

HYDROXYL IN THE MANTLE¹

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ABSTRACT

Four lines of evidence are presented to support the claim that hydroxyl substitutes in limited amounts in certain oxygen point-positions in nominally anhydrous minerals: a) H_2O^+ is present in analyses of these minerals; b) structural formulae are improved in a crystallochemical sense if cation considerations are made the basis for the conversion from weight percent to formula and if $OH + O$ are used to balance the sum of cationic charges and to fill the anion positions in the structure; c) valence-sum calculations indicate some substitution of OH for O in pyroxenes, for example; d) infrared absorption spectra show the presence of hydroxyl in pyroxenes and olivines. The OH -for- O model implies a near-uniform distribution of small amounts of water throughout the mantle and thus eliminates the need for postulating new kinds of high-pressure hydrous phases.

INTRODUCTION

The question of availability of water plays a key role in petrologic discussions because aqueous fluids markedly influence melting phenomena and because they enable chemical transfer of rock constituents. The concentration and the distribution of water are especially critical in the mantle, as most magmas appear to be mantle-derived. The large number of recent investigations of high-pressure stability relationships of amphiboles and micas indicates the importance of this question. These two groups of hydrous minerals provide a possible mineralogical site for water in the upper mantle, but in what form does water occur beyond the stability limit of these phases? In what follows, we examine the hypotheses in the literature and propose an answer based on crystallo-chemical evidence.

WATER IN THE MANTLE: REVIEW OF CURRENT HYPOTHESES

Amphibole, Phlogopite, Titanoclinohumite

The occurrence of amphiboles and phlogopite as apparent primary constituents in peridotitic and eclogitic rocks suggests that these hydrous phases do have a field of stability within the mantle. A number of recent experimental studies fully support this inference. Green and Ringwood (1967, p. 805), Lambert and Wyllie (1968; 1970), Gilbert (1969), and Kushiro (1970) show that amphiboles of various

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compositions are expected to be stable at pressures and temperatures typical of the upper mantle, but that with increasing pressure, their breakdown temperature decreases. This eventual change in the slope of the breakdown curve, from positive to negative, is expected of other hydrous phases as well (Fyfe, 1970); it reflects the decreasing specific volume of water with increasing pressure. As with other hydrous phases, the condition $P(\text{H}_2\text{O}) < P(\text{total})$ serves to decrease the thermal stability of amphiboles at a given pressure. The existing data suggest, therefore, that amphiboles can provide suitable mineralogical sites for water only in the crust and uppermost mantle. Beyond maximum confining pressures of approximately 15 to 25 kbar, depending on composition, mantle amphiboles are expected to break down to the assemblage pyroxene + garnet + an aqueous gas phase (*e.g.*, Wyllie, 1970).

Recent data on the stability of phlogopite suggest that this hydrous phase probably persists beyond the stability limit of amphiboles (Kushiro, Syono, and Akimoto, 1967; Kushiro, 1970) so that its occurrence is to be considered seriously at confining pressures as high as 100 kbar if temperatures do not exceed 1100°C and if $P(\text{H}_2\text{O})$ approaches $P(\text{total})$. The field of stability of phlogopite, unlike that of most amphiboles, expands in gas-absent environments, because the "breakdown" consumes any available gas phase as a reactant and yields an alkaline melt in which water dissolves completely (Yoder and Kushiro, 1969). However, the amount of phlogopite in the upper mantle is limited by the low potassium content of mantle peridotites, so that phlogopite can have only local importance in the upper mantle (Oxburgh, 1964; Wyllie, 1970). Solid solution toward Na-phlogopite (Cárman, 1967) does not seem extensive in phlogopites from ultrabasic nodules (*e.g.*, Lovering and White, 1969).

The occurrence of titanoclinohumite in serpentized kimberlite microbreccia at Moses Rock, Utah, has prompted McGetchin, Silver and Chodos (1970) to propose humites as likely mineralogical sites of water in the mantle. Although well documented as discrete grains and as inclusions in pyrope in the Utah locality, titanoclinohumite has not been found as a conspicuous phase in other mantle-derived rocks, though a possibility exists that humites may have been misidentified as olivine. It seems more probable, however, that titanoclinohumite has only local importance in the upper mantle.

Intergranular Films

The experimental data reviewed above indicate breakdown of known hydrous phases in the uppermost portion of the mantle, proba-

bly at depths less than 100 km. On this basis, Wyllie (1970) suggests the existence of intergranular films of water in eclogite beyond the stability fields of amphiboles. The importance of these films is clear: they can act as media through which specific rock constituents may diffuse (Jahns, Martin, and Tuttle, 1969); their presence can also induce partial fusion of eclogites and peridotites under appropriate conditions of temperature, pressure, and rock composition. The widespread occurrence of CO₂ gas inclusions free of H₂O in the minerals of mantle-derived ultrabasic xenoliths (Roedder, 1965) suggests that CO₂ partitions strongly into a gas phase, although the partition may become less extreme at pressures above 15 kbar (Hill and Boettcher, 1970). In response to the ability of constituents of the low-melting fraction to diffuse through an intergranular film containing H₂O and CO₂, an interstitial melt presumably could form readily. Any silicate melt would dissolve H₂O in preference to CO₂, so that the residence of H₂O in an intergranular film may be short. The presence of such an interstitial silicate melt has been proposed to explain the low-seismic-velocity layer in the upper mantle (Ringwood, 1969; Wyllie, 1970).

