

An explanation of optical variation in yugawaralite

MIZUHIKO AKIZUKI

Institute of Mineralogy, Petrology, and Economic Geology, Faculty of Science, Tohoku University, Sendai 980, Japan

Abstract

Yugawaralites from two localities in Japan consist of growth sectors with variable 2V values and extinction angles. The optical variations cannot be explained on chemical grounds because the mineral shows very little chemical variation but they can be explained on the basis of Al/Si ordering. The $v\{021\}$ sectors (*Pa* setting) are composed of optically triclinic bands, and the $k\{110\}$ sector consists of both triclinic bands and monoclinic homogeneous domains. An electrostatic charge of the Al/Si ordered structure is balanced along a two-dimensional atomic arrangement exposed on the side face of a growth step. If the Si tetrahedron is produced after the calcium ion, the Si ion will be replaced during growth by an Al ion due to the local effect of the calcium ions. When a side plane of growth steps of yugawaralite is not normal to the (010) glide plane, a symmetrical equivalence of two Si sites with respect to the Ca ion will be lost at the surface, and as a consequence ordering will occur and the symmetry of crystal will be reduced. The monoclinic, homogeneous sector might be produced on the very finely kinked surface. The space group of the triclinic sector will be *P1*, while that of the monoclinic sector will be *Pc*.

KEYWORDS: yugawaralite, zeolite, optical variation, Japan.

Introduction

YUGAWARALITE, a monoclinic calcium zeolite ($\text{CaAl}_2\text{Si}_6\text{O}_{16}\cdot 4\text{H}_2\text{O}$), has been discovered at about ten localities in the world since the first description by Sakurai and Hayashi (1952). Although its chemical composition and cell dimensions are very similar for all studied specimens, optical properties, such as 2V values, vary from specimen to specimen, and from sector to sector in each crystal: e.g. the 2V value ranges from $+56^\circ$ to $+89^\circ$ (Sakurai and Hayashi, 1952) and $+78^\circ$ (Harada *et al.*, 1969) for specimens from the type locality, Yugawara, Japan, while it varies from -48° to -72° for specimens from the Chena hot spring area, Alaska (Eberlein *et al.*, 1971) and from -70° to -76° for specimens from Sardinia (Pongiluppi, 1977). The Yugawara specimens are also probably negative, as recently indicated by Harada (1980, pers. comm.). Although an optical sector may be seen distinctly in yugawaralite, no composition variation in Al, Si and Ca was detected between the sectors by electron probe analysis (Eberlein *et al.*, 1971).

Kerr and Williams (1969) showed a perfect Al/Si ordering in a crystal from Iceland, whereas Leimer and Slaughter (1969) found a partial Al/Si

ordering in the crystal from Yugawara, both with symmetry *Pc*.

Anomalous optics and complicated textures have been observed in many zeolites such as analcime, chabazite, stilbite, and harmotome (e.g. Rinne, 1890). Their optical symmetries are lower than both X-ray and morphological symmetries. This anomaly may be due to various origins such as partial chemical alteration, strain, overlapping of fine domains or twins, or ordering.

The crystal structures of feldspars, analcime, chabazite, stilbite, garnet and topaz have been refined by X-ray techniques, so that their optical properties could be directly related to the ordering. Most minerals showing abnormal optics, however, have not been refined with respect to their ordering. The crystal structure of yugawaralite, refined by Kerr and Williams (1969) and Leimer and Slaughter (1969), is not correlated to its optical symmetry.

The objective of the present paper is to describe the growth sectors and optical characteristics of yugawaralite from two localities, and to predict its structure from the standpoint of an order-disorder growth mechanism suggested by Akizuki (1981a).

