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# THE PRESENCE OF HCl IN SCAPOLITES

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## ABSTRACT

The role of hydrogen in scapolite has not as yet been explained. We observe that the anionic valence sums of marialite scapolite are deficient by about 1 *v.u.* for the position predominantly occupied by chlorine. The presence of HCl molecules rather than $Cl^-$ anions can explain this phenomenon as well as the role played by $H^+$ in marialite. To test this hypothesis we obtained infrared spectra on representative samples; the HCl bands were observed. Laser Raman spectra also show the characteristic HCl band at about 2900 $cm^{-1}$ on several samples and on different portions of the same sample. The low water content of scapolites reported throughout the mineralogical literature presented a problem, as it did not provide enough protons to form HCl. However, we have measured water contents in excess of 1 ± 0.05 wt.%, quite sufficient to neutralize the $Cl^-$ ions.

## SOMMAIRE

Le rôle de l'hydrogène dans la scapolite n'a pas encore été élucidé. Le bilan anionique des valences dans les marialites accuse une déficience d'environ 1 *u.v.* dans la sommation des valences qui aboutissent à la position qu'occupe le chlore. La présence de molécules HCl, au lieu d'ions $Cl^-$, expliquerait ce phénomène ainsi que le rôle de l'hydrogène. Nous avons obtenu, sur échantillons typiques, des spectres infrarouges qui montrent les bandes de HCl, étayant ainsi l'hypothèse. Les spectres Raman laser montrent la bande caractéristique de HCl, à ~2900 $cm^{-1}$, dans plusieurs échantillons et en différentes parties d'un même échantillon. La faible teneur en eau, notoire dans les analyses publiées, faisait craindre une insuffisance de protons pour former le HCl, mais de nouvelles analyses nous ont donné des pourcentages d'eau (en poids) de plus de 1 ± 0.05%, très suffisants pour neutraliser les ions $Cl^-$

## INTRODUCTION

Since the publication of Shaw's classical papers on the geochemistry of scapolite (1960), the role of protons in the scapolite structure has baffled mineralogists and crystallographers. Shaw, in the first of these two papers (1960, p. 243), explicitly states, "It is not possible yet to write a structural formula for scapolite," but offers, as "the simplest general formula" for the theoretical marialite end-member, $Na_4[Si_9Al_3O_{24}]Cl$. He continues, "In addition, the possibility should be borne in mind that $OH^-$ may substitute for $O^=$ in the silicate network" (read *aluminosilicate framework).* Such a substitution, however, would disrupt the framework structure locally, as no hydroxyl ion can be bonded to *two* tetrahedral cations, be they both Si atoms, both Al atoms or one of each. In every case the bond-valence sum exceeds the formal valence of OH(-1) by too large an amount. Shaw goes on to explain (p. 244) his "calculation procedure" for converting the chemical analyses (performed by C. O. Ingamells) to formulae: "(*v*) . . . H was not included in the AN (= Cl+C+S+F), owing to uncertainty in its allocation . . .; (*viii*) Any remaining metal was allocated H for OH, in the case of Na and K, or $H_2$ for $(OH)_2$ with Ca, Mg, Fe, Mn and Ti; . . . (*ix*) Residual H was discarded."

In the crystal-structure refinements that followed the appearance of Shaw's papers (Papike & Zoltai 1965, Lin & Burley 1973, Levien & Papike 1976, Peterson 1977), the first three

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*To my relentless, perfectionistic team mate J.D.H.D., in happy expectation of many more years of full-time cooperation.

