Figure 2 gives the relative age and sex distribution of fur seals brought to the site before and after Euro-American contact. About half the males (that is, all adults and subadults) fall into the age class of 5 years and older. Today, mature males do not normally migrate south of the Gulf of Alaska (*12*). During the last 50 years, only four mature males were collected off the coasts of Washington and British Columbia (*13*), and one was collected off the coast of California. Fiscus (*14*) reports that he knows of no earlier records of mature males for the vicinity of Cape Alava.

Because the Ozette Indian village was abandoned shortly after 1900, it is presumed that the uppermost cultural deposits, which contain numerous items of Euro-American manufacture intermixed with fur seal bones, are about that age. The relatively constant high percentages of older males in the midden, compared with the virtual absence of older males in recent populations found locally, indicates that a major change in age composition of males has occurred sometime since approximately 1900. Because mature males still occur in more northerly populations, I can conclude only that there has been a change in the migratory pattern of male fur seals. Speculations about the reasons for this change would be premature, but the evidence is undeniable and it certainly correlates in time with the last major pelagic sealing.

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Band Gap of Forsterite

Abstract. *Optical absorption and reflectivity measurements on synthetic forsterite show that this silicate has a wide band gap of the order of 8.4 electron volts; thus it resembles other pure insulating oxides such as MgO. For natural olivines, in which divalent cations, mainly Fe^{2+}, can replace Mg^{2+}, all the optical absorption bands between the lattice overtones in the infrared and the first excitonic transition at 8.4 electron volts are due to the presence of iron.*

A good electrical insulator is characterized by a wide band gap; that is, between a virtually empty conduction band and an almost filled valence band there is an energy range greater than 3 to 4 ev in which traveling-wave electron states are forbidden.

Unless impurities or defects introduce energy levels within the forbidden gap, the full energy of the band gap must be made available for creation of occupied conducting states. Optical absorption and reflection measurements on iron-free synthetic forsterite, Mg_2SiO_4, demonstrate that it is a wide-gap insulator. When iron, mainly ferrous, is substituted for magnesium as in the mineral olivine, $(Mg,Fe)_2SiO_4$, such optical measurements show that the iron produces energy levels lower than the forsterite band gap. Furthermore, because excitations involving these impurity levels have energies lower than the band gap, impurity effects are probably the dominant conduction processes in natural crystals.

The synthetic forsterites were single crystals produced by the flame-fusion method (*1*), the largest being of centimeter size. It was possible to vary iron content [Fe : (Mg + Fe)] from 0.007 to 1 percent molecular. Furthermore the low iron content permitted the Fe^{3+}:Fe^{2+} ratio to be varied over a wider range than is possible in natural crystals without damage to the crystal; because the crystals were grown in an oxidizing flame, this ratio was rather high in the as-grown crystals but could be lowered by heating in a reducing atmosphere. The crystals were transparent, and samples containing more than about 0.3 percent Fe were lightly tinted; stoichiometry was higher than that listed for natural olivines, and the measured density equalled that calculated from the lattice parameters (*1*).

At energies greater than about 3.3 ev, natural olivines containing Fe of the order of 10 percent molecular show strong absorption that blocks transmission of ultraviolet light through samples thicker than about 0.1 mm. Once it was felt that the apparent absorption edge at 3.3 ev represented the onset of fundamental transitions between valence and conduction bands in the olivine lattice (*2*, *3*) and thus defined the band gap. However, Fig. 1 clearly demonstrates that the apparent absorption edge is simply a result of iron in the crystal: the progressive increase of iron doping progressively increases absorption. The ultraviolet transparency of iron-free forsterite has also been noted for sintered material (*4*) and for single crystals synthesized by the Bridgman method (*5*).

Figure 2 compares transmission by a very thin natural olivine and a synthetic sample (No. 2Lc) of comparable thickness; the iron-free crystal transmits light for another 3 ev beyond the cutoff in the natural crystal. Fundamental transitions in pure Mg_2SiO_4 set in only beyond 7.5 ev, at which point the absorption intensity becomes too great to permit the transition to involve iron and still give reasonable values of oscillator strength. Thus the minimum energy separation for states associated with valence and conduction bands must be greater than 7.5 ev, and absorptions below this energy must be due to impurities.