Observations

Specimens and procedures

The specimens were collected from Toi, Shizuoka Prefecture, and Takinoue in the Kakkonda hot spring area, Iwate Prefecture, Japan. Fig. 1

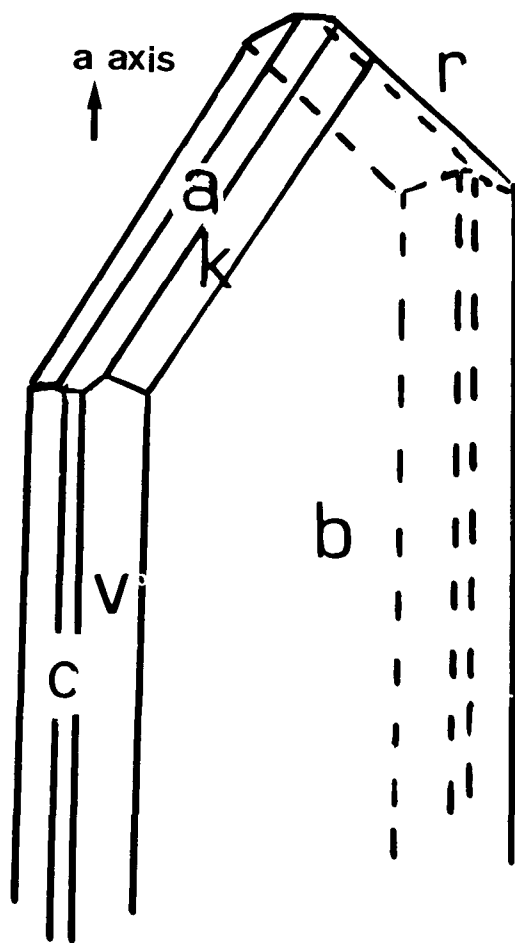


FIG. 1. Typical crystal form of yugawaralite from Toi, Japan. $a(100)$, $b(010)$, $c(001)$, $r(11\bar{1})$ and $v(021)$ faces are shown (Pa setting of Eberlein *et al.*, 1971).

shows a common crystal form of yugawaralite from Toi with indexing after Eberlein *et al.* (1971) and in space group Pa . For the accepted setting in Pc the a and c axes and their intercepts on indices must be interchanged.

The optical properties differ from specimen to specimen or from sector to sector in the same

crystal, whereas the chemical compositions, obtained by electron probe, are homogeneous throughout each crystal. Thin sections with standard thickness, $30\ \mu\text{m}$, were used in order to observe the texture and optical properties. The $2V$ values were measured by both orthoscopic and conoscopic methods on a universal stage using white light. The $2V$ values of all yugawaralites from the two localities are negative. Specimens from the two localities consist of both monoclinic and triclinic sectors. The triclinic sector is produced on the crystal surface inclined to the (010) glide plane, and the monoclinic sector may form on a finely kinked surface. No marked differences of optics and growth textures were observed between specimens from the two localities, in spite of different occurrences.

Toi specimen. Yugawaralite occurs in geodes of altered basalt. The crystals are well-formed, clear, colourless, and tabular, about one centimetre in length and one or two millimetres in thickness. The crystals consist of small $k(110)$, $r(11\bar{1})$, $v(021)$ faces, and a predominant $b(010)$ face with very small $a(100)$ and $c(001)$ faces. The crystal form is similar to that from Yugawara, Japan (Sakurai and Hayashi, 1952).

Fig. 2 shows the sectorial texture in the (010) thin section after removing the $\{010\}$ sector by polishing. The crystal is transparent except at its contact with the country rock, where it is whitish and includes small fluid inclusions. Extinction angles ($a:Y$) are 12° at the $k\{110\}$ and 9 to 11° at the $r\{11\bar{1}\}$ and $v\{021\}$ sectors. The $\{021\}$ and $\{11\bar{1}\}$ sectors have growth bands parallel to each other, while the $\{110\}$ sector is optically homogeneous.

Various morphological changes are observed in the thin sections parallel to the b -axis. The (100) section shows fine growth bands parallel to the (021) and $(0\bar{2}1)$ faces between crossed polars. The optical vibration directions (Z) are symmetrically inclined about 1° to the b -axis in the corresponding $\{021\}$ and $\{0\bar{2}1\}$ sectors showing optically triclinic twinning. The crystal has small (001) face on the surface, and the corresponding $\{001\}$ sector, which is homogeneous and monoclinic, is observed in the crystal as well.

