt (950°C, Larsen and Sørensen, 1987). The observation of pseudo-hexagonal (cyclic) twinning in vitusite-(Ce) implies a precursor with a hexagonal structure. A hexagonal vitusite-(Ce) polymorph cannot be considered as a candidate for this precursor since its stability regime is above the maximum liquidus temperature of apatitic melt; therefore another hexagonal precursor must be considered. This strongly supports the view that the orthorhombic vitusite structure may be present as a result of topotactic transformation of the apatite structure during late-stage hydrothermal activity.

### Conclusions

Vitusite-(Ce) can be considered as an extreme product of Na and RE exchange in apatites. The structure of vitusite can also be considered as an apatite-derived structure, with *cation exchange for fluorine*. In this manner, petrological and chemical similarities between apatite and vitusite are reflected in the crystal structure.

Vitusite can in principle be formed from apatite *sensu stricto* by diffusion of Na and RE for Ca and F, accompanied by a transformation at approaching 80 mol.% substitution. Pseudo-hexagonal twinning observed in vitusite-(Ce) by Rønsbo *et al.* (1979) may provide evidence for such a process.

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