Figure 2 also shows that heating of a synthetic sample in a reducing atmosphere dramatically decreases the absorptions at 4.6 and 6.2 ev. Because the 4.6- and 6.2-ev bands are strongest in crystals that have been heated in an oxidizing atmosphere, the bands must involve mainly Fe^{3+}. The transitions due to Fe^{3+} are so much stronger than those due to Fe^{2+} that the residual Fe^{3+} in natural crystals could account for the strength of the observed near-ultraviolet cutoff (*6*). However, the facts that the near-ultraviolet absorption in natural olivines is a superposition of bands having different centers at 4.0 and 5.0 ev and that other impurities also are present make it difficult to argue that Fe^{3+} alone causes the absorption edge in natural minerals.

The bands in the region between 3 and 7 ev are too strong (oscillator strengths are of the order of 0.1) to be crystal-field transitions taking place only on the iron ions, and must be charge-transfer bands involving transitions between the iron ion and surrounding oxygen ions—that is, between impurity levels in the band gap and the conduction or valence bands. The charge-transfer bands and the crystal-field bands have been discussed (*6*); it is shown that the Fe^{2+} and Fe^{3+} bands in Mg_2SiO_4 between 0.5 and 7 ev are very similar to the same bands that have been identified in MgO.

Peaks in the reflectivity spectrum occur near strong transitions and can reveal transitions in regions where the crystal is too absorbing to transmit light. Figure 3 shows the room-temperature reflectivity spectrum of a synthetic sample having a peak at 8.4 ev. In MgO the lowest fundamental transition at 7.6 ev (*7*, *8*) is an exciton, that is, a bound electron-hole pair which can be created by a photon of energy less than the band gap. In view of the similar energy of the first reflectivity peak in MgO, it is reasonable to suggest that the 8.4-ev reflectivity peak in Mg_2SiO_4 also is an exciton transition. This model extends to the interband transitions the observed similarity of levels within the band gap in the two materials (*6*). If the 8.4-ev peak is an exciton, then the energy needed to put an electron into an intrinsic conducting state in the conduction band is probably even greater than 8.4 ev; Reiling and Hensley (*8*) have estimated 8.7 ev for MgO. In any case, the band gap in Mg_2SiO_4 cannot be less than 7.5 ev.

Olivines are of geophysical interest because they are thought to be the principal mineral phase in the upper 400 km of Earth's mantle (*9*), and in electronic properties they are presumably representative of the dense silicates in this region. While measurements from iron-free crystals are not directly applicable to problems of Earth's interior, they do isolate some effects due to transition metal substitutions.

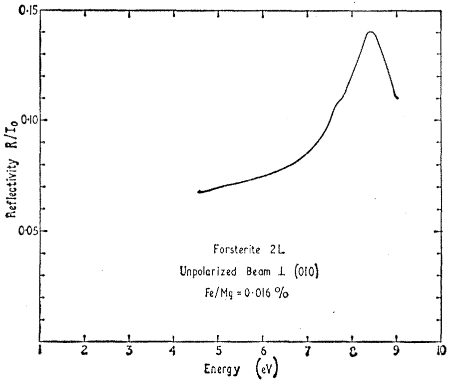

Fig. 3. Room-temperature reflectivity peak at 8.4 ev in synthetic forsterite; surface polished with 0.25-μ diamond paste. Below 5 ev, reflectivity is substantially constant at slightly more than 6 percent.

