of the dynamical theory reveals slight disagreement with these figures. Jeffreys found that the loss of angular momentum by the earth varies as the sixth power of the moon's distance (*2*). This results in a relation between the length of the day and the geologic time scale given by the expression

$$T = 4.5\, a^{13/2} \qquad (1)$$

where $a$ is the distance of the moon relative to its present distance and $T$ is the time in $10^9$ years since $4.5 \times 10^9$ years ago. The dimensionless distance, $a$, during the Middle Devonian era ($T = 4.1$) was 0.986. This implies, if the masses of earth and moon have remained constant since the Middle Devonian, that the moon had a sidereal period equal to 0.981 of the period it has at present, or 26.803 present ephemeris days. Now, the length of the Middle Devonian day from Jeffreys' theory is estimated to be 0.998 of the present ephemeris day. The Middle Devonian sidereal month was, therefore, 26.856 Middle Devonian days long. The length $S$ of the synodic month (the month of the phases) with respect to which coral breeding periodicity has been suggested, is given by

$$S = ME/(E - M) \qquad (2)$$

where $M$ is the length of the lunar sidereal period and $E$ is the length of the year.

Wells, on the basis of astronomical data, finds approximately 339 days in the Middle Devonian year (*3*). Applying Eq. 2, one finds the length of the Middle Devonian synodic month to be 28.8 Middle Devonian days, 0.7 day shorter than the present synodic month. This result is approximately 1.7 days shorter than the length of the lunar cycle which Scrutton obtained from the palaeontological data (*1*). The dynamical treatment gives a Middle Devonian year of nearly 14 rather than 13 lunar months as the count of growth ridges seems to suggest. A difference of 6½ percent between the results of two completely different approaches to the problem, however, is not so serious. Runcorn's analysis (*4*), based upon Kepler's laws of motion applied to the earth-moon system, gives even better agreement.

A number of hypotheses can be advanced to reconcile the differences. Possibly the similarity which exists between the number of diurnal ridges per band on the old corals and the length of the lunar cycle is fortuitous. One species of modern coral has 28 diurnal ridges per band, one and one half less than the number of days per synodic month (Scrutton, *1*); this would make it a highly inaccurate astronomical timepiece. There also exists the possibility that our understanding of the recent history of the earth-moon system is incomplete. For example, excellent agreement is obtained between the observations of Devonian corals and the astronomical calculations if one assumes that the present observed rate of retardation of the earth's rotational period applied during the Middle Devonian era. But since the tide-raising force, which plays a large role in increasing the earth's period of rotation, varies as $a^{-3}$, the moon was certain to have had a far greater effect upon slowing down the earth's rotation in the past when it was nearer the earth.

ANTHONY F. AVENI
*Department of Physics and Astronomy, Colgate University, Hamilton, New York*

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## Kyanite-Sillimanite Equilibrium at 750°C

Abstract. *Reversal of the kyanite-sillimanite inversion has been accomplished hydrothermally at 750°C. The inversion pressure at 750°C is 8.1 ± 0.4 kilobars. The calculated pressure-temperature slope at this point is 17.7± 1.0 bars per degree celsius. Geologically, this result seems more plausible than previous estimates of the location of the boundary. When combined with other work on the relative stability of andalusite, the data indicate that andalusite cannot be stable at a pressure greater than 4.2 kilobars.*

The polymorphism of $Al_2SiO_5$ is one of the most significant features which characterize metamorphic rocks. The andalusite polymorph, of density 3.14 gm/cm$^3$, is restricted to hornfelses, pelitic schists of the lower grades, and some pegmatites. The sillimanite polymorph (density 3.24 gm/cm$^3$) is very characteristic of high-grade schists, gneisses, and granulites. Kyanite (density 3.66 gm/cm$^3$) is found chiefly in medium-grade schists, hydrothermal veins, eclogites, and a few pegmatites and is probably the most widely distributed of the three polymorphs. Because of its high density it is considered to be a product of the most deep-seated kind of metamorphism. The passage of kyanite to sillimanite as the aluminum silicate in rocks of a metamorphic terrane has become established as one of the prime indicators of progressive metamorphism (*1*). The transition is believed to represent increasing temperature of metamorphism at more or less constant pressure.