"Hydroxylated" Pyroxene

The term "hydroxylated" has been applied to a solid solution in which SiO₄ tetrahedra are replaced by four OH groups. Hydroxylated pyroxenes and other hydroxylated silicates are often mentioned as sites for water below the low-seismic-velocity layer in the upper mantle, where rocks are supposedly in a subsolidus condition but devoid of intergranular aqueous films (Lambert and Wyllie, 1970; Fyfe, 1970). The high-pressure synthesis of hydroxylated pyroxenes described as isostructural with orthoenstatite and clinoenstatite has been claimed by C. B. Selar and coworkers (Selar, Carrison, and Stewart, 1967a; 1967b; Selar, 1970) but has not yet been proved by crystal-structure determinations. The authors assign to their run products the formula Mg₂SiH₄O₆ and propose the substitution of every second SiO₄ tetrahedron in the pyroxene chains by four OH groups. We consider this scheme of substitution highly improbable for two reasons which follow.

The authors invoke the case of hydrogarnet as an example of (OH)₄ substitution for SiO₄ groups. In hydrogarnets, such a scheme of substitution has been confirmed by X-ray and neutron diffraction studies and by second-moment nuclear magnetic resonance studies (Cohen-Addad, Ducros and Bertaut, 1967; Cohen-Addad, 1971; Donnay and Allerhand, 1965). The cell volume increases by 19 percent

from $(11.87\text{\AA})^3$ in grossularite (Abrahams and Geller, 1958) to $(12.57\text{\AA})^3$ in hydrogrossularite (Cohen-Addad *et al.*, 1967), which accompanies a 29 percent decrease in calculated densities based on the ideal formulae $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ and $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, respectively. No hydrogen bonding exists between individual OH groups, so that the four OH groups do not constitute one structural unit. Thus the term $(\text{OH})_4$ tetrahedron is, strictly speaking, a misnomer. The oxygen atoms lie at corners of a tetragonal tetrahedron (also called disphenoid, point symmetry $\bar{4}2m$). The four protons lie *outside* the oxygen tetrahedron at a distance of 0.4\AA from the nearest face. As a result, the sizes of $(\text{OH})_4$ and SiO_4 groups differ greatly. In $(\text{OH})_4$ the tetragonal tetrahedron has two edges of 3.17\AA , four edges of 3.39\AA , and a volume of 4.26\AA^3 . The mean O-O distance in the two SiO_4 tetrahedra in, say, pigeonite (Morimoto and Güven, 1970) is 2.66\AA , giving the SiO_4 group a volume of 2.22\AA^3 . The SiO_4 tetrahedron in a typical pyroxene thus occupies only 52 percent of the volume of the oxygen tetrahedron in the $(\text{OH})_4$ group. Moreover, high pressure would make the substitution of SiO_4 by $(\text{OH})_4$ even less likely.

Hydrogarnets contain isolated tetrahedra; in pyroxenes, which are chain silicates, the replacement of an SiO_4 tetrahedron by an $(\text{OH})_4$ group would be accompanied by a tremendous weakening of the chains of tetrahedra. If the oxygen atoms which link adjacent SiO_4 tetrahedra were replaced by OH, they would be involved only in hydrogen bonding with neighbouring SiO_4 tetrahedra. The resulting H--O bonds are several orders of magnitude weaker than Si-O bonds. Even replacement of fewer than half the number of SiO_4 tetrahedra would change the properties of any pyroxene drastically. Thus the inference that the hydroxylated orthopyroxenes and clinopyroxenes synthesized above 40 kbar, 1200°C and 100 kbar, 700°C , respectively, are isostructural with orthoenstatite and clinoenstatite contradicts crystallochemical arguments. This hydroxylation scheme must be considered equally unlikely when postulated for other mantle minerals, as was done by Fyfe (1970). Tetrahedral replacement of SiO_4 by $(\text{OH})_4$ is to be expected only in crystal structures containing isolated tetrahedra and in these, replacement would be expected only in near-surface, low pressure environments because of the marked increase in cell volume that might be expected for the hydroxylation reaction, in analogy with the grossularite-hydrogrossularite example given above. Even garnets in the mantle are unlikely to be hydrogarnets.

Quite a different type of $(\text{OH})_4$ for SiO_4 substitution has been described for hydrosodalite by Bukin and Makorov (1967). The $(\text{OH})_4$ group is said to be internally hydrogen-bonded and more compact.

Rather unusual O-H--O distances are reported and a neutron structure refinement appears imperative before this new type of (OH)₄ group can be profitably discussed.

WATER IN THE MANTLE: PROPOSED MODEL

Most workers in the field agree that the present atmosphere and hydrosphere formed by gradual degassing of the interior of the earth and that the process has not gone to completion (Rubey, 1955). Ringwood (1966, p. 325, 339) suggests that the amount of H₂O still within the earth exceeds that present in the atmosphere, hydrosphere, and sediments "by a substantial factor, perhaps about 5." If distributed over core and mantle, this water would amount to approximately 0.14 weight percent of the mantle; if it were found in the mantle alone, concentrations of 0.20 weight percent would be expected (Harris and Middlemost, 1969). Wyllie (1970, p. 26) proposed 0.1 percent H₂O in the mantle as a whole. A general mechanism is clearly required that will account for the widespread distribution of such small quantities of H₂O within the earth. As one of the requisites, such a mechanism should be independent of specific mantle phases, because they are not likely to be as widely distributed as the water.