The (110) surface consists of both long striations and growth hillock elongated in the direction parallel to the c -axis. The steps of the hillock are of a fine sawtooth pattern and the faces between the steps have very fine striations parallel to the c -axis. The (001) thin section shows $k\{110\}$, $v\{021\}$ and $b\{010\}$ sectors (Fig. 3). The $k\{110\}$ sector is composed of optically triclinic bands ($2V$ value = 76°) in its outer part and an inner monoclinic, homogeneous sector ($2V = 70^\circ$), though the

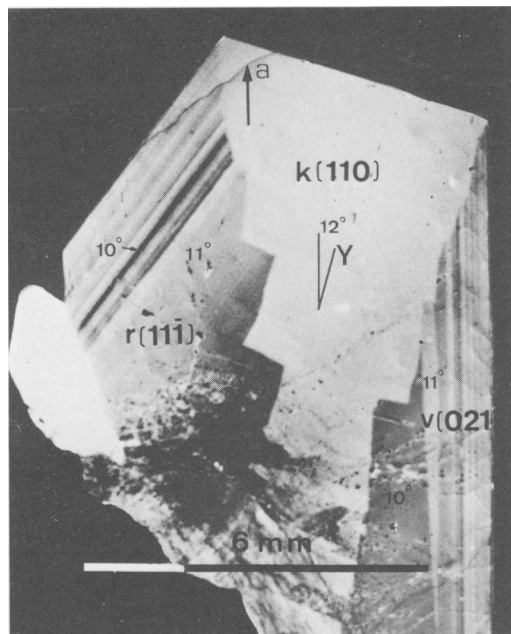


FIG. 2. Polarized photomicrograph showing $k\{110\}$, $r\{11\bar{1}\}$ and $v\{021\}$ sectors in the (010) thin section of yugawaralite from Toi, Japan. The angles between the a -axis and the principal optical vibration axis (Y), which is the extinction angle from the a -axis, are shown on the figure.

$\{110\}$ sector is only homogenous in Fig. 2. The optical extinctions are symmetrical in both the k and the \bar{k} growth bands ($2V = 76^\circ$), suggesting a reflection twinning with respect to (010) (Fig. 3). The extinction direction of the homogeneous $\{110\}$ sector is between those of the two k and \bar{k} bands, suggesting a monoclinic symmetry. The area just below the growth surface has the growth bands, and therefore, the correlation between the homogeneous sector and the surface feature is not observed.

Takinoue specimen. The occurrence and chemical composition of this yugawaralite was described by Chiba *et al.* (1978). The crystals, which are less than 10 mm long, occur as aggregates of tabular crystals within a fine granular quartz vein in altered andesite. The crystals consist of $k(110)$, $r(11\bar{1})$, $v(021)$ and predominant $b(010)$ faces and are elongated parallel to the a -axis.

The granulate quartz crystals (0.01 mm in diameter), overgrown on yugawaralite, have a fibrous texture and show optically wavy extinction, probably due to its low-temperature hydrothermal origin. Since it is difficult to separate

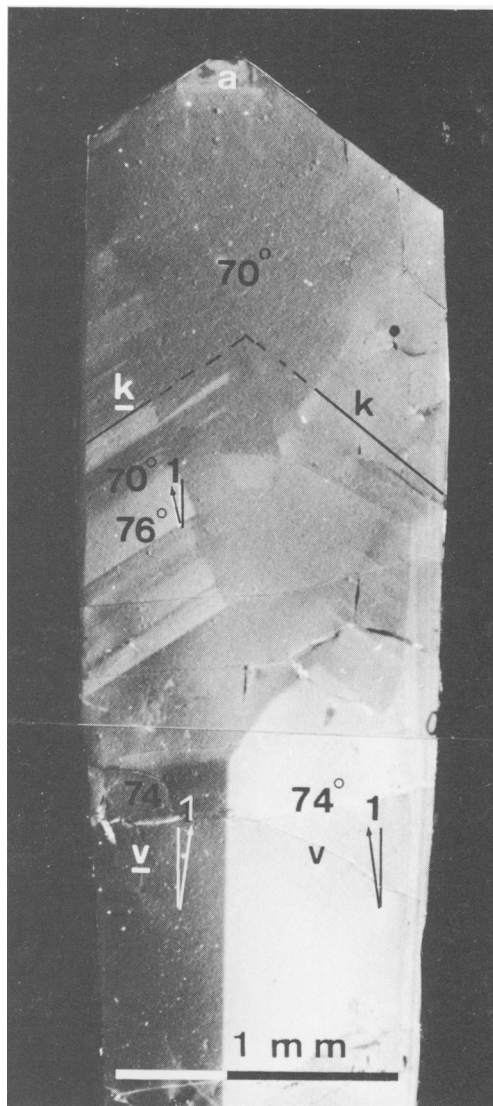


FIG. 3. Polarized photomicrograph showing $k\{110\}$, $v\{021\}$ and small $a\{100\}$ sectors of yugawaralite from Toi, Japan. The a - and b -axes are vertical and horizontal, respectively. The growth band is shown by a solid line, and the growth band assumed in the homogeneous sector is represented by a dashed line. The $2V$ values and extinction angles are shown.

the euhedral yugawaralite crystals from the aggregate in quartz, the growth feature cannot be observed on the surface.