Petrologists have long hoped that experimental determination of the $Al_2SiO_5$ pressure-temperature diagram would elucidate the pressure and temperature conditions which prevailed during different kinds of rock metamorphism. These hopes have been somewhat fulfilled in the last 10-year period by a series of studies which, although they did not define the aluminum silicate equilibrium relations as well as it is now possible to do so, nevertheless demonstrated that kyanite requires quite high pressures for its stability at elevated temperatures and indicated that these pressures are in the range encountered in the earth's crust, though near the upper limit. The findings of Clark *et al.* (*2*) and of Clark (*3*) were the result of experiments made with dry materials at the very high temperatures which were necessary to produce reaction in the sluggish aluminum silicate system. Reversals of the kyanite-sillimanite equilibrium were accomplished above 1300°C in a solid-pressure-medium piston-cylinder apparatus. A long extrapolation to the temperature range of interest (300° to 700°C) was necessary.

A direct determination with dry materials in the crustal temperature range was performed by Bell (*4*) using a rotating-piston Bridgman anvil device. The accelerative effect of high shear stress made it possible to produce reactions in crystalline starting materials in a few hours even at temperatures as low as 300°C. The results for the kyanite-sillimanite equilibrium fell very close to the extrapolation of the Clark data (*3*), which might be considered surprising in view of the pressure variation and uncertainty existing under the flat anvils (*5*) and of the unknown effects of high shear stress as a thermodynamic parameter in influencing the apparent pressure-temperature locations of the equilibrium lines. Bell found a

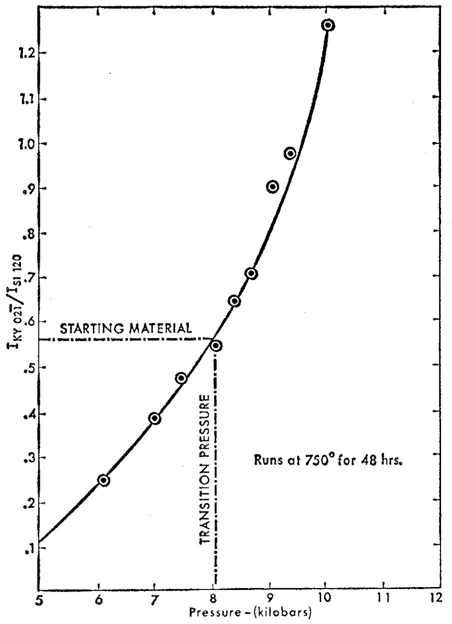

Fig. 1. Ratio of intensities of kyanite 02$\bar{1}$ and sillimanite 120 peaks versus pressure of run at 750°C.

field of stability for andalusite, something that had been regarded as doubtful by many writers (see Weill and Fyfe, *6*), with a triple point among the three polymorphs at 300°C and 8.0 kbar. He found a negative pressure-temperature slope for the andalusite-sillimanite equilibrium line, with sillimanite on the high-temperature side. This result has since been strikingly vindicated by the improved entropy measurements of Pankratz and Kelley (*7*). A pressure-temperature field of stability for andalusite is now regarded as established.

Weill and Fyfe (*6*) demonstrated by measuring solubilities of aluminum silicate in fused cryolite at 1010°C and 1 atm that the order of decreasing stability at those conditions is sillimanite, andalusite, kyanite. Weill (*8*) measured weight gain or loss of an andalusite crystal after treating it with steam for 70 days at 700°C and 3.0 kbar in the presence of kyanite or sillimanite powder and showed that the relative order of stability at those conditions is again sillimanite, andalusite, kyanite. The way in which this evidence serves to restrict possible $Al_2SiO_5$ pressure-temperature diagrams will be shown later.

