

Nahcolite (NaHCO_3) in inclusions in apatites from some E. African ijolites and carbonatites

A. H. RANKIN AND M. J. LE BAS

Department of Geology, University of Leicester, LE1 7RH

SUMMARY. Nahcolite (NaHCO_3) is identified and recorded for the first time from an igneous rock. Often associated with it is another carbonate mineral tentatively identified as kalicine¹ (KHCO_3), which has not previously been recorded as a primary mineral in any rock. These minerals occur in inclusions in apatite crystals in ijolites and carbonatites, and indicate that both ijolite and carbonatite magma must have been considerably richer in soda and potash than is indicated by the chemical analyses of the rocks. The identification was made by a combination of microchemical, solubility, crystallographic, and optical determinations.

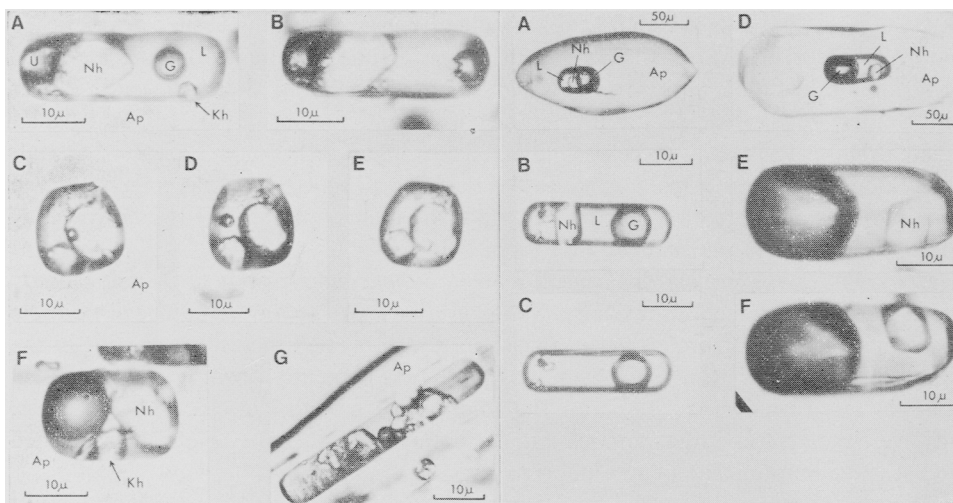
FLUID inclusions in minerals can provide a unique opportunity of studying the physical and chemical nature of crystallizing fluids. The presence of daughter minerals that have precipitated from the fluid inside the inclusion as it cooled are particularly useful in determining the actual composition of this fluid, although the difficulties posed by their minute size and inaccessibility often precludes a definite identification of such phases (Roedder, 1972, p. JJ19). By a combination of optical, crystallographic and chemical methods, it has been possible to show that nahcolite is present in inclusions in apatites from ijolites and carbonatites of the Wasaki, Ruri, Homa, and Tororo complexes of East Africa, described by King, Le Bas, and Sutherland (1972).

Investigation of the bicarbonate daughter minerals within inclusions prior to extraction. Primary aqueous inclusions containing precipitated daughter phases are present in the apatites from some East African carbonatites and ijolites (Le Bas, Mills, and Rankin, 1972; Rankin and Le Bas, 1973), and although the exact nature and composition of these inclusions varies from sample to sample, a characteristic feature of many of these fluid-filled cavities is the existence of highly birefringent, water-soluble, crystalline daughter phases such as are now reported as nahcolite (NaHCO_3).

These crystals are observed within the inclusions as minute (less than 10 μm), colourless, anisotropic solids exhibiting very high interference colours, usually third order (figs. 1 and 2). Crushing-stage studies (Roedder, 1970) in dilute acidified (HCl) glycerol show that these birefringent solids dissolve instantly with rapid effervescence and evolution of gas bubbles when the acid medium comes into contact with them, which, coupled with the high birefringence, is indicative of a carbonate mineral. Similar studies showed that this carbonate phase dissolves instantly without any apparent reaction when the inclusion is opened in pure distilled water on the microscope crushing-stage. This marked solubility in an aqueous medium would further suggest that this phase is an alkali carbonate.

¹ Kalicinite (Groth, 1898) is a spelling variant of kalicine (Pisani, 1865).

