

vary greatly with changes in nitrate concentration (2).

Water collected from below the thermocline at five stations in the Peru current, which has low oxygen and high nitrite concentrations (11), were examined for nitrate reduction to molecular nitrogen. Twenty-four experiments were conducted with water containing oxygen concentrations from 0.11 to 0.37 ml per liter and nitrite from 0.05 to 3.23 $\mu\text{g-atom}$ per liter. We found no evidence of the reduction of nitrate to molecular nitrogen in these experiments. Apparently in this water nitrate reduction does not proceed at significant rates beyond nitrite, if indeed these large concentrations of nitrite are the result of biochemical reduction of nitrate, as suggested by Brandhorst (12).

Production of molecular nitrogen in the ocean is presumed to be biochemically mediated. Microorganisms such as *Pseudomonas*, which are capable of reducing nitrate to molecular nitrogen, have been isolated from the water and the sediments. It is unlikely that gaseous nitrogen is produced by any mechanism other than bacterial denitrification. Gas chromatographic and mass spectrometric studies of anaerobic fermentation of sewage sludge by Brezonik and Lee (13) showed that nitrogen gas is not produced by any mechanism other than bacterial reduction of nitrate. The nonenzymatic (Van Slyke) reaction for the conversion of ammonia, amino acids, and nitrite to molecular nitrogen occurred only with a pH less than 3.

This study indicates that denitrification is a significant process in oxygen-deficient sea water by which microorganisms convert nitrate and certain intermediate products (nitrite, and so

on) to molecular nitrogen. Determination of the critical concentration of oxygen at which reduction to molecular nitrogen occurs requires further study. We are now of the opinion that oxygen must be absent, or present perhaps at concentrations of less than 0.10 ml per liter, in order to have significant molecular nitrogen production. Probably most of the denitrification in water masses of the type studied occurs in a narrow zone near the sulfide-oxygen interface, where large concentrations of nitrate and little or no oxygen are present (10).

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ily distinguished by their optical properties (Table 1) and the data from x-ray powder diffraction patterns.

Previous chemical analyses of shattuckite, including those recently reported by Sun (3) and Newberg (4), have been hampered by the difficulty of obtaining a sample free of other intimately admixed minerals, such as planchéite, ajoite ($\text{Cu}_6\text{Al}_2\text{Si}_{10}\text{O}_{29} \cdot 5\frac{1}{2}\text{H}_2\text{O}$), quartz, and hematite. A recent analysis by Vlisidis (see 5) of carefully purified samples conforms closely to the formula $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$. This formula was further supported by a crystallographic study (6) and has now been finally established by a complete structure analysis.

The crystal unit cells of shattuckite and planchéite were determined by the Buerger precession method, and the parameters are given in Table 1. The optical properties and unit-cell parameters for shattuckite agree closely with those reported by Newberg (4). Because of their fibrous nature, suitable crystals for single-crystal study are difficult to isolate, and the x-ray patterns often show a uniform streaking of reflections normal to the *c*-axis. Nevertheless, complete three-dimensional intensity data have been collected for both crystals, and thus a satisfactory refinement of their detailed structures is made possible.

The structure of shattuckite was first solved by locating the Cu positions through a straightforward interpretation of the *c*-axis Patterson projection. The phases determined by the Cu atom structure factors were used to calculate a preliminary electron density map which revealed all the other atoms in the structure. Full-matrix, least-squares refinement of the atomic parameters and an overall temperature factor have been carried out separately on 131 (*h0l*) reflections and 79 (*0kl*) reflections, to a conventional reliability factor of 0.122 for the former and 0.093 for the latter. Since the interatomic distances still have rather high uncertainties at this stage, refinement is being continued with three-dimensional data.

The structure consists of $(\text{CuO}_2)_n$ layers similar to the $\text{Mg}(\text{OH})_2$ layers in brucite, normal to the *b*-axis, centered at *b* = 0 and $\frac{1}{2}$. The oxygen atoms on both sides of the layer are provided by OH groups and the unshared oxygen atoms of $(\text{SiO}_3)_n$ chains which are parallel to the *c*-axis. These chains are nearly identical in configuration to the well-

Shattuckite and Planchéite: A Crystal Chemical Study

Abstract. *The orthorhombic crystal structures of shattuckite, $\text{Cu}_5(\text{SiO}_3)_4(\text{OH})_2$, and planchéite, $\text{Cu}_8(\text{Si}_4\text{O}_{11})_2(\text{OH})_4 \cdot \text{H}_2\text{O}$, have been solved. Shattuckite contains silicate chains similar to pyroxene in a complex association with copper atoms, while the closely related planchéite contains silicate chains similar to amphibole.*

As an initial phase of a program to establish the chemical and structural nature of the copper silicates, the crystal structures of shattuckite and planchéite have been solved and partially refined with two-dimensional data. Because of the scarcity of material and close asso-

ciation with other copper silicate minerals, the chemical composition of these two minerals has been in doubt ever since shattuckite was first reported by Schaller (1), and planchéite was first mentioned by LaCroix (2). Although similar in appearance, they can be read-