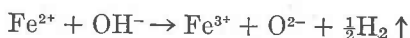
We submit that hydroxyl groups, to the extent of less than one weight percent H₂O+, replace oxygen atoms in certain crystallographic (Wyckoff) point-positions of the structures of nominally anhydrous mantle phases such as feldspars, garnets, olivines, spinels, and pyroxenes, or of their high-pressure breakdown products. The same phenomenon, OH-for-O substitution, is expected in the crust and can provide a general means of storing small quantities of H₂O in rocks at any depth. We find evidence for this type of substitution in: (a) the presence of H₂O+ in analyses of anhydrous minerals; (b) the improved structural formulae resulting from OH-for-O substitution; (c) valence-summation results, which in the past have led to the discovery by neutron diffraction of the type of limited substitution proposed here (Tippe and Hamilton, 1971); and (d) direct determination of OH, by infrared spectra for instance, in reputedly anhydrous minerals. Small amounts of OH substituting for O would not have been detected even in high precision X-ray refinement because of the low scattering power of protons and the very small effect, if any, that this substitution would have on cell dimensions.

H₂O+ in analyses of essentially anhydrous minerals

Compilations of the best available wet chemical analyses of common igneous and metamorphic minerals (Deer, Howie, and Zussman,

1963) show the scarcity of truly anhydrous silicates. Out of 47 plagioclase analyses (Deer, Howie, and Zussman, 1963, v. 4, pp. 108–120) for example, only one is reported to be water free: H_2O+ values reported separately in analyses of olivines, garnets, feldspars, nephelines and pyroxenes are not negligible (Fig. 1). We are well aware that H_2O+ values represent the least reliable data in wet chemical analyses. Nevertheless, the present-day practice of ignoring all H_2O+ for “dry” mineral analyses, and of considering all H_2O+ structural water for hydroxy minerals, is arbitrary. As an illustration, let us consider pyroxenes and amphiboles. The analytical techniques used for the two mineral groups are nearly the same; the OH environment, if we recognize that pyroxenes have some OH-for-O substitution, is similar in the two structure types. Thus, there is no reason for treating the reported H_2O+ of pyroxenes differently from that of amphiboles. Yet, in the interpretation of chemical analyses, the reported H_2O+ is systematically rejected as unreliable in the case of pyroxenes, whereas it is accepted as valid, fully converted to OH and seriously discussed in the case of amphiboles.

Kaersutite (Fig. 1) has been considered as a possible water-bearing mantle phase. Its typically low analytical H_2O+ content has been attributed to the reaction



which could take place upon heating in nature or in the laboratory. Wilkinson (1961) has, however, pointed out that the reported ferric iron content of kaersutites is low, so that the above explanation of its low H_2O+ appears an unlikely one. Even if all of the kaersutite H_2O+ is converted to OH, the idealized formula is closer to $AX_2Y_5Z_8O_{23}(OH, F)$ than to $AX_2Y_5Z_8O_{22}(OH, F)_2$, (Wilkinson, 1961). Thus a replacement of OH by O, the reverse substitution of the one which we propose for pyroxenes, is indicated here, and the evidence for it is taken from analytical values obtained for H_2O+ . Such anionic replacement of OH by O in hydroxy minerals in general has received considerable attention in the past (*e.g.*, Belov and Litvinskaya, 1966; Rimsaite, 1970).

Improved structural formulae

It is not necessary to rely on the analytical H_2O+ value in order to derive a structural formula that includes OH ions. The procedures we have used are illustrated with a feldspar and a pyroxene example. The feldspar formula heretofore has been routinely referred to 32 oxygen atoms per cell (Table 1). We choose instead to convert the