Measured thermodynamic data for the $Al_2SiO_5$ polymorphs are now good enough to permit geologically meaningful calculation of the kyanite-sillimanite equilibrium if one point on the curve could be reliably determined. The most important measurements are those of the heat capacities (*7*) and molar volumes and thermal expansions (*9*).

The determination of the pressure of the kyanite-sillimanite equilibrium was carried out hydrothermally at 750°C in the talc-pressure piston-cylinder apparatus with a 1-inch diameter (2.54 cm) pressure cavity. The pressures between 0 to 15 kbar are known to ± 0.4 kbar by calibration determinations based on the melting curve of LiCl, the Bi(I)–Bi(II) transition and the calcite–aragonite transition in the temperature range 400° to 600°C (*10*). The magnitude of the pressure loss due to friction is 13.1 percent of the nominal pressure and is independent of sample temperature below 800°C. The precision of pressure determination is not quite as good as can be achieved in some kinds of gas-pressure apparatus, but this lack is counterbalanced by extreme ease of operation and low-temperature gradients over the sample, the accuracy obtainable being adequate for the present purposes.

Starting materials for most of the runs were ground natural kyanite and sillimanite, mixed intimately in about equal proportions (under acetone). The minerals were analyzed with the electron microprobe. The kyanite was from Litchfield, Connecticut. Its major impurity was 0.93 percent of $Fe_2O_3$. The sillimanite was from Lisenz, Tyrol. It had 0.76 percent of $Fe_2O_3$ and 0.10 percent of $TiO_2$; x-ray properties of the starting materials are given in Table 1.

The minerals were sealed with water in platinum capsules and held at 750°C and high pressure for 48 hours; the reaction mixture was quenched to room temperature at pressure in about 2 minutes. Chromel-p-alumel thermocouples were in contact with the sample capsules. The capsules were cut open and the charge was reground and sprinkled onto a thin uniform layer of vaseline on a glass plate for x-ray scanning. Growth of one phase relative to the other was detected by change of relative peak-heights of sillimanite and kyanite diffraction spectra. It was usually possible to tell the direction of the reaction qualitatively by comparing the diffractogram chart of the initial mixture with the diffractogram after the run, without measuring peak heights. The relative peak heights in the starting material were very reproducible, as judged from eight different vaseline preparations of the ground material, which indicated that it would be possible to refine the method by measuring the peak heights.

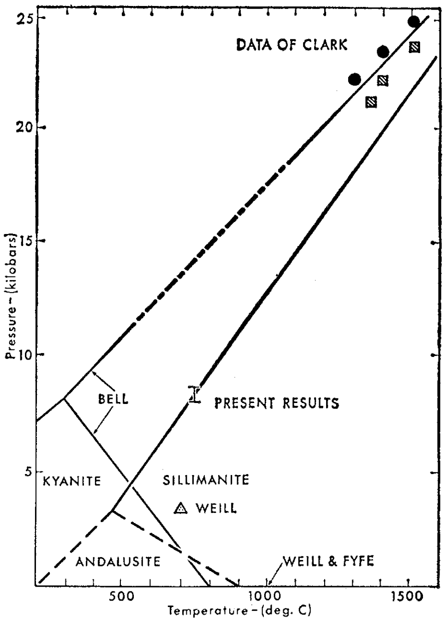

Fig. 2. Phase diagram of $Al_2Si0_5$ (heavy lines) based on present results and data of Weill (*8*) and Weill and Fyfe (*6*). Also shown are reversals of Clark (*3*) and of Bell (*4*) (lighter lines).