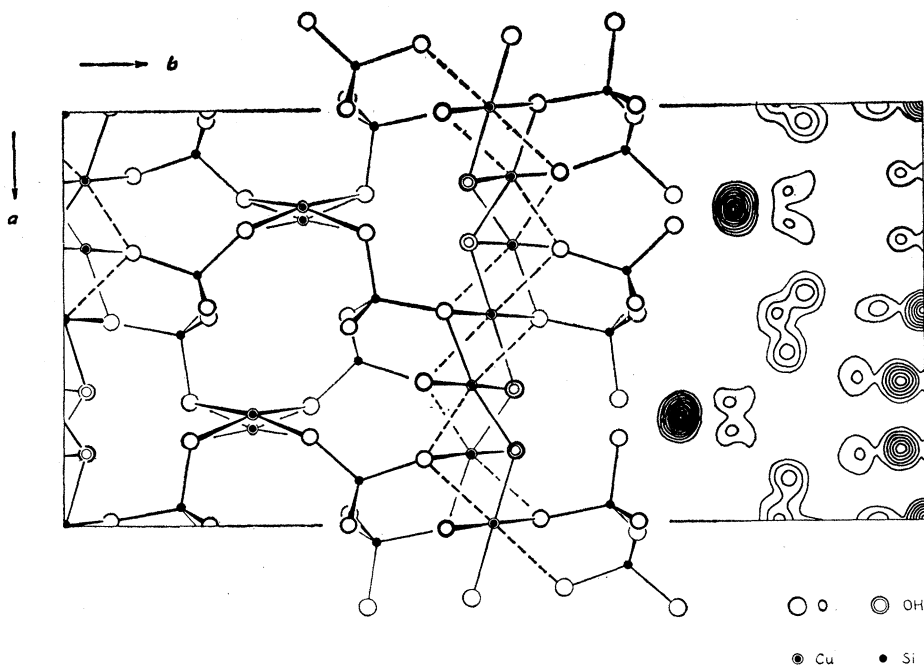


Fig. 1. The structure of shattuckite projected along the c -axis, showing the silicon-oxygen bonds as solid lines and the copper-oxygen bonds as dashed lines. One unit cell is contained within the rectangle. A representation of the electron density projection is shown at the right of the unit cell.

known zigzag chains in pyroxene. Those unshared oxygen atoms not involved in the copper-oxygen sheet are joined to those of opposite layers by additional Cu atoms forming ladder-like $(\text{CuO}_2)_n$ chains parallel to the c -axis. These features are shown in a projection of the structure along the c -axis in Fig. 1. Of the three types of Cu atoms present, two are located in the layer network in octahedral coordination showing the strong tetragonal distortion commonly exhibited by Cu(II). The third type is located in the latter chains in approximately square coordination.

The structure of planchéite has now

Table 1. Crystallographic data for shattuckite from Ajo, Arizona, and planchéite from La Rioja, Argentina.

Property	Shattuckite	Planchéite
$n\alpha$	1.753 ($\parallel b^*$)	1.697 ($\parallel c^*$)
$n\beta$	1.782 ($\parallel a^\dagger$)	1.718 ($\parallel b^\ddagger$)
$n\gamma$	1.815 ($\parallel c^\S$)	1.741 ($\parallel a^\ddagger$)
$2V$ (calc.)	88°	$88\frac{1}{2}^\circ$
Space groups	$Pcab$	$Pcnb$
a	9.876 Å	19.04 Å
b	19.812 Å	20.01 Å
c	5.381 Å	5.27 Å
Z	4	4
D (x-ray)	4.138 g/cm ³	3.85 g/cm ³
D (meas.)	4.11 g/cm ³	3.65-3.80 g/cm ³

* Very pale blue; $\dagger$ pale blue, $\ddagger$ blue, $\S$ deep blue.

also been solved in a similar manner. It is found to be a simple extension of the shattuckite structure in which the silicate chain is doubled along the a -axis to form a chain closely similar to that in amphibole. A molecule of water is inserted on the twofold axes in the structure to fill the void formed by the hexagonal rings in the amphibole-like chain. The structure analysis establishes the formula conclusively as $\text{Cu}_8(\text{Si}_4\text{O}_{11})_2(\text{OH})_4 \cdot \text{H}_2\text{O}$. In view of the prevailing difficulties of obtaining homogeneous samples, this result is consistent with the best chemical analyses, with the exception of a small excess of water in the latter. Also, infrared measurements, while showing the presence of OH groups but not H_2O in shattuckite, indicate the presence of both in planchéite.

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Rare Earths in European Shales:

A Redetermination

Abstract. The rare-earth elements in a composite of European shales originally analyzed by Minami in 1935 have been analyzed by neutron activation. The apparent europium deficiency and the differences in relative elemental abundances for the rare earths from American and Russian sediments, as inferred from the older values, are obviated.

In 1935 Minami (1) measured the rare-earth element contents (lanthanides plus yttrium) of three composites of European and Japanese shales by an x-ray spectrographic technique. The resulting values, and those obtained by Noddack (2) for rare earths in meteorites, furnish the most striking example known of the Oddo-Harkins rule that, in nature, the relative elemental abundance of an element of even atomic number tends to exceed that of either of the elements of adjacent, odd atomic numbers. Goldschmidt (3) inferred from the data that after partial separations of the members of the rare-earth group had been effected by certain (unspecified) processes of igneous rock formation, processes of weathering and sediment formation mixed the rare earths back into their average crustal relative abundances. This and other conclusions based on Minami's data appear to have greatly influenced Goldschmidt's general views of geochemical processes and thus, to some extent, the development of the field of geochemistry. Minami's values have been used in nearly all compilations of terrestrial elemental abundances; general features of the rare-earth abundance distribution he observed were corroborated by Sahama (4).

Modern techniques of analysis have made possible such accurate determinations of rare earths that small differences (0 to 10 percent) in elemental abundances can be observed; thus, further consideration must be given to the accuracy of the specific values reported by Minami. Using neutron activation analysis, Haskin and Gehl (5) found relatively little variation in the abundance distributions of the rare earths among ten specimens of limestone, sandstones, and shales. By averaging the relative abundances for seven of the samples, they obtained a distribution similar to that found by Minami;