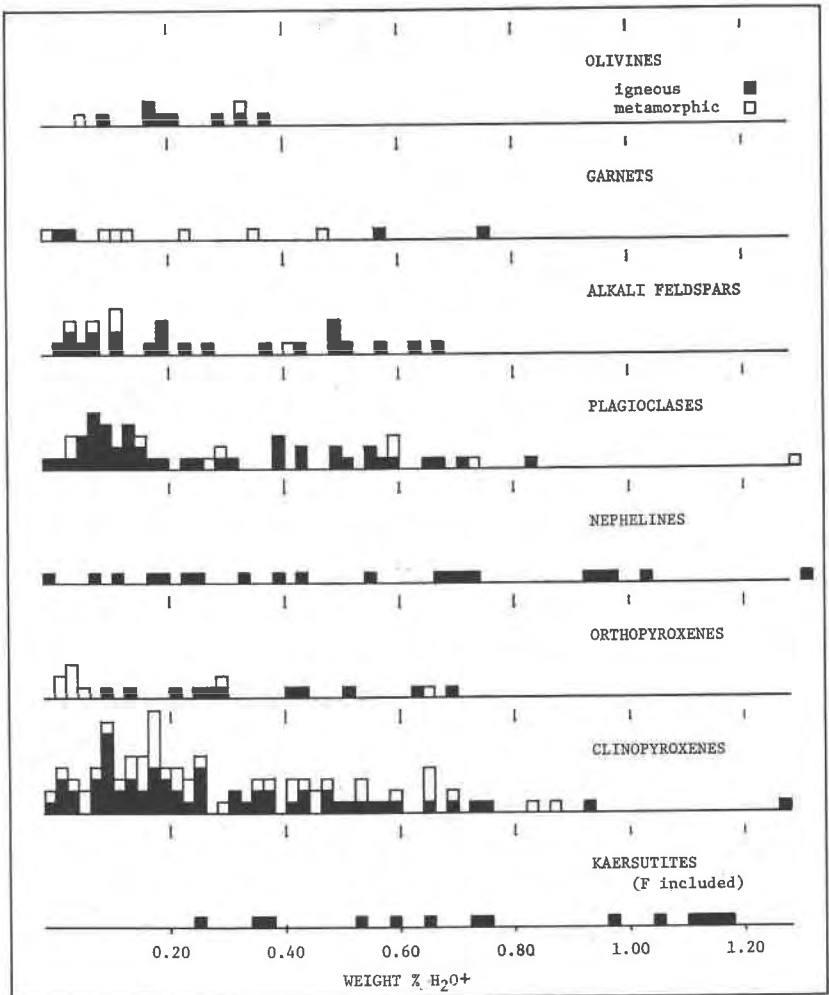


FIG. 1. Histogram showing H₂O⁺ reported in anhydrous igneous (black squares) and metamorphic minerals (open squares). Data on olivines, garnets, feldspars, nephelines, and pyroxenes are from the compilations of Deer, Howie, and Zussman, vol. 1, 2, and 4 (1962, 1963). Shown on the bottom line are H₂O⁺ values (F included when reported) for the amphibole kaersutite (Deer, Howie, and Zussman, vol. 2, 1963; Best, 1970). Note that on the basis of reported H₂O⁺ values, many nominally anhydrous phases contain as much water as do most kaersutites.

Table 1

Anorthite from volcanic tuff, Otaru City, Hokkaido, Japan				
Oxides	Wt%	Constituents of formula	No. of ions on the basis of	
			32 O	16 (Si +Al +Fe)
SiO ₂	43.79	Si	8.133	16.028
Al ₂ O ₃	35.79	Al	7.835	
Fe ₂ O ₃	0.43	Fe ³⁺	0.060	
MgO	0.33	Mg	0.091	3.969
CaO	18.69	Ca	3.720	
Na ₂ O	0.42	Na	0.152	
K ₂ O	0.03	K	0.006	* 0.114
H ₂ O+	0.59	OH	—	
H ₂ O-	0.06	O	32.000	
Total	100.13			31.886

* OH based on charge balance requirement combined with assumption of 32 anions per cell.

Takubo, J., anal.; quoted from Deer, Howie, & Zussman, 1963, v. 4, p.120, No. 5.

sum of tetrahedral cations, Si, Al, Fe³⁺, B, to 16 and to calculate the total cationic charge, including the charge from X = Na, K, Ca, that must then be balanced by 32 anions. The charge sum usually amounts to less than 64 by an amount Δ , say, which is set equal to the OH content, thus balancing the formula $X_xZ_{16} [O_{32-\Delta}(OH)_\Delta]$. The analytical value of x turns out to be equal to or less than 4.00; Δ values range from 0.01 to 0.30 for the analyses quoted in Deer, Howie, and Zussman, 1963, v. IV). The only assumption we have added to the usual one of full occupancy of anionic sites, is that of full occupancy of tetrahedral cation sites, which appears a justifiable one for a framework structure. The decision to consider only Al, B, and Fe³⁺ as admissible substituents for Si in feldspars rests on literature data for effective ionic radii and coordination numbers (Shannon and Prewitt, 1969).

To evaluate the hydroxyl content in the chemical formula of pyroxenes, without relying on the experimental H₂O+ value, requires a different approach from that used for the feldspars. This is so because the cation positions with coordination numbers 4, 6, and 8,

namely T , $M(1)$, and $M(2)$ in space group $C2/c$, are partly occupied by ions that are associated with more than one coordination number. Thus we cannot base the conversion from analysis to formula on any one cation point-position. Moreover, the slight omission solid solution known to occur occasionally in $M(2)$ sites rules out the use of the sum of all cations as a basis for conversion. The occupancy of the T sites can, however, be estimated from the known $T-O(2)$ distance (Clark, Appleman, and Papike, 1968; 1969), and the Si content thus obtained can be used to establish a conversion factor. The implicit assumption that Si is only 4-coordinated in pyroxenes is a safe one.

Other conversion factors must, of course, be selected for other mineral groups. In each case all available crystallochemical information must be taken into account to arrive at the best possible choice.

Valence-summation results

The correlation of bond valence with bond strength combined with Pauling's principle of local neutralization of charges, enables us to distinguish O^{2-} from OH^- and from H_2O in a crystal structure determined by X-rays (Donnay and Allman, 1970). In hydroxide and hydrate phases, anionic valence sums which deviate significantly from their expected integral values are indications of hydrogen bonding. By taking unbonded oxygen approaches into account, hydrogen bonds can be located as was shown in kernite (P. H. Coppens and G. Donnay, priv. comm.), in pumpellyite (Allmann and Donnay, 1971), and in haidingerite (Donnay and Donnay, 1972). If the compound is essentially anhydrous, a significant lowering of a valence sum from its ideal value is an indication of anion substitution, with an anion of lower valence replacing the one of higher valence, namely OH^- replacing O^{2-} in the cases we are considering here.

