cell dimension of the fcc phase of Pr was determined as 4.88 Å.

Compression studies up to 40 kb (*4*) and electrical resistance measurements up to 100 kb (*5*) have been made on Nd. No evidence of allotropy was found in these studies. Our x-ray data reveal that Nd transforms from the hexagonal structure (*A3′*, La type) to an fcc structure at a pressure which is estimated to be in the 50 kb range. At this pressure and room temperature a unit-cell dimension of 4.80 Å was determined for the fcc phase.

Table 1 summarizes the results on the high-pressure fcc modifications of these rare-earth metals. The unit-cell dimensions (a_0) for these modifications are listed along with the corresponding approximate pressures at which the values were determined.

The similarities observed among the metals La, Ce, Pr, and Nd are of interest not only from the usual electronic aspect, but also from the viewpoint of allotropy as we have demonstrated in this report. It would be of interest to study the cubic close-packed structures of La, Pr, and Nd at higher pressures in an effort to detemine if Ce is the only metal in this group which undergoes an electronic transition. From the results of this work it appears that pressures considerably higher than those attainable with the present pressure cell would be required to carry out this study.

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17 February 1964

Ferric Tourmaline from Mexico

Abstract. *Dark brown crystals, up to 10 mm long, occur in rhyolite at Mexquitic, San Luis Potosí, Mexico. They are short prismatic, showing* $\{11\bar{2}0\}$, $\{30\bar{3}0\}$, $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, *with* c/a *0.4521, measured with a goniometer, and distinct* $\{11\bar{2}0\}$ *cleavage. With an unusual combination of cell dimensions, high density, high refractive indices, and extreme birefringence, this tourmaline falls outside the known elbaite-schorl and schorl-dravite series. A chemical analysis, recalculated on the basis of cell volume and density, gives close to the theoretical 150 atoms per cell, whether the iron is ferrous or ferric, but the physical properties indicate a ferric tourmaline.*

In the spring of 1962 specimens of brilliant dark-brown crystals on a rhyolite matrix were being sold by dealers in the western states as enstatite from San Luis Potosí, Mexico. The precise locality where this mineral was found (*1*), according to R. V. Gaines, is Mexquitic near San Luis Potosí City. The perfection of crystal form and the remarkable nature of the paragenesis (a magnesium-rich pyroxene is incompatible with the geochemistry of rhyolite, in which the ferromagnesian minerals normally have a high ratio of iron to magnesium) raised doubts concerning the validity of the identification of this mineral as enstatite. Its optical properties showed that it was not a pyroxene; its morphology and an x-ray powder photograph identified it as tourmaline. Because the optical properties and the density lay well outside the range of known tourmalines, the present investigation was undertaken.

Typical specimens show individual crystals up to 10 mm in length and 5 mm in thickness attached to the rhyolite and embedded in a clayey material. This material has a mean refractive index about 1.50 to 1.51, birefringence about 0.01, and an x-ray powder photograph shows a single halo at $d = 4.0$ to 4.5 Å; it is tentatively identified as allophane. Small crystals of sanidine are present in this clayey material.

The tourmaline crystals have short prismatic habit. The following forms have been identified and measured on the two-circle goniometer: $\{11\bar{2}0\}$, $\{30\bar{3}0\}$, $\{10\bar{1}1\}$, $\{02\bar{2}1\}$, leading to the axial ratio $(c/a)_{\text{gon}} = 0.4521$. The crystals are dark brown, almost black, with a bronze schiller; the streak is yellow-brown. The mineral has distinct prismatic cleavage in contrast to the very poor cleavage usually reported for tourmaline. It is optically negative; (indices of refraction) $\omega = 1.735$ (yellow-brown), $\epsilon = 1.655$ (very pale yellow), both ±0.003. The birefringence, 0.080, is extreme for a tourmaline; the maximum birefringence for tourmaline recorded by Deer, Howie, and Zussman (*2*, p. 306, anal. 1) is 0.035. The cell dimensions were obtained from single-crystal and diffractometer data. The diffractometer data were refined by least squares (*3*); $a = 15.873$, $c = 7.187$ Å, standard deviation 0.002 Å, giving $(c/a)_{\text{x-rays}} = 0.4528$. This combination of cell dimensions is also unusual: on a graph of c plotted against a (Fig. 1) this tourmaline falls outside the solid-solution series elbaite-schorl and schorl-dravite.

Density (D) determinations showed many of the crystals to contain small quartz inclusions. The pure mineral has $D = 3.31 \pm 0.01$ g/cm^3, a value which is outside the range for known tourmalines, 3.03 – 3.25 (*2*, p. 300).

