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Oxidation state of iron in neptunite from Mössbauer spectroscopy.

By G. Michael Bancroft, *University Chemical Laboratories, University of Cambridge, England,* Roger G. Burns,* *Department of Mineralogy and Petrology, University of Cambridge, England* and A. G. Maddock, *University Chemical Laboratories, University of Cambridge, England.*

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The Mössbauer spectrum of neptunite has been recorded at room temperature. This spectrum indicates that at least 95 % of the iron is present as high spin Fe^{2+}, and that titanium is present as Ti^{IV}

The rare mineral neptunite,

$$LiNa_2K(Fe,Mn,Mg)_2Ti_2O_2(Si_8O_{22}),$$

is found associated with alkaline subsilicic rocks (Heinrich & Quon, 1963). It occurs as an alteration product of narsarsukite (Flink, 1901), sphene (Nockolds, 1950) and eudialyte (Bondam & Sörensen, 1959), and Stewart (1959) suggested that neptunite forms under conditions of lower oxygen partial pressure. Recently, the crystal structure of neptunite was described by Borisov, Klevtsova, Bakakin & Belov (1965) and Cannillo, Mazzi & Rossi (1966). Borisov *et al.* used a manganiferous neptunite from the Kola peninsula, whereas a ferriferous neptunite from San Benito County, California, was employed by Cannillo *et al.* The neptunite structure consists of pyroxene chains linked together into a three-dimensional network of SiO_4 tetrahedra. Both Ti and (Fe,Mn) occur in octahedral coordination, and chains of linked octahedra, sharing edges, form bands within the silicate framework. In their respective structures, Borisov *et al.* (1965) and Cannillo *et al.* (1966) imply that Ti and (Fe,Mn) occur in distinct octahedra with Ti in the octahedron with the smaller average metal–oxygen distance. However, Borisov *et al.* (1965) note that, because of the small difference between the Ti and (Fe,Mn) octahedra and the unusual pleochroism, it is possible that neptunite contains Ti^{3+} and (Fe^{3+},Mn^{3+}) ions of comparable radii. Chemical analyses of neptunite (Flink, 1895; Sjöström, 1895; Bradley, 1909; Louderback, 1910; Fersman, 1926; Bussen, Denisov, Kravchenko-Berezhnoi & Uspenskaya, 1965; Cannillo *et al.*, 1966) are invariably expressed as weight percentages of TiO_2, FeO and MnO. This is because it is impossible to analyse by wet chemical techniques titanium(III) coexisting with iron(III), although there may be indications of the existence of Ti^{3+} ions in a structure. Thus, analyses of titan-augites (Deer, Howie & Zussman, 1963) quote iron as ($FeO+Fe_2O_3$) and titanium as TiO_2, even though the violet colour and absorption spectra (Chesnokov, 1959; Burns, unpublished work) show that Ti^{3+} ions are present. It is possible to identify the oxidation state of iron in neptunite directly, and titanium indirectly, by Mössbauer spectroscopy, which provides a rapid method for characterizing iron in minerals (Bancroft & Burns, 1966).

The Mössbauer instrumentation (Bancroft, Maddock & Ward, 1966) and technique for silicate minerals (Bancroft, Burns & Maddock, 1967*a*) are described elsewhere. A two-millicurie source of ^{57}Co in stainless steel was used. This gave a miminum line width of 0·35 $mm.sec^{-1}$ with sodium nitroprusside as absorber. Total counts in excess of 2×10^5 per channel were recorded, and statistical errors in peak positions were considerably smaller than the assigned instrumental drift ($\pm$0·02 $mm.sec^{-1}$ or 0·5 channels).

Room temperature measurements were made on a neptunite from San Benito County, California. A computer analysis of the spectrum (Stone, 1966) showed that it was best fitted to two Lorentzian curves of equal intensity with line widths of 0·42 $mm.sec^{-1}$, and there was no evidence for any other lines. Values for the chemical isomer shift and quadrupole splitting were 1·26 and 2·65 $mm.sec^{-1}$, respectively, relative to the value $-0{\cdot}16$ $mm{\cdot}sec^{-1}$ for the chemical isomer shift of sodium nitroprusside. These values for neptunite are compared in Table 1 with those obtained (Bancroft, Burns & Maddock, 1967*b*) for fayalite, tephroite, and orthoferrosilite (octahedral Fe^{2+}) and andradite and epidote (octahedral Fe^{3+}). It is immediately obvious from inspection of the data in Table 1 that iron in the neptunite structure occurs as octahedral Fe^{2+} ions, which implies that the oxidation state of titanium is Ti^{IV}.