The tourmaline variety buergerite, although not a mantle mineral, may serve as an example. Its structure was accurately determined by Barton (1969). The substitution of OH and F for $O(3)$, a corner shared by two aluminum octahedra and one ferric iron octahedron, was indicated by the low valence sum of 1.64 v.u. associated with this anion (Table 2). Hydrogen bonding could not be called on to account for it since there were no OH groups or H_2O molecules available. The neutron-diffraction study of Tippe and Hamilton (1971) shows a proton peak corresponding to 8 percent atomic replacement of O by OH at the correct distance from $O(3)$, thus confirming OH -for- O substitution. Neutron diffraction cannot tell us about additional F -for- O substitution, because the scattering cross sections for O and F

Table 2
Valence Summation for buergerite, NaFe₃³⁺B₃Al₆Si₆O₂₇(O,F,OH)₄
R_{3m}, Z=3

Cations ^b		ix _{9a} in 9a	v ₁ Fe in 9b	iii _{9b} in 9b	v ₁ Al in 18c	iv _{9i} in 18e	Σv (V.O.)	Anton Chemistry
Antions ^c	in 9a	v.u. ^a	v.u. ^a	v.u. ^a	v.u. ^a	v.u. ^a		
iii	0(1) in 9a	2.111	3 ^d (0.352) 0.351				1.05	F ^e
iv	0(2) in 9b	2.517 (0.175) ^f 0.154	2.003 (0.502) 0.501	1.379 (0.980) 0.974			2.14	0 ^m
iii	0(3) in 9b		1.942 (0.597) 0.595		2 ^e 1.897 (0.523) 0.522		1.64	0 ^m , OH, F
iii	0(4) in 9b	2.788 (0.094) ^g 0.088				1.620	2.06	0 ^m
iii	0(5) in 9b	2.679 (0.124) 0.117		3		1.626	2.05	0 ^m
iii	0(6) in 18c		1.989 (0.522) 0.521		1.924 (0.485) 0.484	1.620	1.99	0 ^m
iii	0(7) in 18c				1.979 (0.409) 0.408	1.602	1.96	0 ^m
iii	0(8) in 18c				1.931 (0.425) 0.474		2.01	0 ^m
L(A) ^e		2.678	2.006	1.364	1.919	1.617		
L(B) ^e		3.149	2.365	(1.020) 1.013	(0.529) 0.527	1.618		
L(C) ^e		5.686	5.588	1.870	1.919	2.118		
v ₁ (v.u.)		1.107/9=0.123	2.989/6=0.498	3/3=1.000	2.951/6=0.492	3.956/4=0.989		
Σv (v.u.)		(1.179) 1.107	(2.997) 2.990	(3.020) 3.000	(2.936) 2.931	3.956		

are too similar. On the basis of valence sum and chemical considerations, it appears reasonable to add the small amount of F given by the chemical formula to this position.

The pyroxene omphacite may serve as a second, more pertinent example, although its neutron-diffraction study has not as yet been carried out. Its structure refinement has been reported by Clark *et al.* (1969) on a crystal from Hareidland, Norway. Using their occupancy assignments, the valence summation (Table 3) leads to a prediction of OH-for-O(2) substitution, since $\Sigma_c O(2)$ has a value of 1.76 v.u., which is significantly less than 2.00. The chemical analysis of J. Ito in Schmitt (1963) does show 0.50 wt percent H₂O+. The excess of 0.20 v.u. for the valence sum of O(3) is also of interest. It may be an indication of π bonding for this bridging oxygen atom since the angle Si-O(3)-Si is 137.5°, considerably larger than the other five angles (Table 3) subtended by Si and M(2) cations at O(3).

For many of the feldspars for which accurate structure data are available, valence sums tend to be low for the so-called OC position of monoclinic species and the OC(o) position of triclinic ones. The valence sums range from 1.80 to 1.89 v.u., and it is not certain that this is low enough for the fact to be significant. A recent, highly precise neutron study of a Lacher See sanidine (Brown, Hamilton, Prewitt, and Sueno, 1971) showed no evidence of the presence of protons. A neutron-diffraction study of a pegmatitic orthoclase from the Pala district of Southern California, selected because of its high analytical water content of 0.68 weight percent H₂O (S. Horska, priv. comm.), was performed by E. Prince. He reports (priv. comm.) that the amount of OH substituting for O in any one given position is below the observable amount, namely less than 3 atomic percent. It must be stressed in this connection that the need for accurate chemical



^a Occupancies and bond lengths from Barton (1969).

^b Na = 1/3 (Na_{2.49}Ca_{0.39}K_{0.05}□_{0.07}); Fe³⁺ = 1/9 (Fe³⁺_{5.99}Al_{2.65}Ti⁴⁺_{0.18}Mg_{0.08}Mn²⁺_{0.05}□_{0.05}) B = B; Al = 1/18 (Al_{16.32}Fe³⁺_{0.93}Fe²⁺_{0.56}Ti_{0.04}Mg_{0.02}Mn_{0.02}□_{0.11}) Si = 1/18 (Si_{17.20}B_{0.80}).

^c Cell content: 3[O₂₇(O_{2.51}F_{1.03}OH_{0.46})].

^d Superscript in upper left corner denotes number of bonds reaching anion.

^e Superscript in upper right corner denotes number of bonds reaching cation.

^f The valence strength in parentheses is the one obtained directly from the equations (Donnay and Allmann, 1970). Next to it is the normalized value.