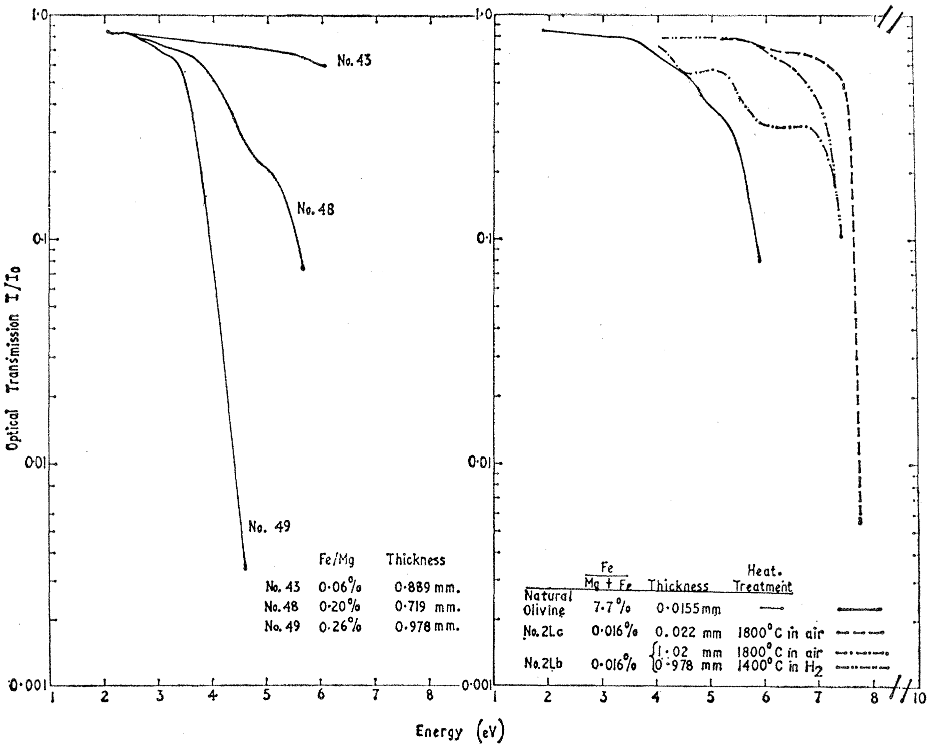

Fig. 1 (left). Optical transmission in samples of synthetic forsterite: increasing ultraviolet cutoff with increasing iron content. Measurements were made at room temperature with unpolarized light and unoriented samples. Fig. 2 (right). Comparison of transmissions: in two of the curves the ultraviolet cutoff in a very thin natural crystal is contrasted with the extended range of transmission in the slightly thicker synthetic No. 2Lc. The transmission curves for No. 2Lb show the decreased absorption (enhanced transmission) that results from heating of the crystals in a reducing atmosphere. Measurements were made at room temperature with unpolarized light and, for the synthetic samples, with beam parallel to the crystal *b*-axis.

Since the band gap for intrinsic electronic semiconduction is so high, one must discard the hypothesis (*2*, *3*) that intrinsic conductivity in conduction and valence bands is significant in olivines. Some preliminary measurements (*6*) of electrical conductivity of the synthetic specimens show them to be quite good insulators, similar to the simpler oxides MgO or Al_2O_3. Since energy levels below 7.5 ev in olivines are due to iron, it is far more likely that electronic transport takes place through the interactions of localized electrons on impurity sites. The question of whether charge-transfer transitions can contribute appreciably to conduction depends on the lifetime of the resulting electrons or holes and on their mobility. Photoconduction in gadolinium iron garnet (*10*) indicates that charge transfer may create holes in the valence band (positive polarons), but the absence of detectable photoconductivity in olivines (*3*, *5*) and the extremely low mobilities (*5*, *6*) of possible carriers make quantitative discussion of a similar conduction method in olivines difficult at the present time.

Knowledge that the energy of formation of excitons in forsterite is 8 to 9 ev is relevant to discussions of heat transport by excitons in Earth's mantle. Such excitations must be created in large numbers and have great mobility in order to transfer a perceptible amount of energy. The low-energy excitations tied to substitutional iron are probably too immobile to be important, while the number of any forsterite excitons near 8 ev, presumably of greater mobility, will be inconsequentially fewer than the number calculated when the formation energy was taken to be of the order of 1 ev (*11*, *12*) because of the exponential dependence upon activation energy. Barring very remarkable effects of pressure, one can say that excitonic energy transport is of negligible importance for the thermal conductivity of mantle materials.

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Cyanovinyl Phosphate: A Prebiological Phosphorylating Agent?

Abstract. *Cyanovinyl phosphate may be prepared by the addition reaction of phosphate to cyanoacetylene. Kinetic studies have established that cyanovinyl phosphate undergoes a slow pseudo-first-order hydrolysis in aqueous solution. Cyanovinyl phosphate converts uridine to uridine monophosphate and phosphate to pyrophosphate.*

There have been several reports describing the synthesis of the pyrophosphate bond and the alkyl phosphate bond under potential prebiological conditions. Potassium cyanate effects the conversion of orthophosphate to pyrophosphate but only on an apatite surface (*1*). Pyrophosphate and nucleotides are produced by the thermal condensation of orthophosphate and nucleosides under anhydrous conditions (*2*). Unfortunately these syntheses proceed only under rather restrictive conditions. A more attractive mode for the prebiotic synthesis of alkyl phosphates and pyrophosphates is one which will proceed in dilute aqueous solution and as such may have taken place on the primitive earth in a large body of water. However, experiments designed with this goal in mind have yielded negative results (*3*).

Recently it has been proposed that cyanoacetylene has a central role in prebiological synthesis (*4*). It is one of the major products resulting from the action of an electric discharge on methane-nitrogen mixtures. Cyanoacetylene has been converted to cytosine on treatment with cyanate or cyanogen and it has been converted to asparagine and aspartic acid with cyanide and ammonia (*4*). The conversion of cyanoacetylene to cyanovinyl phosphate and the possible role of this high-energy phosphate compound as a prebiological phosphorylating agent are discussed in this report.