Yugawaralite from Takinoue occurs as aggregates of two or three crystals aligned almost parallel to their (010) planes (Fig. 4). Since the crystals

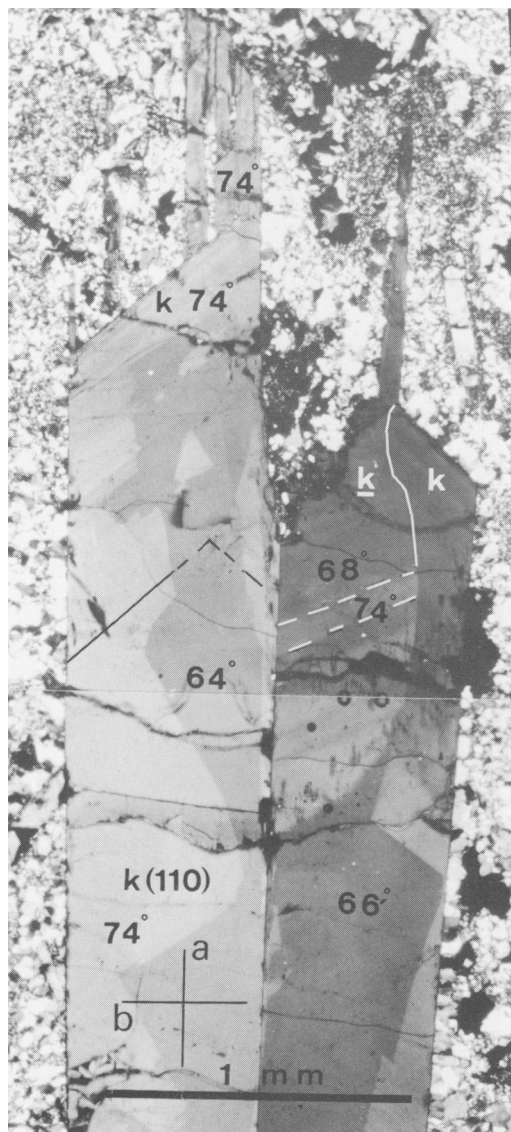


Fig. 4. Polarized photomicrograph showing $k\{110\}$ sectors of yugawaralite from Takinoue, Japan. The a -axis is roughly vertical and the b -axis is roughly horizontal. The $2V$ values and growth bands are indicated. Minerals around the two large yugawaralites are small yugawaralite and quartz crystals.

grew within fine quartz crystals, it was difficult to identify correctly the sectors in the section from their morphology. Some thin yugawaralites protrude in the direction parallel to the a -axis on the large crystal (Fig. 4). Their optical properties are similar to those of the large crystals. The section

which is nearly parallel to the b -axis shows texture similar to that of the Toi crystals, with banded and homogeneous sectors. The $2V$ values are about 74° in the banded sector, and vary from 64° to 68° in the homogeneous sector. The growth band and the assumed growth band in the sector are shown by solid and dashed lines, respectively, showing a habit change during growth. The $\{010\}$ sectors are not found in the crystal at all in spite of crystals with a prominent (010) face. The (010) face is not produced by crystal growth on (010) , but is the result of the growth of (110) , $(11\bar{1})$ and (021) faces on a more or less optically homogeneous core. Although morphological orientation cannot be exactly determined, because of small and aggregate crystals, the k and $\bar{k}\{110\}$ sectors may be in a triclinic twin relation in common with those in the Toi specimen.

Discussion

Cause of optical anomalies in silicates. Other silicates, such as adularia (Akizuki and Sunagawa, 1978), topaz (Akizuki *et al.*, 1979), analcime (Akizuki, 1981a), chabazite (Akizuki, 1981b), garnet (Akizuki, 1984), stilbite (Akizuki and Konno, 1985), and harmotome (Akizuki, 1985) consist of optical sectors which correlate with the growth planes or the vicinal surfaces. It has been suggested that the optical properties are a result of the ordered arrangements of two kinds of atom which are produced during crystal growth.