TABLE 3. VALENCE SUMMATION FOR OMPHACITE, $M(1)M(2)Si_2O_6$ FROM HAREIDLAND, NORWAY^a
 $c_2/c_3; z=4$

Anions	Cations		viii		iv		$\sum v$		Anion Chemistry
	vi	vii	viii	iv	v	vi	vii	viii	
	M(1) in 4e O A	M(2) in 4e O A	M(2) in 4e O A	T in 8f λ	T in 8f λ	T in 8f λ	v.u.	v.u.	
iv	2.095	*	2.364	*	1.612				
0(1) in 8f	0.338 2.032	*	(0.257) ^c	0.255	(1.038)	1.036	2.01	0 ⁼	
iii	1.994	*	2.356	*	1.585				
0(2) in 8f	0.404		(0.260)	0.256	(1.097)	1.095	1.76	0 ⁼ , OH ⁻	
iv			2.512	*	1.657				
0(5) ^d in 8f			(0.205)	0.202	(0.947)	0.945	2.20	0 ⁼ π bonded	
			2.747		1.668				
			90.131	0.129	(0.925)	0.923			
\bar{L} (Å)	2.040		2.495		1.6305				
L_{max} (Å)	2.652		3.164		2.130				
p_i	3.446		3.729		3.264				
v_i	2.240/6=0.375		1.680/8=0.210		4.000/4=1.000				
$\sum v$ (v.u.)	2.242		(1.706)	1.680	(4.007)	3.999			

* Two bonds reaching cation

^aOccupancies and bond lengths from Clark et al. (1969).

^b $M(1) = Mg_{0.545}Al_{0.240}Fe^{2+}_{0.217}$

$M(2) = Ca_{0.590}Na_{0.320}Mg_{0.057}Fe^{2+}_{0.053}; T=Si$

^cThe valence strength in parentheses is the one obtained directly from the equations (Donnay and Allmann, 1970). Next to it is the normalized value.

^dBond angles subtended at O(5): Si-O(5)-Si=137.5°
 Si-O(5)-M(2)=101.6, 90.0, 117.2, 92.5°
 M(2)-O(5)-M(2)=113.8°

data and for a refined structure determination limits the applicability of the valence-summation procedure as a means of pinpointing OH-for-O substitution.

Direct determination of hydroxyl groups in near-anhydrous minerals

Neutron-diffraction studies have already been mentioned as a powerful direct method of determining the positions and occupancies of protons in crystal structures, provided, of course, that the percentage substitution of OH-for-O is sufficiently high in any one crystallographic position to lead to observable H positions in the difference map. This will require highly accurate neutron data, if

substitutions as low as 5 atomic percent are to be detected. Single crystal infrared absorption spectra provide a second experimental approach for ascertaining the presence of hydroxyl groups and their orientations. In this way, hydroxyl groups have been identified in forsteritic olivines and in pyroxenes (White and Keester, 1965). Professor J. Zemann and coworkers have surveyed many minerals and have reported the presence of OH in, for example, all three Al_2SiO_5 modifications (Beran and Zemann, 1969; Beran, 1970). Spectral study has been combined with thermogravimetric analyses to study quantitatively the concentration of hydroxyl groups in selected pyroxenes and garnets (W. A. Sabine and C. Frondel, priv. comm., 1970).

The presence of hydroxyl groups in natural and synthetic quartz has been proved with single-crystal infrared absorption spectra by a number of investigators (*e.g.*, Brunner, Wondratschek, and Laves, 1961; Bambauer, Brunner, and Laves, 1969). Dodd and Fraser (1965; 1967) have correlated the results of their spectral studies with changes in the coefficient of elastic wave attenuation, acoustic Q , and changes in indices of refraction; they found the zones rich in hydroxyl to be related to episodes of rapid crystal growth. The data of Ballman, Dodd, Kuebler, Laudise, Wood, and Rudd (1968) indicate that in their syntheses substitution of Fe^{3+} for Si^{4+} balances the OH-for-O replacement, the extent of which is always small, not exceeding a few hundred hydroxyl groups per million oxygen atoms. These low concentrations are not surprising since the introduction of one OH into the quartz structure greatly weakens the bond between the two affected, adjacent silicon tetrahedra. Indeed, if a limited amount of OH substitution is tolerated in quartz, a framework structure, larger amounts of such substitution may be expected for less highly polymerized silicates.

DISCUSSION

The small amounts of OH-for-O substitution proposed above can reasonably be expected to take place not only in silicate minerals, especially those with non-bridging oxygen atoms, but also in other oxide structures such as spinels and the modifications of TiO_2 (Beran and Zemann, 1971). An analogous substitution, SH-for-S, should be looked for in sulfides. Our model accounts for amounts of water in the range of 0.1 to 0.2 weight percent evenly distributed throughout the mantle, in contrast to models based on known hydrous phases, such as phlogopite and amphiboles, which are limited to the uppermost regions of the mantle. It also eliminates the need for postulating novel kinds of hydrous phases for the major portion of the mantle that lies below the low-seismic-velocity layer. The proposed anionic sub-

stitution, however, need not be restricted to the mantle. Water is plentiful in most crustal environments, so that crustal minerals may be expected to contain somewhat larger amounts of OH than their mantle analogues. For any chemically balanced substitution reaction, changes in partial molar volumes of reactants and products with increasing pressure will determine the influence of pressure on our mechanism (W. T. Holser, priv. comm., 1971). The small extent of OH-for-O substitution proposed would lead to very small increases or decreases in molar volumes of crystalline phases, depending on which compensating cation substitution is proposed.

Determination of distribution coefficients of OH between crystal and coexisting fluid may provide a direct estimate of the activity of water at the time of formation of specific crustal or mantle assemblages. Also of importance to petrologists is the range of temperatures at which the small amounts of structurally bound water could be released from nearly anhydrous minerals. As mentioned above, some OH may be involved in internal oxidation reactions upon heating if the mineral contains, for example, ferrous iron. Where this is not the case, however, release of hydroxyl is to be expected only upon destruction of the crystal structure near the solidus temperature. A reliable H_2O+ analysis should therefore use a flux to ensure destruction of the structure. Differential thermal analysis and thermogravimetric analysis, performed on a portion of the same specimen, should help distinguish tightly bound chemisorbed water from structural hydroxyl groups.