TABLE 1. ANIONIC BOND-VALENCE SUMS OF MARIALITE ON-8*

| Cations<br>Anions | $^{viii}\left[\begin{matrix}\mathrm{Na}_{0.73}\mathrm{Ca}_{0.18}\\ \mathrm{K}_{0.05}\ \square_{0.04}\end{matrix}\right]$ | $^{iv}\mathrm{Si}_{1.00}$ $T(1)$ | $^{iv}(\mathrm{Al}_{0.65}\mathrm{Si}_{0.35})$ $T(2)$ † | $^{iv}(\mathrm{Si}_{0.73}\mathrm{Al}_{0.27})$ $T(3)$ † | $\Sigma_C v$ (v.u.) |
|---|---|---|---|---|---|
| $^{ii}$O(1) |  | 1.594(5) Å<br>1.027(9) v.u.<br>1.607(5)<br>1.002(9) |  |  | 2.03(1) |
| $^{iii}$O(2) | 2.350(6) Å<br>(0.426)0.404 v.u. |  | 1.688(5)<br>0.845(8) | 1.644(5)<br>0.944(9) | 2.19(2) |
| $^{iii}$O(3) | 2.516(7)<br>(0.248)0.235 |  | 1.693(7)<br>0.837(11) | 1.646(7)<br>0.941(12) | 2.01(2) |
| $^{iii}$O(4) | 2.500(7)<br>(0.261)0.248 |  | 1.690(7)<br>0.841(11) | 1.639(7)<br>0.954(13) | 2.04(2) |
| $^{iv}$O(5) | 2.868(6)<br>(0.071)0.067<br>2.817(7)<br>(0.092)0.087 | 1.612(6)<br>0.992(11) | 1.699(6)<br>0.827(9) |  | 1.97(1) |
| $^{iv}$O(6) | 2.882(7)<br>(0.065)0.062<br>2.945(6)<br>(0.038)0.037 | 1.619(6)<br>0.979(11) |  | 1.673(7)<br>0.892(12) | 1.97(2) |
| $^{iv}$Cl$^-$etc. | 3.021(7)<br>0.000 |  |  |  | 0.00 |
| $\bar{L}$ (Å) | 2.697 for O's only | 1.608 | 1.6925 | 1.6505 |  |
| $L_{\max}$(Å) | 3.036 " " " | 2.130 | 2.2145 | 2.165 |  |
| $p$ | 7.956 " " " | 3.080 | 3.242 | 3.208 |  |
| $v_i$(v.u.) | 1.140/8 | 1.000 | 0.8375 | 0.9325 |  |
| N.F. | 0.949 for O's only |  |  |  |  |
| $\Sigma_A v$ (v.u.) | 1.140 " " " | 4.000 | 3.350 | 3.730 |  |

* Sample analyzed and described by Shaw (1960); bond lengths from Lin & Burley (1973). Shaw's formula was used to calculate $L_{\max}$ and $v_i$: $(\mathrm{Na}_{0.73}\mathrm{Ca}_{0.18}\mathrm{K}_{0.05}\square_{0.04})_{\Sigma 1}\left[\mathrm{Si}_{1.00}(\mathrm{Al}_{0.65}\mathrm{Si}_{0.35})(\mathrm{Si}_{0.73}\mathrm{Al}_{0.27}\right]_{\Sigma 4}\left[\mathrm{O}_{5.89}(\mathrm{OH})_{0.11}\right]_{\Sigma 6}\left[\mathrm{Cl}_{0.18}(\mathrm{CO}_3)_{0.05}\square_{0.02}\right]_{\Sigma 1/4}$.

† Occupancies by Si and Al determined from $\bar{L}$ relation given for aluminosilicate framework structures by Ribbe & Gibbs (1969).

of which were performed on specimens described by Shaw, no attention was paid to the role played by the hydrogen atoms in the structure; no hydrogen atoms were located on difference electron-density maps. To investigate the role of hydrogen, one of us (G.D.) studied the anionic bond-valence sums of Shaw's ON-8 marialite sample, using the bond lengths found by Lin & Burley (1973), for want of better marialite data (Table 1). The atomic coordinates had unfortunately been obtained from a least-squares refinement based on a chemical formula (p. 1273) different from that given by Shaw (1960, p. 241), for reasons that are not explained. Deer *et al.* (1963, p. 324) give the Shaw formula, which we check to two decimal places. The bond-valence sums prove satisfactory, except for the position occupied predominantly by chlorine; the bond lengths suggest that chlorine receives practically no bonds from tetrahedral or from eight-coordinated cations. The low bond-valence sum for chlorine (Table 1) can only be explained by proposing molecular HCl in the channels of the structure, a hypothesis that also accounts for the role of hydrogen in scapolite. The findings are reminiscent of a similar situation found in apophyllite, $\mathrm{KCa_4(Si_4O_{10})_2F_{1-x}(HF)_x(H_2O)_{8-x}(OH)_x}$ with $x \sim 1$ (Prince 1971), where a neutron refinement of the structure revealed a proton adjacent to fluorine, and a mass-spectrometric analysis (performed by T. C. Hoering & G.D. at the Geophysical Laboratory; *in* Prince 1971), confirmed the presence of molecular HF.

## EVIDENCE FOR PRESENCE OF HCl

The calculation of an anionic bond-valence sum, as presented by Donnay & Allmann (1970), involves only one anionic species — oxygen. Here, however, we are dealing with chlorine, besides oxygen, and the procedure must be modified. The presence of 20 ionic percent of $\mathrm{CO_3}$ in the Cl position does not affect the procedure: the oxygen ions of the carbonate group are at normal Na–O distances. We ignore the carbonate substitution for that reason.