The chemical analysis in percentage by weight, made by H. B. Wiik (*4*), is as follows: SiO_2, 33.19; TiO_2, 0.46; Al_2O_3, 30.87; FeO, 18.6; MnO, 0.20; MgO, 0.17; CaO, 0.36; Na_2O, 3.40; K_2O, 0.08; H_2O^+, 0.42; H_2O^-, 0.02; B_2O_3, 11.5; F, 1.77; total, 101.04, less O for F, 0.72, 100.32. Wiik remarks that although the iron is reported as

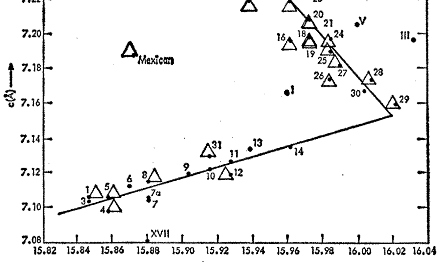

Fig. 1. Cell dimensions of tourmalines. The literature data and reference numbers are from Epprecht (*10*). The composition, when known, is shown by the position of the point inside the triangle: elbaite (lower left), schorl (lower right), dravite (upper corner).

Table 1. Change in optical properties accompanying iron oxidation.

Fe_2O_3 (% by wt.)	FeO (% by wt.)	Index of refraction (β)	Birefringence ($\gamma - \alpha$)
	Hornblende before heating		
9.23	16.51	1.6980 (dark green)	0.0196
	Hornblende after heating		
23.40	4.12	1.7690 (dark brown)	0.0940
	Triphylite		
0.00	24.33	1.687 (colorless)	0.006
	Ferrisicklerite		
27.20	0.59	1.795 (brown)	0.040

FeO, it may well be present, at least in part, as ferric iron. The drastic treatment required to get the mineral in solution (H_2SO_4 + HF in a closed tube under pressure at 300°C) makes it impossible to discriminate between the two forms of iron by wet chemical analysis. We have tried to do this with the help of electron-spin resonance (*5*). The spectra obtained at liquid-nitrogen temperature and at room temperature show a broad peak which indicates the presence of Fe^{+++} or Mn^{++} or both. No calibration standards were available to give quantitative estimates of the amounts.

On the basis of cell volume and density, the cell content was calculated from the analysis, the iron being taken to be either all ferrous or all ferric. In the first case we obtain $Na_{3.42}$ $K_{0.05}$ $Ca_{0.20}$ $Fe^{++}_{8.07}$ $Ti_{0.18}$ $Mg_{0.13}$ $Mn_{0.00}$ $Al_{18.84}$ $B_{10.30}$ $Si_{17.17}$ $O_{86.44}$ $F_{2.01}$ $(OH)_{1.46}$, with 149.26 atoms per cell. In the second case we get $Na_{3.34}$ $K_{0.05}$ $Ca_{0.20}$ $Fe^{+++}_{7.90}$ $Ti_{0.17}$ $Mg_{0.13}$ $Mn_{0.09}$ $Al_{18.46}$ $B_{10.10}$ $Si_{16.82}$ $O_{88.64}$ $F_{2.85}$ $(OH)_{1.42}$, with 150.17 atoms per cell. In either case, Fe^{++} or Fe^{+++}, the number of atoms is close to 150, which is the number of atomic sites in the cell of the crystal structure (*6*).

At first sight this tourmaline is not chemically unusual; it is a very nearly pure iron tourmaline, low in hydroxyl ions and somewhat high in fluorine. But the sum of univalent anions is only about one third of the expected 12 per cell, which indicates that $O^{=}$ substitutes for OH^-; the balance of charges can be maintained by a concomitant replacement of Fe^{++} by Fe^{+++} (as in the series annite-oxyannite, *7*, p. 95). Further considerations in favor of this interpretation are the following. The observed high density is, of course, a consequence of the small cell volume (Fig. 2). A small cell volume would be expected if all or most of the usual Fe^{++} ions were replaced by the smaller Fe^{+++} ions in the oxyannite-type core of the structure. Excess boron might replace silicon, keeping the somewhat shrunk six-membered ring of tetrahedra of the right size for the three ferric-iron octahedra to share the apical oxygens.

Table 2. Comparison of tourmalines from the Urals and from Mexico.