A three-dimensional crystal structure of a growth hillock is produced by the piling up of a two-dimensional atomic arrangement when the solution is lower in supersaturation. According to Pauling's second rule, the local charge balance must be maintained in a three-dimensional structure. Thus tetrahedra which are directly coordinated by alkali ions are preferentially occupied by aluminium in zeolites, because of the local charge balance. The electrostatic charge on the growth surface however is not balanced in a direction perpendicular to the surface and therefore an ionic crystal can grow continuously. The charge balance should be maintained along the two-dimensional structure exposed on the growth surface as well as within the crystal.

The two-dimensional atomic arrangements exposed on a growth step surface of an aluminosilicate differ among different kinds of surfaces. If the tetrahedron is produced after a large cation is in the channel, an aluminium ion will preferentially occupy the tetrahedron, whereas if the tetrahedron is produced prior to the cation lodging, a silicon ion will occupy the site. Thus, the degree of the Al/Si ordering may differ from sector to

sector. If the vicinal surface is normal to a mirror or glide plane, the two symmetric sites will be equivalent on the step surface, resulting in disordered arrangements. Conversely, if the vicinal surface is inclined to the mirror or the glide plane, the two symmetric sites in a crystal will not be equivalent on the surface, thus ordering will occur and the symmetry of the crystal will be reduced. The morphological mirror plane changes into the twin plane due to the symmetrically ordered arrangements.

Numerous minerals with sectors controlled by ordering are found in hydrothermal veins, but few are found in rocks formed at higher temperatures, because atoms can more easily attain a stable position on growth surfaces at higher temperatures and the crystals grow homogeneously ordered or disordered. However, an irregularly ordered structure, produced at low temperature, is frozen in its growth, and the texture is heterogeneous as noted at the start of this section.

Optical anomalies in yugawaralites, a probable mechanism. The chemical compositions of yugawaralite from all the known localities are very similar to each other, but its optical properties vary from specimen to specimen and from sector to sector. Eberlein *et al.* (1971) found no compositional variation in Al, Si and Ca by electron microprobe analysis of Alaskan yugawaralite and they suggested that the optical variations may be related either to differences in atomic Al/Si distribution below the detection limit of the probe or to trace-element distribution. However, the sectorial twin and the difference of symmetry between the sectors cannot be interpreted by the slight difference of chemical composition or the trace-element distribution, but only by Al/Si ordering. In yugawaralite, the calcium ion is surrounded by four oxygens of the framework and four water molecules in one of the main channels. These four oxygens belong to Al tetrahedra shown in the crystal structure of yugawaralite (Kerr and Williams, 1969) as Al(1) and Al(2) in Fig. 5, and the side faces of growth steps parallel to (021) are also indicated in this figure. The Al(1) tetrahedron is produced prior to the Ca ion on the steps and the Al(1') tetrahedron is produced after the Ca ion. The Al(2) tetrahedron is produced after the Ca-ion on the step, whereas the Al(2') tetrahedron is in contact with the Ca-ion on the same step. This suggests that both the Al(1') and Al(2) sites will be preferentially occupied by aluminium ions due to the local effect of the calcium ions. On the other hand, the Al(1) site will be preferentially occupied by silicon.

Although the Al(1) and Al(1') tetrahedra and the Al(2) and Al(2') tetrahedra are equivalent

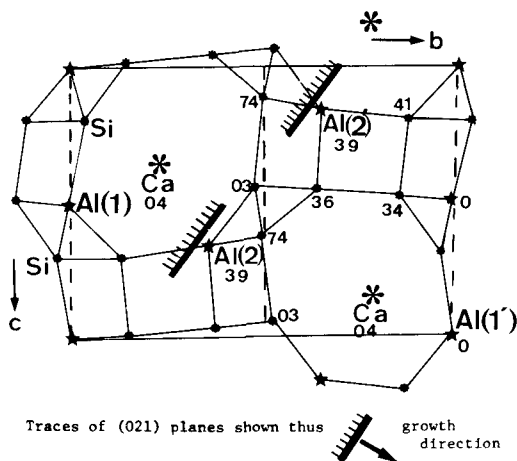


FIG. 5. Crystal structure of yugawaralite projected on the *a-b* plane (after Kerr and Williams, 1969) with (021) growth steps. Only Si, Al and Ca sites are shown in the figure. Numbers in parentheses denote Z-coordinates in hundredths (*Pa* setting of Eberlein *et al.*, 1971).