Cyanovinyl phosphate may be prepared in dilute solution by the addition of $10^{-4}M$ cyanoacetylene to $0.1M$ phosphate at pH 7 to 9. The product is obtained in over 90 percent yield as measured by the intensity of its absorption maximum at 225 mμ (E = 14,000) (pH 7). Cyanovinyl phosphate may be synthesized on a preparative scale by heating 100 ml of a solution containing 0.1 mole of Na_2HPO_4 and 0.01 mole of cyanoacetylene at 60°C for 1 hour. The inorganic phosphate is then precipitated with 0.1 mole of barium acetate after dilution to 500 ml with water. The barium salt of cyanovinyl phosphate, (1.1 g, 35 percent) is then precipitated from the filtrate by addition of 350 ml of ethanol. Analysis: calculated for $C_3H_2NO_4PBa \cdot H_2O$: C, 11.91; H, 1.33; N, 4.63; P, 10.21. Found: C, 11.67; H, 1.55; N, 4.97; P, 10.69.

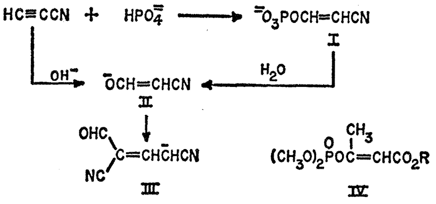
The cyclohexylamine salt was prepared from the barium salt by the procedure of Tener (*5*). Analysis: calculated for $C_{15}H_{30}N_3O_4P$: C, 51.86; H, 8.71; N, 12.10; P, 8.92. Found: C, 51.88; H, 8.81; N, 12.15; P, 8.58.

The structure of cyanovinyl phosphate follows from the method of synthesis, the elemental analyses, the ultraviolet spectrum (*6*), and infrared absorption (KBr) at 2235 cm^{-1} (CN) and 1650 cm^{-1} (C=C).

This appears to be a general synthesis of alkyl cyanovinyl phosphates. For example, the addition reaction of ethyl phosphate to cyanoacetylene may be observed by the appearance of an absorption maximum at 220 mμ.

Cyanovinyl phosphate is an exceptionally stable enol phosphate. The kinetics of its hydrolysis at pH 7, 9, and 11 were followed spectrophotometrically at 60°C and 100°C. When the hydrolyses were performed at pH 7 and pH 9, compounds II and III could be detected by absorption maxima at 248 mμ and 310 mμ, respectively. The same compounds are produced by the action of base on cyanoacetylene (*4*). At pH 11 only a small level of II was apparent. This is to be expected, since compound II is readily cleaved at high pH and also it does not condense to III in strong base (*4*).

The hydrolysis was pseudo-first-order and pH-independent in the pH range 7 to 11 (the kinetic data at 100°C are plotted in Fig. 1) with half-lives of 0.049 day ($K_1 = 14.1$ day^{-1}) at 100°C and 4.9 days ($K = 0.14$ day^{-1}) at 60°C. Half-lives for hydrolysis of 300, 10^3, and 10^4 days were obtained by extrapolation of a log K versus $1/T$ plot to 30°, 20°, and 0°C, respectively. These data may be contrasted with the hydrolysis of IV (R = H), which has a half-life of 2 days at pH 11 and 30°C (*7*).



Since the rate of hydrolysis is pseudo-first-order and pH-independent over a wide range, the reaction mechanism probably involves the attack of a water molecule on the cyanovinyl phosphate anion.

Enol phosphates are known to be efficient phosphorylating agents in nonaqueous systems. However, the high reactivity of enol phosphates precludes their use in aqueous systems (*8*). The stability of aqueous solutions of cyanovinyl phosphate prompted our investigation of its properties as a possible prebiological phosphorylating agent.

We found that orthophosphate is converted to pyrophosphate, and uridine to uridine-5′-phosphate, by an aqueous solution of cyanovinyl phosphate. A 2 to 4 percent yield of pyrophosphate is obtained when 0.3 ml of $0.2M$ ammonium cyanovinyl phosphate is heated for 18 hours at 85°C with $0.25M$ orthophosphate in the pH range 6 to 8 (*9*). Addition of 0.025 to 0.05 g of calcium phosphate, a catalyst for some phosphorylation reactions (*1*), did not enhance the yield of pyrophosphate. Uridine-5′-phosphate (UMP) was synthesized in 3.9 percent yield (based on