Locality	ω	ϵ	$\omega - \epsilon$	Density (g/cm³)
Urals (schorl)	1.668	1.633	0.035	3.218
Mexico	1.735	1.655	0.080	3.31

Optical properties too suggest that iron is present in the ferric state. As Eugster and Wones (*7*, p. 96) showed for their synthetic annite-oxyannite compositions, the indices of refraction increase as the ratio of Fe^{+++} to Fe^{++} increases. Other examples can be found in the literature. Barnes (1930) (*8*) oxidized a hornblende by heating in air at 800°C (see Table 1).

Similar changes result from the oxidation of triphylite, $Li(Fe,Mn)PO_4$, to ferrisicklerite, which is isostructural with triphylite, but with all the iron in the ferric state and some lithium removed to maintain charge balance. The pertinent properties of triphylite and ferrisicklerite from Varuträsk (*9*) are shown in Table 1.

Similarly we can contrast the Mexican tourmaline with a schorl from the Urals with comparable composition, except that practically all its iron is reported to be in the ferrous state (*2*, p. 306, anal. 1) as shown in Table 2. Thus the physical and optical data support the view that in the Mexican material the iron is in the ferric state. We are dealing with a new variety of tourmaline, the formula of which will be written as follows to show the presumed ionic substitutions: $(Na_{3.34}K_{0.05})$ $(Fe^{+++}_{7.90}$ $Ti_{0.17}$ $Mg_{0.13}$ $Mn_{0.09}$ $Al_{0.46}$ $Ca_{0.20})$ $Al_{18.00}$ $B_{8.92}$ $(Si_{16.82}$ $B_{1.18})$ $O_{80.91}$ $(O_{7.73}$ $F_{2.85}$ $OH_{1.42})$. Note that the excess of Al over 18 is placed with the octahedral cations, that enough B is added to Si to raise the total to 18 tetrahedral cations and enough O to the univalent anions to raise their total to 12. Except for the high sodium-potassium value (3.39 instead of 3), the number of ions in the various crystallographic positions would thus be satisfactory: 8.95 octahedral cations, 8.92 boron ions, and 80.91 oxygen ions are equal to the theoretical values 9, 9, and 81, within the limits of error of the analysis (150.17 atoms instead of 150).

Note added in proof. E. White of

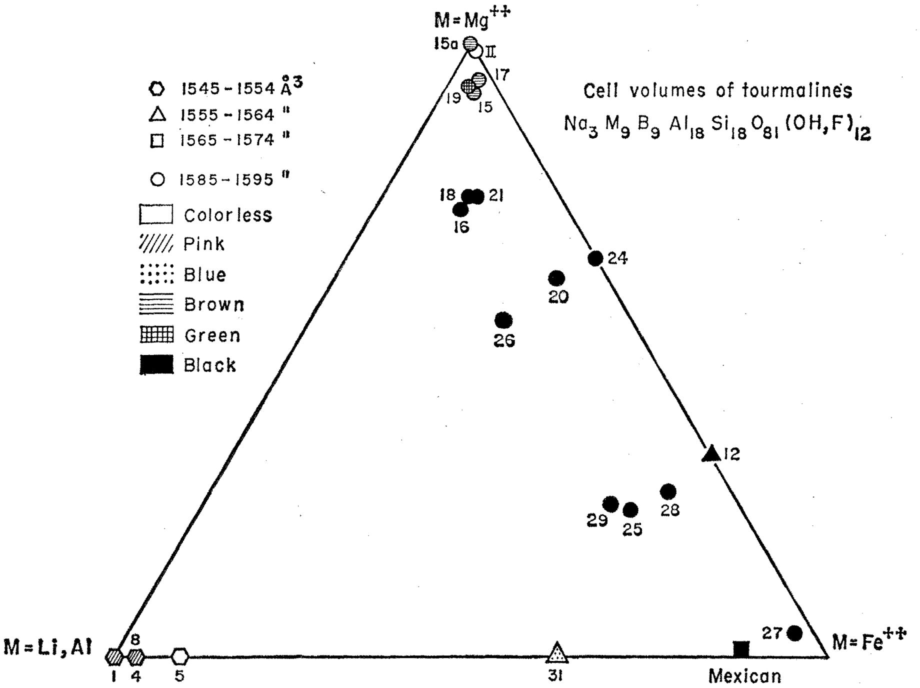

Fig. 2. Cell volumes for tourmalines of known compositions; the literature data and reference numbers are from Epprecht (*10*).

the Materials Research Laboratory, Pennsylvania State University, has informed us that his study of the FeK absorption edge shows more than 90 percent of the iron to be in the ferric state.