Flame emission micro-techniques have been used to study the alkalis present within the inclusions and the results have demonstrated that sodium is present in substantial amounts in the aqueous fluids. Aqueous extracts leached from crushed apatite samples containing abundant inclusions have further shown, using an EEL flame



FIGS. 1 and 2: FIG. 1 (left). A. Three-phase inclusion in apatite (Ap) showing gas bubble (G), aqueous solution (L), nahcolite (Nh), ?kalicine (Kh), and unidentified anisotropic solids (U). B. As A, rolled through $c. 90^\circ$, showing normal habit of nahcolite, and 'disappearance' of the ?kalicine crystal. If it is taken that the disappearance is due to viewing it with α vibration in the plane of the photograph, then the crystal outlines observed in A may be correlated with the $\{210\}$ and $\{100\}$ forms in fig. 6b. C, D, E. Inclusion in apatite showing nahcolite crystals in several orientations. F. Inclusion in apatite with nahcolite (Nh) and suspected kalicine (Kh) showing normal habits. G. Tubular inclusion in apatite, with great abundance of various carbonates, principally nahcolite. The host rock in each case is Usaki ijolite pegmatite (U366). FIG. 2 (right). A. Apatite crystal (Ap) containing large three-phase primary inclusion containing gas (G), liquid (L), and nahcolite daughter mineral (Nh). B. Similar inclusion to A containing well-formed nahcolite crystal (Nh) with small amounts of other carbonate daughter minerals and an unidentified black opaque mineral alongside. Viewed in polarized light with plane of polarization \perp to length of inclusion. C. Same inclusion as B viewed in polarized light with plane of polarization parallel to length of inclusion. It shows the exact match of the refractive index of the liquid with the approximate α vibration direction of the nahcolite. D. Primary three-phase inclusion in apatite, similar to A. E. Enlargement of inclusion in D, showing euhedral nahcolite (Nh). F. As E, but rolled $c. 90^\circ$, showing different view of nahcolite crystal. The host rock in each case is the Wasaki carbonatite (U876).

photometer, that sodium is always in excess of potassium. The sodium to potassium weight ratios (wt. Na^+ : wt. K^+) range from 1.3:1 to 3.8:1 for the extracts from ijolite apatites and from 3.1:1 to 16.0:1 for those from carbonatite apatites.

Another most useful observation is the extreme difference in refractive indices of the alkali carbonate. In some orientations the index matches exactly that of the aqueous fluid within the inclusions, whilst in other orientations it exceeds that of the fluid (figs. 2B and C). The refractive index for pure water is 1.333 and seldom exceeds about 1.39 for saturated aqueous solutions of inorganic salts. Concentrated solutions of

alkali carbonates are no exception, for example $n_D = 1.3409$ for a 6% NaHCO_3 solution and $n_D = 1.3652$ for a 15% $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ solution (Weast, 1965, pp. D127–D165).

Water-soluble carbonates of sodium and potassium that possess an index of refraction less than 1.39 are restricted to nahcolite (NaHCO_3 , $\alpha = 1.376$) and kalicine (KHCO_3 , $\alpha = 1.380$) (Winchell and Winchell, 1964, p. 89). No other synthetic or naturally occurring water-soluble sodium or potassium carbonates having an index of refraction less than 1.405 are known to exist (Winchell and Winchell, 1964; Porter and Spiller, 1956). Nor do the properties correspond to those of natron and trona. These preliminary studies therefore indicated that alkali bicarbonates are present and, since soda is in excess of potash, suggested that nahcolite would be expected to be the dominant bicarbonate daughter phase within the inclusion, and this is confirmed by the optical and crystallographic data given below.