A run was made at 9.3 kbar with the same starting materials and an excess of added natural quartz. The reaction was also reversed with synthetic kyanite and sillimanite prepared as follows. The kyanite was prepared hydrothermally (750°C, 24 hours, 15.7 kbar) from ground natural quartz and $Al(OH)_3$ (Baker) seeded with a trace of the Litchfield kyanite. The charge was completely converted to kyanite and quartz. The kyanite had a slightly larger unit cell than the natural kyanite (Table 1). The size of the crystals was uniformly between 5 and 10 microns. The kyanite was completely converted to sillimanite in 48 hours at 750°C and 6.0 kbar by the hydrothermal method with a trace of Lisenz sillimanite. The synthetic sillimanite had unit-cell constants indistinguishable from the Lisenz material.

Reactions in 48 hours were much greater than might have been supposed in view of the known sluggishness of aluminum silicate reactions. Runs at 750°C were performed at pressures of 11.8 and 15.4 kbar, in which natural sillimanite inverted completely to kyanite. In a run at 6.1 kbar natural kyanite inverted almost completely to sillimanite. Reactions at pressures between these showed intermediate degrees of reaction. The materials in runs in which the capsule leaked (that is, the charge came out dry) showed no reaction.

Table 1. Cell constants of starting material and overgrowths.

| $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (deg) | $\beta$ (deg) | $\gamma$ (deg) |
|---|---|---|---|---|---|
| *Lisenz sillimanite* | | | | | |
| 7.482 | 7.669 | 5.782 | | | |
| *Sillimanite overgrowth (750°C, 7.0 kbar, 48 hr)* | | | | | |
| 7.481 | 7.666 | 5.783 | | | |
| *Litchfield kyanite* | | | | | |
| 7.116 | 7.850 | 5.564 | 89.88 | 101.29 | 105.98 |
| *Kyanite overgrowth (750°C, 11.6 kbar, 48 hr)* | | | | | |
| 7.116 | 7.848 | 5.561 | 89.93 | 101.28 | 105.96 |
| *Synthetic kyanite (750°C, 15.7 kbar, 24 hr)* | | | | | |
| 7.125 | 7.847 | 5.571 | 89.92 | 101.20 | 106.02 |

The direction and degree of reaction for the definitive runs are shown in Fig. 1. The transition pressure at 750°C for the equilibrium between sillimanite and kyanite is 8.1 ± 0.4 kbar.

The runs showing large amounts of reaction were examined microscopically. Overgrowths on mineral grains were obvious and abundant. The overgrowths on kyanite grains were especially evident, being limpid and geometrical, in contrast to the darker surfaces and ragged edges of the ground natural kyanite fragments.

Overgrowths of kyanite and sillimanite were scanned slowly with x-rays, a corundum internal standard being used. No change in the *d*-spacings from those of the original materials could be distinguished (Table 1). A small amount of corundum could be distinguished in most of the quenched charges, both by x-ray diffraction and optically. In addition an unidentified weak peak at 28.5 degrees ($2\theta$, Cu radiation) appeared in some of the diffractograms. The corundum and the unknown substance, probably a hydrous aluminum silicate, are presumably products which precipitated from the vapor phase upon quenching. The run with excess quartz showed the unknown phase but not the corundum. The quartz was present in its original amount in the quenched charges. There was no melting.

The equilibrium was reversed by seeding synthetic sillimanite with a small amount of Litchfield kyanite and heating at 750°C and 9.3 kbar of water pressure. After 48 hours there was substantial growth of kyanite.

The resulting transition pressure at 750°C of 8.1 kbar is substantially lower than the 14.1 kbar at 750°C given by the Clark (*3*) extrapolation. The slope of the transition at that temperature can be calculated from the measured entropies and volumes of the minerals at 1 atm. The entropies at 25°C for kyanite and sillimanite given by Todd (*11*) and high-temperature heat-capacity measurements of Pankratz and Kelley (*7*) were used to determine entropies, at 750°C and 1 atm, of 69.20 cal/deg-mol for kyanite and 71.54 cal/deg-mol for sillimanite, giving a $\Delta s$ of 2.34 cal/deg-mol for the reaction. At an elevated pressure $P$, the entropy change ($\Delta s$) is corrected by the approximate formula