The present proposal supersedes the concept of completely anhydrous mineral structures: limited anion substitution may be as universal as cation substitution. Many detailed studies, especially structure refinements by neutron diffraction, will be needed fully to establish the nature of water in rock-forming minerals and to give information on the limits of solubility of OH in different structure types. May we venture the hope that our paper will lure other investigators into this field of study.

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REFERENCES

- ABRAHAMS, S. C., AND S. GELLER (1958) Refinement of the structure of a grossularite garnet. *Acta Crystallogr.* 11, 437-441.

- ALLMANN, R., AND GABRIELLE DONNAY (1971) Structural relations between pumpellyite and ardennite. *Acta Crystallogr.* **B27**, 1871-1875.
- BALLMAN, A. A., D. M. DODD, N. A. KUEBLER, R. A. LAUDISE, D. L. WOOD, AND D. W. RUDD (1968) Synthetic quartz with high ultraviolet transmission. *Appl. Opt.* **7**, 1387-1390.
- BAMBAUER, H. U., G. O. BRUNNER, AND F. LAVES (1969) Light scattering of heat-treated quartz in relation to hydrogen-containing defects. *Amer. Mineral.* **54**, 718-724.
- BARTON, RANDOLPH, JR. (1969) Refinement of the crystal structure of buergerite and the absolute orientation of tourmalines. *Acta Crystallogr.* **B25**, 1524-1533.
- BELOV, J. V., AND G. P. LITVINSKAYA (1966) New ideas about isomorphic substitutions. *Vest. Moskovskovo Univ., Ser. IV*, **6**, 17-27 (in Russian).
- BERAN, A. (1970) Ultrarotspektroskopischer Nachweis von OH-Gruppen in den Mineralen der AlSiO-Modifikationen. *Anz. math.-naturwiss. Kl. Osterr. Akad. Wiss.* Nr. 10, 184-185.
- , AND J. ZEMANN (1971) Messung des Ultrarot-Pleochroismus von Mineralen. XI. Der Pleochroismus der OH-Streckfrequenz in Rutil, Anatas, Brookit und Cassiterit. *Tschermaks Mineral. Petrogr. Mitt.* **15**, 71-80.
- BEST, M. G. (1970) Kaersutite-peridotite inclusions and kindred megacrysts in basanitic lavas, Grand Canyon, Arizona. *Contrib. Mineral. Petrology*, **27**, 25-44.
- BROWN, G. E., W. C. HAMILTON, C. T. PREWITT, AND S. SUENO (1971) Neutron diffraction study of Al/Si ordering in sanidine (abstr.) *Geol. Soc. America, Abstr. Progr.* **3**, 514.
- BRUNNER, G. O., H. WONDRAUSCHKEK, AND F. LAVES (1961) Ultrarotuntersuchungen uber den Einbau von H in natuerlichen Quarz. *Z. Elektrochem.* **65**, 735-750.
- BUKIN, V. I., AND YE. S. MAKAROV (1967) Crystal structure of hydrosodalite according to neutron diffraction analysis. *Geochemistry*, **4**, 19-28.
- CARMAN, J. H. (1967) The high- and low-temperature stability of sodium-phlogopite $\text{NaMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ (abstr.) *Trans. Amer. Geophys. Union*, **48**, 224-225.
- CLARK, JOAN R., DANIEL E. APPLEMAN, AND J. J. PAPIKE (1968) Bonding in eight ordered clinopyroxenes isostructural with diopside. *Contrib. Mineral. Petrology*, **20**, 81-85.
- , ———, AND ——— (1969) Crystal-chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Amer. Spec. Pap.* **2**, 31-50.
- COHEN-ADDAD, CLAUDINE (1971) Etude du composé $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_{1.15}(\text{OH})_{7.4}$ par absorption infrarouge et diffraction des rayons X et des neutrons. *Acta Crystallogr.* **A27**, 68-70.
- , P. DUCROS, AND E. F. BERTAUT (1967) Etude de la substitution du groupelement SiO_4 par $(\text{OH})_4$ dans les composés $\text{Al}_2\text{Ca}_2(\text{OH})_{12}$ et $\text{Al}_2\text{Ca}_2(\text{SiO}_4)_{2.15}(\text{OH})_{3.36}$ de type grenat. *Acta Crystallogr.* **23**, 220-230.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962; 1963) *Rock-forming Minerals*, **1**, **2**, and **4**. John Wiley and Sons Inc., New York, N. Y.
- DODD, D. M., AND D. B. FRASER (1965) The 3000-3900 cm^{-1} absorption bands and anelasticity in crystalline α -quartz. *J. Phys. Chem. Solids* **26**, 673-686.
- , AND ——— (1967) Infrared studies of the variation of H-bonded OH in synthetic α -quartz. *Amer. Mineral.* **52**, 149-160.
- DONNAY, GABRIELLE, AND A. ALLERHAND (1965) Possible application of nuclear