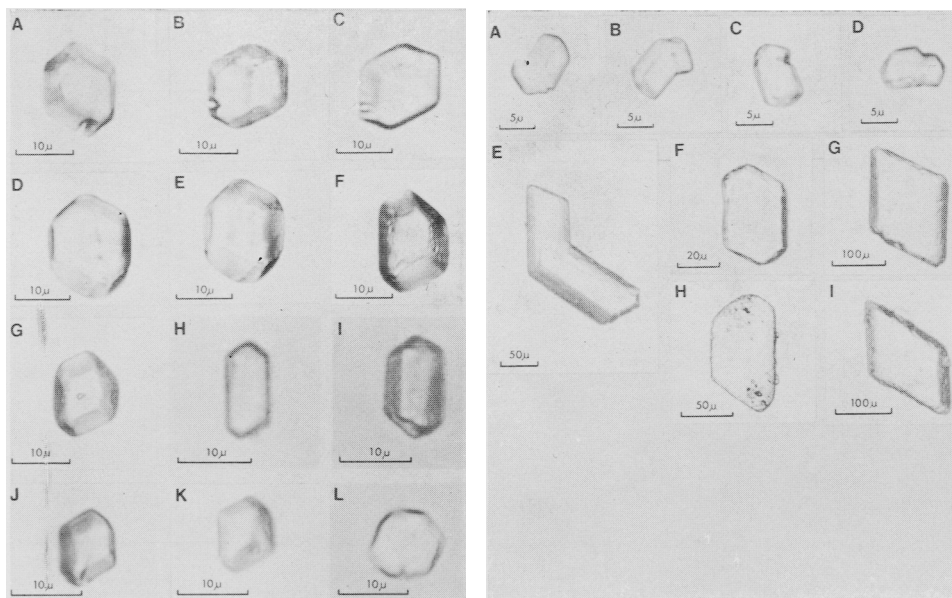
Extraction and crystallographic measurements of nahcolite. In spite of the exceedingly small size of the nahcolite crystals, which rarely exceed $10 \mu\text{m}$, it has been possible to extract the solids from large (up to $150 \mu\text{m}$) well-formed inclusions present in the apatites from a few specimens (U876, U366, U785) by gently opening the cavities in suitable oils (usually $n = 1.56$) on the microscope crushing-stage. In most cases, however, the crystal either remains lodged within the inclusions or else it is crushed and scattered among the apatite debris as minute fragments.

The crystal morphology (fig. 3) at first suggested low symmetry orthorhombic but the subsequent discovery of twinned crystals (fig. 4A–D) indicated monoclinic symmetry. Due to the close coincidence of the α vibration direction with the pole to the (101) face, which is prominent (fig. 5), the crystals give the appearance of having straight extinction, apparently confirming the orthorhombic symmetry. The true monoclinic symmetry was determined by plotting stereographically all the morphological data from twinned and untwinned crystals (fig. 6A) of nahcolite extracted from the inclusions. The difficulty of the identification largely arises from the fact that for nahcolite $\beta = 93^\circ 19'$ giving near orthorhombic symmetry in some orientations.

Refractive index measurements on the extracted specimens gave: $\alpha 1.378 \pm 0.003$, $\beta 1.502 \pm 0.005$, $\gamma 1.579 \pm 0.003$, which compare favourably with those obtained by Fahey (1962) for nahcolite from the Green River Formation ($\alpha 1.375$, $\beta 1.498$, $\gamma 1.583$, all ± 0.002). In shattered specimens the minute nahcolite fragments sometimes showed a marked conchoidal fracture but on other occasions good cleavages were visible though the directions could not be ascertained. Some of the crystals extracted could be rolled into various orientations directly under the microscope by gently stirring the immersion oil ($n = 1.54$) with a fine-pointed steel probe. These crystals together with those *in situ* within the inclusions were photographed in various orientations at high power and the photomicrographs enlarged (figs. 1–4). Interfacial angles and also angles to edges were measured from these photomicrographs and further measurements were made directly on the microscope-stage. The results of numerous measurements on five extracted crystals from U366 and U876 were used to determine the axial ratios. One of the extracted crystals showed perfect twinning (fig. 4A), which is a

characteristic feature of synthetic nahcolite crystals (Winchell and Winchell, 1964, p. 89), as shown in fig. 4E.