Taking into account the quantitative sensitivity of the measurement the present study indicates that at least 95 % of the iron is in the Fe^{2+} oxidation state, and indicates that titanium is present as Ti^{IV}. Thus, at the present time, the only unequivocal occurrences of the Ti^{3+} ion in silicate minerals are titan-augite (Chesnoskov, 1959; Burns, unpublished work) and the titaniferous phlogopite fitzroyite (Burns, unpublished work). The possibility remains, however, that Ti^{3+} might also occur in some titaniferous amphiboles, garnets and biotites.

Table 1. *Mössbauer parameters for iron in silicate minerals*

Mineral	Chemical isomer shift ($mm.sec^{-1}$)	Quadrupole splitting ($mm.sec^{-1}$)	Width at half height ($mm.sec^{-1}$)
Neptunite	1·26	2·65	0·42
Fayalite $Fa_{96{\cdot}1}$	1·27	2·90	0·41
Knebelite $Fa_{31{\cdot}1}$	1·27	2·81	0·40
Orthoferrosilite $Fs_{86{\cdot}4}$			
M_2 position	1·24	2·00	0·35
M_1 position	1·26	2·45	0·35
Andradite	0·50	0·58	0·35
Epidote	0·45	2·02	0·40

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* Present address: Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand.

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Classification of crystalline substances by crystal systems, crystal classes, Bravais lattices and space groups.

By W. NOWACKI, T. MATSUMOTO and A. EDENHARTER, *Abteilung für Kristallographie und Strukturlehre, Universität Bern, Bern, Switzerland**

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A totality of 8795 substances of known space group was arranged according to space groups, and within one space group according to chemical categories. Two tables give the realization in absolute numbers and in percentages of the 41 most frequent space groups (≥ 3 %). It was found that the statistics of 1948 (*Crystal Data*, Part I) were already representative; no fundamental changes are to be observed during the subsequent period.

All substances listed in the second edition of Part II of *Crystal Data* (Donnay, Donnay, Cox, Kennard & King, 1963) with a definite space group (and in addition some others) were arranged according to space groups. In the first edition of Part I (Donnay & Nowacki, 1954) 3782 substances were worked through; in the meantime the number increased to 8795. The substances were again divided into chemical categories I to VI [inorganic compounds: I = elements and alloys, including arsenides, borides, hydrides, carbides, nitrides, phosphides and silicides; II = sulphides, sulphosalts, selenides and tellurides; III = oxides and hydroxides; IV = halides, including oxyhalides; V = bromates, chlorates, iodates, carbonates, nitrates, sulphates and tellurates, in which the bonding with oxygen is essentially covalent (Niggli's crystalline compounds of the first kind); VI = aluminates, antimonates, arsenates, borates, cerates, chromates, columbates, ferrites, germanates, manganates, molybdates, osmates, phosphates, platinates, praseodymates, rhenates, silicates, stannates, tantalates, titanates, tungstates, uranates, vanadates and zirconates, in which the bonding with the oxygen is more heteropolar (= Niggli's crystalline compounds of the second kind)] and VII (organic compounds); category VII was again subdivided into 6 (7) divisions [VIIa = inorganic compounds with organic radicals; azides, carbonyls, cyanides, organometallic compounds, siloxanes and silicones; VIIb = aliphatic; VIIc = carbocyclic–alicyclic; VIIc$_2$ = carbocyclic–aromatic; VIId = heterocyclic and VIIe = complex or of unknown constitution]. The following tables were obtained: *A.* Main Table, giving for each space group the substances crystallizing in it (with formula and/or name, reference), arranged according to categories; *B.* Tables of statistical data: (*a*) Distribution of crystalline substances among the 219 space groups (absolute numbers), (*b*) *ditto* (percentages), (*c*) among the 14 Bravais lattices (absolute numbers), (*d*) *ditto* (percentages), (*e*) among the 32 crystal classes (absolute), (*f*) *ditto* (percentages), (*g*) among the 7 crystal systems (absolute), (*h*) *ditto* (percentages), (*i*) among symmorphic, (*), hemisymmorphic (′) and asymmorphic space groups (absolute), (*j*) *ditto* (percentages), (*k*) distribution among the 41 most frequent space groups (absolute) and (*l*) *ditto*, relative (percentages ≥ 3 %).

Tables *B*, (*k*) and (*l*), are given here as Tables 1 and 2. The numbers in parentheses are those of the first edition (Donnay & Nowacki, 1954). The total percentages in Ta-

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* Contribution no. 172.