to each other in the three-dimensional structure, respectively, they are not always equivalent to each other in the two-dimensional structure exposed on the surface during growth. If the growth steps on a yugawaralite crystal move in the direction inclined to the glide plane, the *Pc* symmetry will be reduced to *P1* due to the Al/Si ordering. If the steps move in a direction normal to the mirror plane, the Al/Si disorder would remain, and therefore, the symmetry *Pc* will be maintained in the domain. Also, the disordered structure will form on a finely kinked surface (Akizuki, 1985).

The *v*(021) face is inclined to the mirror plane, and therefore, the {021} sector with growth bands is triclinic. Since the *k*(110) face is inclined to the mirror plane as well, the corresponding sector should be non-centrosymmetric and triclinic. The banded sector is triclinic, whereas the homogeneous sector is monoclinic. The homogeneous sector might be produced on a more finely kinked face during growth than that observed on the surface.

Kerr and Williams (1969) and Leimer and Slaughter (1969) refined the structure in the non-centrosymmetric space group *Pc*. Unfortunately, they did not report the optical properties of the specimens used for their study. It may be difficult to identify the triclinic symmetry in X-ray analysis, because of the small degree of triclinicity. The piezoelectric and pyroelectric effects (Eberlein *et al.*, 1971) indicate that yugawaralite has a non-

centrosymmetric space group. The crystal showing optically triclinic $P1$ symmetry may be monoclinic Pc in X-ray analysis.

A metastable crystal growth is explained in terms of a non-centrosymmetric phenomenon, because the electrostatic charge is balanced on the crystal surface, not in the three-dimensional structure. Therefore, many metastable zeolites such as thomsonite, laumontite, gismondine, harmotome, gmelinite, epistilbite, heulandite, stilbite and brewsterite show piezoelectric and pyroelectric effects and optically sectorial textures in spite of their centrosymmetric structures in X-ray analysis (Ventriglia, 1953).

Acknowledgements

The author is most grateful to Dr R. Nawaz for critical reading and correcting the manuscript. I thank Dr M. Aoki, Miyagi University of Education for supplying the samples.

References

Akizuki, M. (1981a) *Lithos* **14**, 17–21.
 — (1981b) *Am. Mineral.* **66**, 403–9.

- (1984) *Ibid.* **69**, 328–38.
 — (1985) *Ibid.* **70**, 822–8.
 — and Konno, H. (1985) *Ibid.* **70**, 814–21.
 — and Sunagawa, I. (1978) *Mineral. Mag.* **42**, 453–62.
 — Hampar, M. and Zussman, J. (1979) *Ibid.* **42**, 237–41.
 Barrer, R. M. and Marshall, D. J. (1965) *Am. Mineral.* **50**, 484–9.
 Chiba, T., Aoki, M. and Konno, H. (1978) *J. Tohoku Branch, Geol. Soc. Japan* **9**, 15 [in Japanese].
 Eberlein, C. D., Erd, R. C., Weber, F. and Beatty, L. B. (1971) *Am. Mineral.* **56**, 1699–717.
 Harada, K., Nagashima, K. and Sakurai, K. (1969) *Ibid.* **54**, 306–9.
 Kerr, I. S. and Williams, D. J. (1969) *Acta Cryst.* **B25**, 1183–90.
 Leimer, H. W. and Slaughter, M. (1969) *Z. Krist.* **130**, 88–111.
 Pongiluppi, D. (1977) *Can. Mineral.* **15**, 113–4.
 Rinne, F. (1890) *Sitz. Akad. Wissen. Berlin* **46**, 1163–207.
 Sakurai, K. and Hayashi, A. (1952) *Sci. Rep. Yokohoma Nat. Univ. Ser. II*, **1**, 69–77.
 Ventriglia, U. (1953) *Rend. Soc. Mineral. Ital.* **9**, 268–9.

[Manuscript received 7 July 1986: revised 3 October 1986]