The eight-coordinated cation (Na,Ca,...)$^{1.14+}$ that heads column 1, Table 1, forms seven bonds with oxygen ions and presumably one more with the hypothetical chlorine ion, a bond that is reported to be 0.10Å longer than the sum of the Shannon (1976) radii for $^{viii}\mathrm{Na}^+$ and $^{iv}\mathrm{Cl}^-$.

Because of the large difference, namely 0.36Å, between the oxygen and chlorine effective ionic radii, the mean bond-length $\bar{L}$, the maximum bond-length $L_{max}$ and the exponent $p$ are evaluated for the seven Na–O bonds first, although the ideal bond valence $v_i$ remains 1.140/8. When this is done, the sum of only the seven Na–O bond valences, 1.201*v.u.*, already exceeds the cationic formal valence, 1.140*v.u.*, so that there is no bond valence left over to assign to the Na–Cl bond. Instead a normalization factor, *N.F.*, of 0.949 is needed to reduce the bond-valence sum to its required value, even with a zero Na–Cl bond valence. The resulting anionic bond-valence sums (Table 1, last column) are in the normal range, falling between 1.97 and 2.04*v.u.*, with the exception of the O(2) value of 2.19*v.u.*, which is close to the upper limit observed in silicate structures. The surprisingly short Na–O(2) bond length of 2.350(6)Å, together with the *T*(2)–O(2) and *T*(3)–O(2) bond lengths, both of which are less than their $\bar{L}$ value, accounts for this high anionic bond-valence sum and forms the most interesting structural feature of scapolites. That this feature is not restricted to specimen ON-8 can be gathered from a recent refinement of a 77% meionite specimen (Peterson 1977); it shows a similarly short Ca–O(2) bond length of 2.351(1)Å, 0.13Å less than the sum of the radii, as compared with a Na–O(2) value of 2.350Å for ON-8, 0.17Å less than the sum of radii.

The conclusion to be drawn from Table 1 is that a bond valence of zero *v.u.* best describes the Na–Cl "bond", a conclusion that would be unacceptable if chlorine were present as a $Cl^-$ ion, the pair of ions $Na^+$ and $Cl^-$ having an electronegativity difference of 2.1 units and forming strong ionic bonds in, say, NaCl. If, however, chlorine is present in molecular HCl, its bond-valence sum as well as the structural role of hydrogen in scapolite are explained.

Table 2 gives an alternate way of checking the bonding role of chlorine in the structure; the cationic bond-valence sums are here calculated with chlorine assumed to be present as $Cl^-$. Abnormally large deviations from the formal cationic valence sums would indicate this assumption to be erroneous. All oxygen atoms but O(1) present a problem similar to that of the alkali ion in Table 1, because they are bonded to Na as well as to two tetrahedral cations. We treat them the way the alkali ion was treated above; $\bar{L}$, $L_{max}$ and $p$ are calculated for the tetrahedral bonds alone but their $v_i$s are based on *all* bonds formed by oxygen atoms. The $(OH)_{0.11}$ appearing in the formula (Table 1, first footnote) is assigned to O(6) because it re-