- magnetic resonance to order-disorder studies in the hydrogrossularite series. *Carnegie Inst. Wash. Year Book*, **64**, 210-212.
- , AND R. ALLMANN (1970) How to recognize O^{2-} , OH^- , and H_2O in crystal structures determined by X-rays. *Amer. Mineral.* **55**, 1003-1015.
- DONNAY, J. D. H., AND GABRIELLE DONNAY (1972) Haidingerite II. From valence summation to hydrogen bonding. *Kristall Technik*, **7**, 17-20.
- FYFE, W. S. (1970) Lattice energies, phase transformations, and volatiles in the mantle. *Phys. Earth Planet. Interiors*, **3**, 196-200.
- GILBERT, M. C. (1969) Reconnaissance study of the stability of amphiboles at high pressure. *Carnegie Inst. Wash. Year Book*, **67**, 167-170.
- GREEN, D. H., AND A. E. RINGWOOD (1967) An experimental investigation of the gabbro to eclogite transformation and its petrological application. *Geochim. Cosmochim. Acta*, **3**, 767-833.
- HARRIS, P. G., AND E. A. K. MIDDLEMOST (1969) The evolution of kimberlites. *Lithos*, **3**, 77-88.
- HILL, R. E. T., AND A. L. BOETCHER (1970) Water in the Earth's mantle: melting curves of basalt-water and basalt-water-carbon dioxide. *Science*, **167**, 980-982.
- JAHNS, R. H., R. F. MARTIN, AND O. F. TUTTLE (1969) Origin of granophyre in dikes and sills of tholeiitic diabase. (abstr.) *Trans. Amer. Geophys. Union*, **50**, 337.
- KUSHIRO, I. (1970) Stability of amphibole and phlogopite in the upper mantle. *Carnegie Inst. Wash. Year Book*, **68**, 245-247.
- , Y. SYONO, AND S. AKIMOTO (1967) Stability of phlogopite at high pressures and possible presence of phlogopite in the earth's upper mantle. *Earth Planet. Sci. Lett.* **3**, 197-203.
- LAMBERT, I. B., AND P. J. WYLLIE (1968) Stability of hornblende and a model for the low-velocity zone. *Nature*, **219**, 1240-1241.
- , AND P. J. WYLLIE (1970) Melting in the deep crust and upper mantle and the nature of the low-velocity zone. *Phys. Earth Planet. Interiors*, **3**, 316-322.
- LOVERING, J. F., AND A. J. R. WHITE (1969) Granulitic and eclogitic inclusions from basic pipes at Delegate, Australia. *Contrib. Mineral. Petrology*, **21**, 9-52.
- MARTIN, R. F., AND GABRIELLE DONNAY (1971) Is water ubiquitous in the upper mantle? (abstr.) *Trans. Amer. Geophys. Union*, **52**, 370.
- MCGETCHIN, T. R., L. T. SILVER, AND A. A. CHODOS (1970) Titanoclinohumite: a possible mineralogical site for water in the upper mantle. *J. Geophys. Res.* **75**, 255-259.
- MORIMOTO, N., AND N. GÜVEN (1970) Refinement of the crystal structure of pigeonite. *Amer. Mineral.* **55**, 1195-1209.
- OXBURGH, E. R. (1964) Petrological evidence for the presence of amphibole in the upper mantle and its petrogenetic and geophysical implications. *Geol. Mag.* **101**, 1-19.
- RIMSAITE, J. (1970) Structural formulae of oxidized and hydroxyl-deficient micas and decomposition of the hydroxyl group. *Contrib. Mineral. Petrology*, **25**, 225-240.
- RINGWOOD, A. E. (1966) The chemical composition and origin of the earth. In P. M. Hurley (ed.) *Advances in Earth Science*. MIT Press, Cambridge, Mass. p. 287-356.
- (1969) Composition and evolution of the upper mantle. *Amer. Geophys. Union, Monogr.* **13**, 1-70.

- ROEDDER, E. (1965) Liquid CO₂ inclusions in olivine-bearing nodules and phenocrysts from basalts. *Amer. Mineral.* **50**, 1746-1782.
- RUBEY, W. W. (1955) Development of the hydrosphere and atmosphere with special reference to probable composition of the early atmosphere. *Geol. Soc. Amer. Spec. Pap.* **62**, 631-650.
- SCHMITT, H. H. (1963) *Petrology and Structure of the Eiksundsdal Eclogite Complex, Hareidland, Sunnmøre, Norway*. Ph. D. Thesis, Harvard Univ.
- SCLAR, C. B. (1970) High-pressure studies in the system MgO-SiO₂-H₂O. *Phys. Earth Planet Interiors*, **3**, 333.
- , L. C. CARRISON, AND O. M. STEWART (1967a) High-pressure synthesis of a new hydroxylated pyroxene in the system MgO-SiO₂-H₂O. (abstr.) *Trans. Amer. Geophys. Union*, **48**, 226.
- , ———, AND ——— (1967b) High-pressure synthesis and stability of hydroxylated clinoenstatite in the system MgO-SiO₂-H₂O. (abstr.) *Geol. Soc. Amer. Spec. Pap.* **115**, 198.
- SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925-946.
- TIPPE, ARMIN, AND WALTER C. HAMILTON (1971) A neutron-diffraction study of the ferric tourmaline buergerite. *Amer. Mineral.* **56**, 101-113.
- WHITE, W. B., AND K. L. KEESTER (1965) Optical absorption spectra of iron in the rock-forming silicates (abstr.) *Amer. Crystallogr. Assoc. Meet. Abstr.* **II-2**.
- WILKINSON, J. F. G. (1961) Some aspects of the calciferous amphiboles, oxyhornblende, kaersutite, and barkevikite. *Amer. Mineral.* **46**, 340-354.
- WYLLIE, P. J. (1970) Ultramafic rocks and the upper mantle. *Mineral. Soc. Amer. Spec. Pap.* **3**, 3-32.
- YODER, H. S., AND I. KUSHIRO (1969) Melting of a hydrous phase: phlogopite. *Amer. J. Sci.* **267-A** (Schairer volume), 558-582.

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