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3 December 1963 ■

Ferrosilite ($FeSiO_3$): Synthesis at High Pressures and Temperatures

Abstract. *The $FeSiO_3$ (ferrosilite) end member of the pyroxene series is not known as a pure mineral in nature and cannot be synthesized at atmospheric pressure. It is readily synthesized, however, at pressures from 18 to 45 kb and temperatures from 1150° to 1400°C. Its refractive indices approach those predicted for ferrosilite and it melts incongruently to an Fe_2SiO_4-rich liquid plus quartz.*

Under high pressures and temperatures ferrosilite ($FeSiO_3$, with the pyroxene structure) has been synthesized for the first time. It has also been synthesized independently by S. Akimoto and colleagues at the University of Tokyo. Although $FeSiO_3$ is an important constituent of many pyroxenes, it occurs rarely if at all as a discrete phase. The only suspected occurrence is in lithophysae of some obsidians, where pyroxenes are found whose optical properties are similar to those extrapolated to $FeSiO_3$ from pyroxene solid solutions (*1*); their scarcity and small grain size have prevented chemical analysis.

Attempts at experimental synthesis, either in evacuated tubes or in controlled atmospheres at low pressures, have failed. Starting materials with the bulk composition $FeSiO_3$ crystallize to fayalite (Fe_2SiO_4) plus SiO_2 (*2*). Bowen has suggested the possibility that fayalite grows metastably, thus masking ferrosilite stability (*1*).

We first made ferrosilite during preliminary runs to determine the stability of fayalite in crimped but unsealed platinum capsules in single-stage piston-and-cylinder high-pressure apparatus. Inasmuch as the internal heating element of the apparatus is a graphite sleeve, the reaction $2C + O_2 = 2CO$ might buffer the partial pressure of oxygen in the capsule, thus reducing the fayalite to SiO_2 plus metallic Fe. After several hours at 20 kilobars and 1250°C, the charge was mainly fayalite with minor magnetite and a phase thought to be ferrosilite from its optical properties. Apparently, loss of Fe by alloying with the platinum container, with concomitant oxidation of some FeO to magnetite, drove the bulk composition of the iron silicate slightly toward $FeSiO_3$.

The identification of ferrosilite was confirmed by runs made on the $FeSiO_3$ composition. Proper proportions of Fe, Fe_2O_3, and SiO_2 were reacted in an evacuated silica glass tube to yield an equimolar mixture of fayalite and quartz. This material was packed in Fe capsules with tightly fitting lids and used in high-pressure runs. The new phase was synthesized under conditions ranging from 1150°C at 18 kb to 1400°C at 45 kb (Table 1). Reaction was nearly complete, with small amounts (1 to 5 percent) of fayalite plus quartz or coesite apparently shielded by inclusion in the major phase. Thus the composition of the new phase must lie near $FeSiO_3$. The presence of the Fe capsule suggests that the Fe_2O_3 content, if any, should be small.

Ferrosilite melts incongruently in the range 20 to 40 kb to an Fe_2SiO_4-rich liquid plus quartz; melting relations at higher pressures have not yet been determined. The liquid quenches rarely to glass and more commonly to fayalite or to fayalite plus ferrosilite with a distinctive texture. Ferrosilite synthesized just below the incongruent melting temperature is orthorhombic; this inverts in a few hours at room temperature and pressure to a polysynthetically twinned monoclinic form. It is not yet clear whether the orthorhombic polymorph forms stably or metastably. At temperatures roughly 100°C below that of incongruent melting, ferrosilite crystallizes as a monoclinic form in which twinning is simple or absent.

Preliminary optical properties for the monoclinic form are:

$$n_X = 1.764 \pm 0.002$$
$$n_Y = 1.767 \pm 0.002$$
$$n_Z = 1.792 \pm 0.002$$
$$Z \wedge c = 31^\circ \pm 1^\circ$$
$$(+)2V = 25^\circ \pm 5^\circ$$

where n_X, n_Y, and n_Z are the principal indices of refraction, $Z \wedge C$ is the angle between the principal optic direction Z

Table 1. Results of selected runs on $FeSiO_3$ composition with different starting materials. Explanation of abbreviations: fay, fayalite; qtz, quartz; fs, ferrosilite; coes, coesite; quench, quench products including glass, fayalite, and ferrosilite.

P (kb)	*T* (°C)	Duration (hr)	Results
	Fayalite and quartz		
18	1150	23	fs; minor fay, qtz
20	1200	14	fs; minor fay, qtz
20	1300	14	qtz + quench
30	1300	1	fs; minor fay, qtz
30	1400	1	qtz + quench
40	1400	1	fs
40	1450	1	qtz + quench
	Fayalite and coesite		
45	1400	1	fs
	Ferrosilite		
14	1000	31	fay + qtz + fs