TABLE 2. CATIONIC BOND-VALENCE SUMS OF MARIALITE ON-8

| Anions<br>Cations | $^{ii}O(1)$ | $^{iii}O(2)$ | $^{iii}O(3)$ | $^{iii}O(4)$ | $^{iv}O(5)$ | $^{vi}O(6)$<br>$O_{0.89}OH_{0.11}$ | $^{iv}Cl^-$ *etc* | $\sum_A v$(v.u.) | Formal anion charge | Δ(v.u.) |
|---|---|---|---|---|---|---|---|---|---|---|
| $^{viii}$Na *etc.* | - | 2.350(6)Å<br>(0.404v.u.)<br>0.465 | 2.516(7)<br>(0.235)<br>0.299 | 2.500(7)<br>(0.248)<br>0.313 | 2.868(6)<br>(0.067); 0.116<br>2.817(7)<br>(0.087); 0.150 | 2.882(7)<br>(0.059); 0.107<br>2.945(6)<br>(0.035); 0.064 | 3.021(7)$^4$<br>0.250(4) | 1.51 | 1.14 | 0.37 |
| *T*(1) | 1.595(5)<br>1.012(9)<br>1.607(5)<br>0.988(9) | | | | 1.612(6)<br>(0.545)<br>0.942 | 1.619(6)<br>(0.499)<br>0.907 | | 3.85 | 4.00 | -0.15 |
| *T*(2) | - | 1.688(5)<br>(0.639)<br>0.735 | 1.693(7)<br>(0.637)<br>0.812 | 1.690(7)<br>(0.635)<br>0.802 | 1.699(6)<br>(0.458)<br>0.792 | | | 3.14 | 3.35 | -0.21 |
| *T*(3) | - | 1.644(5)<br>(0.695)<br>0.800 | 1.646(7)<br>(0.698)<br>0.889 | 1.639(7)<br>(0.701)<br>0.885 | | 1.673(7)<br>(0.447)<br>0.812 | | 3.39 | 3.73 | -0.34 |
| *$\bar{L}$(Å) | 1.601 | 1.666 | 1.670 | 1.665 | 1.656 | 1.646 | 3.021 | | | |
| *$L_{max}$(Å) | 2.130 | 2.190 | 2.190 | 2.190 | 2.172 | 2.148 | 3.490 | | | |
| *$p$ | 3.023 | 3.179 | 3.212 | 3.171 | 3.209 | 3.279 | - | | | |
| $vi$(v.u.) | 2/2 | 2/3 | 2/3 | 2/3 | 2/4 | 1.89/4 | 1/4 | | | |
| $\sum_c v$(v.u.) | 2.000 | 1.738 | 1.570 | 1.584 | 1.157 | 1.040 | 1.000 | | | |
| *N.F.* | 1.000 | 1.151 | 1.274 | 1.263 | 1.729 | 1.817 | 1 | | | |
| $\sum_c v$(v.u.) | 2.000 | 2.000 | 2.000 | 2.000 | 2.000 | 1.890 | 1.000 | | | |

* Calculated for O-*T* bonds only

$L_{max}$ is the weighted mean average of the appropriate values for *T*(1), *T*(2) and *T*(3) (see Table 1).

[4] The superscript indicates the multiplicity of the bond evaluated at $Cl^-$.

ceives much the lowest bond-valence sum. Its $v_i$ value is thus reduced to 1.89/4. The O–Na bond valences are transferred from Table 1. When they are added to the calculated O–*T* bond valences, the anionic sums turn out to be appreciably too low (their values, not usually listed, are here given in the antepenultimate row of Table 2), so that the normalization factors (*N.F.*) become correspondingly high. The cationic bond-valence sums of Na and *T*(3) are certainly unacceptable values, as expected if the $Cl^-$ assumption is incorrect.

## EXPERIMENTAL PROCEDURES

As neither structure refinement by neutron diffraction nor mass-spectrometric data on scapolite were available to us, we approached Professor J. Zemann (Vienna) with a request for infrared analysis of the ON–8 sample kindly supplied to us by Lin & Burley. Dr. Zemann passed the sample to Dr. A. Beran who observed the HCl bands without difficulty. The spectrum should routinely have been repeated after all the hydrogen in the sample was replaced by deuterium. Unfortunately, scapolite resists deuteration so that the check could not be carried out, and the results could not be considered conclusive.

We then turned to laser Raman spectroscopy. The spectra were recorded at room temperature on a Jarrell–Ash 25-300 spectrometer equipped with a photon-counting detection system, using the yellow 514.5 nm line of an $Ar^+$ laser (Coherent Radiation Ltd., model 52G) for excitation. The laser power at the sample was 200–400 mW. A small piece of a scapolite crystal was pressed manually into the surface of a ball of wax mounted on an X-ray goniometer head. In all, twelve spectra were recorded from two representative chlorine-rich scapolite crystals, one of which was ON–8. Different mounting waxes were used, and the laser beam was focused onto different positions on the surface of the crystal. All the samples gave extremely strong fluorescence backgrounds and consequently high count rates, and very slow scan speeds were necessary to obtain the spectra. The bands, which were clearly discernible (±3cm$^{-1}$) above the background for each sample (under the appropriate instrumental settings), are as follows: ~ 2900 (w, br), ~1100(vw,br), 770(vw,br), 540 (m), 460(s), 290(vw,br), 260(w), 160(m), 50(vvs) cm$^{-1}$. The 2900 cm$^{-1}$ band (Fig. 1) is of particular interest here. The existence of this weak, broad peak on top of the strong fluorescence background (1200–3400 cm$^{-1}$) was clearly established by its appearance in all the spectra recorded, including duplicate scans. The use of different mounting waxes ensured that this band was not an artifact resulting from one of the waxes. We attribute the 2900 cm$^{-1}$ band to the presence of small amounts of HCl in the scapolite crystals; the characteristic band for diatomic HCl occurs at 2886 cm$^{-1}$. The origin of the strong fluorescence in Figure 1 is unclear; this is an everyday problem in Raman spectroscopy, particularly where polymers and minerals are concerned.