Results of crystallographic measurements. Some of the crystals of nahcolite measured are shown in figs. 3 and 4. The measurements, made with a simple goniometer, were plotted on a stereographic projection and at first, when it was believed the mineral



FIGS. 3 and 4: FIG. 3 (left). A, B, C. Three views of single nahcolite crystal extracted from inclusion in apatite from the Usaki ijolite pegmatite (U366). A is viewed down [010]. D, E, F. Another extracted nahcolite crystal from U366. F is viewed down [010]. See also fig. 5. G. Another nahcolite crystal from U366, resting on side pinacoid. H. Nahcolite crystal elongated along (101) extracted from a primary inclusion in apatite from the Sokolo carbonatite (U785). Viewed down [010]. I. As H, rolled about length of crystal. J, K, L. Three views of rolled nahcolite crystal extracted from a primary inclusion in apatite from the Wasaki carbonatite (U876). K is viewed down [010]. FIG. 4 (right). A, B, C, D. Four views of twinned nahcolite crystal from Usaki ijolite pegmatite (U366). See also fig. 5. E. Twinned crystal of synthetic nahcolite showing same habit as in A. F. Normal habit of synthetic nahcolite, comparable with those in fig. 3. G. Common habit of synthetic nahcolite, as in fig. 2B. H, I. Normal habits of synthetic kalicinite. They are similar to F and G as discussed in text.

was orthorhombic, an apparent close fit of the axes and some prominent faces to those of pirssonite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) was obtained though the habit was unusual; but, because the crystals were completely water-soluble and pirssonite is only partially soluble in water, this possibility had to be ruled out. When the twinned crystal was discovered and the monoclinic symmetry realized, the data were replotted (fig. 6A) and nahcolite recognized, and later confirmed by refractive index determinations.

Owing to the difficulty of measuring accurately the crystallographic angles of all the faces from the highly enlarged photographs, some use had to be made of the properties of zones of faces and the Law of Rational Indices to improve the measurements. Location of the optical vibration directions also assisted in the construction of

the stereogram (fig. 6A). The axial constants obtained are $a:b:c::0.755:1:0.355$ (± 0.01), $\beta = 93.5^\circ$, which compare favourably with the values quoted in Dana (Palache *et al.*, 1951, p. 134) of $0.7645:1:0.3582$, $\beta = 93^\circ 19'$.

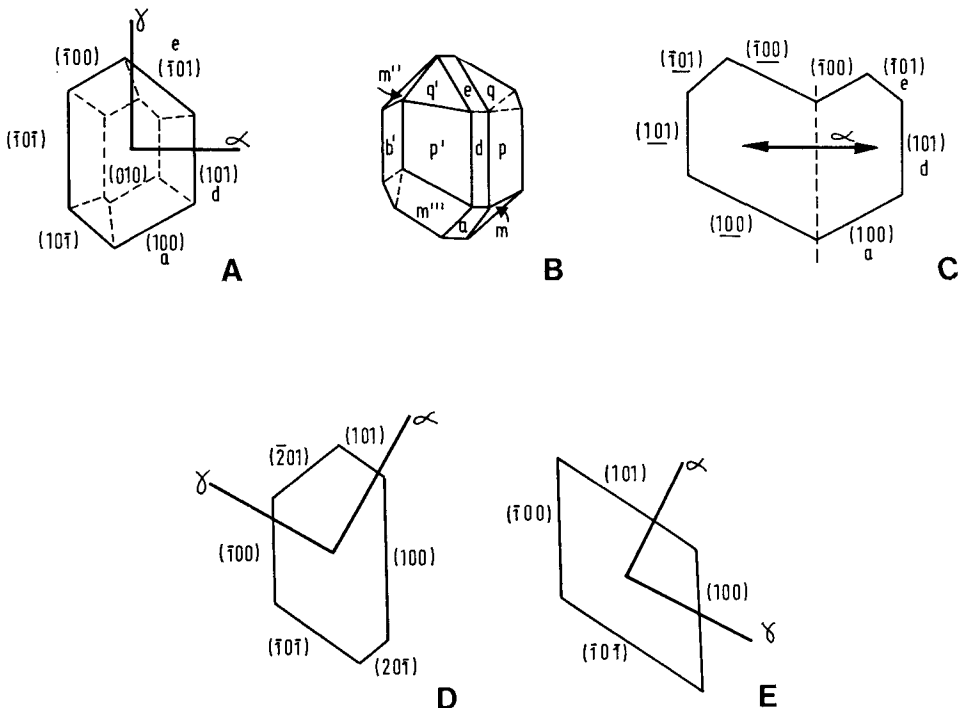


FIG. 5. A. Nahcolite crystal showing the normally developed outline of faces and optical orientation. Drawn from fig. 3F. B. Nahcolite crystal drawn from several photographs including figs. 3D and E. This is the normal habit. Letters correspond to those in fig. 6A. C. Twinned crystal of nahcolite as illustrated in fig. 4A, showing composition plane (dashed) and the α vibration direction, which is common to both halves of the twin. D. Kalicine crystal, as in fig. 4H, with faces indexed. E. Kalicine crystal, as in fig. 4I, showing optical orientation of common habit with α at 7° to the normal to (101).