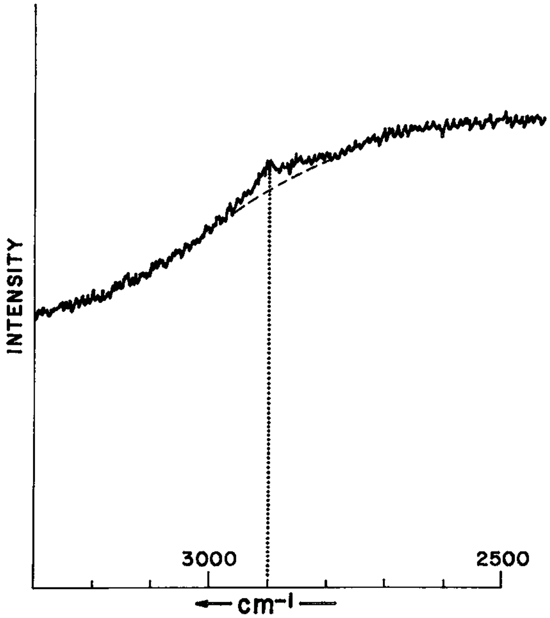

FIG. 1. Laser Raman spectrum of scapolite ON–8 in the 3300–2500 cm$^{-1}$ region. Conditions: $Ar^+$ excitation, 514.5 nm (400 mW); slit widths, 5 cm$^{-1}$ time constant 4 sec; scan speed, 20 cm$^{-1}$ min$^{-1}$.

The low $H_2O$ values reported for scapolites in the literature probably reflect the higher than normal temperatures required to free the pro-

TABLE 3. $H_2O$ AND $CO_2$ CONTENTS OF REPRESENTATIVE SCAPOLITES*

| ROM No. | Locality | wt. % $H_2O$ | wt. % $CO_2$ |
|---|---|---|---|
| M33540 | Hwy #507, 0.8 km south of Gooderham, Haliburton Co. Ont. | 1.03 | 1.07 |
| M33132 | Lot 40, Range "D" South, Grattan Tp., Renfrew Co. Ont. | 1.06 | 4.03 |
| M23661 | Pusunsaari, Pitkaranta, Finland | 0.89 | 3.71 |
| M16647 | Lots 24 & 25, Conc. VI, Monteagle Tp. Hastings Co. Ont. | 0.36 | 1.59 |

* Specimen ON-8 was not available for water determination. An accuracy of ±0.05 wt. % is associated with $H_2O$ contents.

tons from the HCl molecules in the channels. The present method of water determination eliminates such pitfalls as follows: the sample is weighed into a molybdenum foil which is shut mechanically and placed into a platinum bucket suspended in a glass apparatus. The apparatus is evacuated at 150°C overnight to remove all adsorbed water. The sample is then decomposed by induction heating to 1500°C, with $CO_2$, $H_2O$ and HCl being condensed at liquid-nitrogen temperature. Any non-condensable gases are pumped away after exposure to CuO at 500°C to oxidize CO and $H_2$ to $CO_2$ and $H_2O$. The $CO_2$ is then separated by lowering the trap temperature, and its volume is measured manometrically. The $H_2O$ and HCl are then passed over uranium metal at 800°C, and the liberated $H_2$ is measured manometrically (Bigeleisen *et al.* 1952). The purity of the $H_2$ is checked with a mass spectrometer. As Table 3 shows, the water content can be determined with accuracy well beyond that of previous methods. Water contents above 1 wt.% $H_2O^+$ are rare in the literature. The values reported here are relatively high, and quite sufficient to neutralize the $Cl^-$ ions.

## CONCLUSION

All available evidence suggests that marialite accommodates its $H^+$ and $Cl^-$ ions in the form of HCl molecules. The ideal formula of the end-member is written $Na_4[Si_2(Al,Fe^{3+})]_4O_{24}\cdot HCl$; the $CO_3^{2-}$ and $SO_4^{2-}$ groups are likely to be present as $HCO_3^-$ and $HSO_4^-$ ions, although they have not been investigated in our study of chlorine-rich scapolite compositions. A neutron refinement of the ON–8 specimen is highly desirable, as it would locate the protons in the structure. The actual Si/Al ratio of ON–8, which contains 18% meionite, is 2.27, certainly closer to 2 than to 3, the ratio required by the formula for marialite as formerly written — $Na_4[Si_3Al]_3O_{24}Cl$.

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