The principal form developed is $\{010\}$ and most crystals when extracted from the inclusions rest on this face (fig. 3A, C, F, G, H, J, K). In that orientation, the forms $\{100\}$, $\{101\}$, and $\{10\bar{1}\}$ are seen in profile with the angles between the poles being 62° , 50° , and 68° . These measurements ($\pm 1^\circ$) were repeated on numerous different crystals from photomicrographs and directly under the microscope. The α vibration direction lies less than 1° away from the pole to (101) and towards the c axis. Other forms present on all the crystals are $\{110\}$, $\{111\}$, and $\{1\bar{1}1\}$. The twinned crystal (fig. 4A) has its composition plane parallel to (101).

Other bicarbonate daughter minerals. Even though nahcolite has been positively identified within the inclusions it became apparent during the course of these investigations in view of the presence of potassium as well as sodium within the inclusions that kalicine (KHCO_3) might also be present, particularly in specimens that gave a high

Na⁺: K⁺ weight ratio. When two or more seemingly identical bicarbonate phases are observed within the inclusions (fig. 1) it is feasible to suppose that one of them may be kalicine (probably the smaller one), particularly since Roedder (1972, p. JJ19) cites evidence to suggest that, in general, only one single crystal of a precipitated daughter phase would be expected within a fluid-filled inclusion. Kalicine has never been

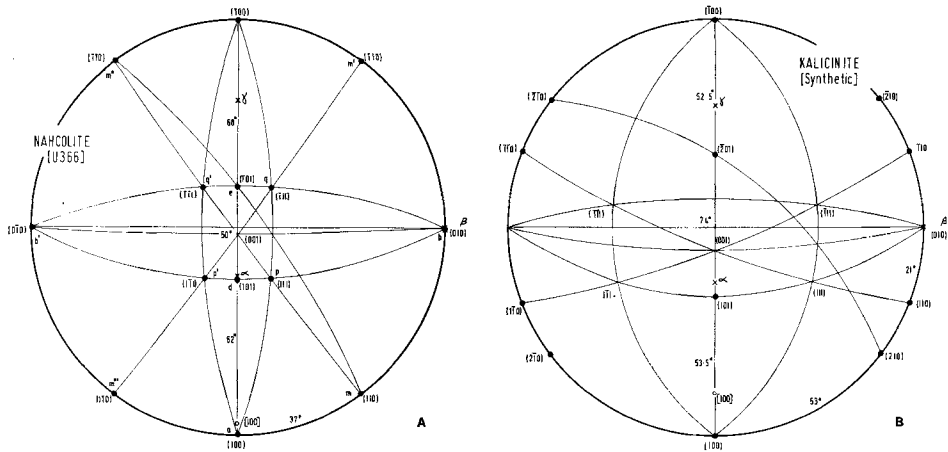


FIG. 6. A. Stereogram of nahcolite derived from angular measurements of natural crystals as shown in figs. 3 and 4. B. Stereogram of kalicine constructed from data for synthetic crystals. Note the similarities of some of the zones and the optical orientation with those of nahcolite. Dots indicate faces identified, other faces also likely to be present are also plotted. X indicates vibration directions.

observed before in a rock, the only known previous occurrence was ‘found as a result of recent decomposition under a dead tree at Chypis, Canton Wallis, Switzerland’ (Palache *et al.*, 1951, p. 136). It is also said to occur with trona in Hungary (*ibid.*).

The crystallographic distinction between nahcolite and kalicine is not easy as they appear to have similar habits (fig. 4, F, G, H, I). The principal forms of kalicine are {101}, {20 $\bar{1}$ }, {100}, and {110} according to Porter and Spiller (1956, M. 387), giving the angles 74°, 52.5°, 53.5°, 74°, 52.5°, 53.5° in the [010] zone, with α vibration only 7° from the pole of (101) (fig. 6B).

However, some synthetic crystals show the forms {010}, {101}, and {100} with only minor development of {110} faces; such crystals usually rest on (010), being the larger face, and are elongated parallel to the (101) face giving near-straight extinction optics. The {001} and {210} forms also seem to be likely faces. It has not been possible positively to identify crystals of either the Porter and Spiller habit or the ‘synthetic’ habit, though several daughter minerals with crystallographic outlines approximating to one or other of these are suspected to be kalicine (fig. 1A, B).

The origin and significance of bicarbonate daughter minerals within the inclusions. The primary aqueous inclusions containing bicarbonate daughter minerals must be considered as trapped portions of the environment of crystallization of the host apatite. In the case of the two ijolites studied, which show no secondary alteration,

(U366, U271), the amount of bicarbonate present within the inclusions varies from a few % to about 80 % by volume of the inclusion. This variation is real, and even though necking-down processes (Roedder, 1962) have been operative to a certain degree, many inclusions that still show this variation appear to be completely unaffected by any subsequent changes after they have formed.

Primary silicate-melt inclusions are also present within these apatites. These inclusions, which consist of minute crystals of silicate minerals embedded in a glassy matrix, are co-genetic with the bicarbonate-rich inclusions. The environment of crystallization of the ijolites is therefore considered to be a silicate melt with an associated carbonate-rich fluid (seen as the nahcolite-bearing inclusions), which, because of the variable amount of water present, ranged from a true carbonate melt to a dilute aqueous fluid analogous to the 'carbothermal solutions' postulated by Wyllie (1966, p. 345).

The possibility that carbonatites could have originated from such a source is highly probable in view of these observations, and it is also evident that such fluids carry large amounts of alkalis, which confirms the view held by von Eckermann (1948) that alkalis must have been present in substantial amounts in carbonatite magma. Further confirmation is provided by the occurrence at Oldoinyo L'Engai volcano of natro-carbonatite lava (Dawson, 1966).

The presence of nahcolite, which never exceeds about 30% by volume of the inclusions in the carbonatite apatites, enhances the view held above and since the inclusions are trapped portions of a homogeneous aqueous fluid, this fluid must constitute part of a fluid carbonatite magma.

Acknowledgements. We wish to thank Dr. R. J. King for providing reference samples of some of these minerals from other described localities. One of us (A. H. R.) gratefully acknowledges the financial assistance provided by N. E. R. C. during the tenure of a research studentship.

REFERENCES

- DAWSON (J. B.), 1966. In *Carbonatites*, ed. TUTTLE (O.F.) and GITTINS (J.), New York (Interscience), 155-58.
- ECKERMAN (H. VON), 1948. *Intern. Geol. Congr. 18th Sess., Great Britain*, 3, 94.
- FAHEY (J. J.), 1962. *U.S.G.S. Prof. Paper* 405.
- KING (B. C.), LE BAS (M. J.), and SUTHERLAND (D. S.), 1972. *Journ. Geol. Soc.* **128**, 173.
- LE BAS (M. J.), MILLS (A. A.), and RANKIN (A. H.), 1972. *Nature*, **239**, 215.
- PALACHE (L.), BERMAN (H.), and FRONDEL (C.), 1951. *The System of Mineralogy*, 7th edn, 2, New York and London (Wiley and Sons).
- PORTER (M. W.) and SPILLER (R. C.), 1956. *The Barker index of crystals*, 2 part 2. Cambridge (Heffer and Sons).
- RANKIN (A. H.) and LE BAS (M. J.), 1973. *Journ. Geol. Soc.* **129**, 319.
- ROEDDER (E.), 1962. *Sci. Amer.* **207**, 38-47.
- 1970. *Schweiz. Min. Petr. Mitt.* **50**, 41-58.
- 1972. *U.S.G.S. Prof. Paper* 440-JJ.
- WEAST (R. C.), 1965. *Handbook of Chemistry and Physics*, 46th edn, Ohio (The Chemical Rubber Co., Ohio).
- WINCHELL (W.) and WINCHELL (A. N.), 1964. *The Microscopical Characters of Artificial Inorganic Solid Substances*, New York (Academic Press).
- WYLLIE (P. J.), 1966. In *Carbonatites*. Ed. TUTTLE (O.F.) and GITTINS (J.), New York (Interscience), 311-52.

[Manuscript received 12 July 1973]