$$\Delta S(P) \approx \Delta S(0) - \Delta(V_0\alpha)P/J$$

where $V_0$ is the molar volume at 1 atm and 750°C, $\alpha$ is the molar thermal expansion at these conditions, and $J$ is the heat-work equivalence. Substituting $V_0\alpha = 1.255 \times 10^{-3}$ cm$^3$/deg-mol for sillimanite and $V_0\alpha = 1.335 \times 10^{-3}$ cm$^3$/deg-mol for kyanite (Skinner *et al.* *9*), and if $P$ is 8100 bars and $J$ is 41.31 (bar-cm$^3$)/cal, the entropy change at 8100 bars becomes 2.35 cal/deg-mol. The volume change of the reaction at 750°C and 1 atm is 5.488 cm$^3$/mol, according to Skinner *et al.* (*9*). There are no reliable compressibility data available at the present time for the two phases. A glance at typical values for minerals in the data of Birch *et al.* (*12*) shows, however, that $\Delta V$ for the reaction at 8.1 kbar is quite unlikely to change by more than 0.2 cm$^3$/mol from the 1 atm value. The slope of the reaction is thus 17.7 ± 1.0 bar/°C by the Clausius-Clapeyron relation. This gives a value of 21.4 kbar at 1500°C, not far from the 24.0 value given by Clark (*3*). The probable curvature, owing to change of the heat capacity difference at higher temperatures, would make the value still lower in pressure at 1500°C, perhaps by another kbar. The temperature intercept at 1 atm for the reaction is 290°C. The maximum curvature conceivable would only raise this temperature by about 30°C. The slope of 17.7 bar/deg is considerably greater than the slope of 13.2 bar/deg found by Clark (*3*). Clark recognized that his experimental data were not consistent with the available room-temperature thermodynamic data, but thought that the decrease in $\Delta S$ at high temperature would result in a slope in agreement with his experiments. The new high-temperature entropy data show, however, that the slope at 1500°C is not likely to be less than 17.0 bar/deg.

The calculated slopes of the kyanite-andalusite boundary and the andalusite-sillimanite boundaries are, respectively, 10.9 bar/deg and −8.0 bar/deg. The experiments of Weill and Fyfe (*6*) and Weill (*8*) serve to put further restrictions on the $Al_2SiO_5$ diagram. Both sets of experiments were apparently performed at pressures higher than the andalusite-sillimanite boundary and at pressures lower than the kyanite-andalusite boundary at the given temperatures. With this information and the calculated slopes of the boundaries, the statement may be made that andalusite cannot be stable at a pressure greater than 4.2 kbar. An aluminum silicate diagram, based on the present results, which is consistent with the data of Weill and Fyfe (*6*) and Weill (*8*) is given in Fig. 2, along with the determinations of Clark (*3*) and Bell (*4*). The dashed portions are conjectural. Clark assumed a friction correction of −8 percent for his apparatus. A friction correction of −16 percent would bring his data into accord with this result. The friction correction for runs on hard, dry materials at very high temperatures has still not been satisfactorily determined. The high pressure of the aluminum silicate triple point (8.0 kbar) found by Bell (*4*) may be a result of the necessity of considerable overpressing needed to create the high-pressure phases at the expense of low-pressure ones at a finite rate.

An outstanding problem resulting from the acceptance of the Clark kyanite-sillimanite data was the source of the high pressures to produce kyanite. At a temperature of 500°C, for instance, 10.5 kbar would be necessary to stabilize kyanite. This would necessitate nearly 35 km of vertical travel of kyanite-bearing rocks in the metamorphic cycle, unless some scheme of pressure generation other than burial could be invoked. Clark (*3*) postulated a "tectonic overpressure" of as much as 3.7 kbar, caused by mountain-building forces and supported by the strength of the rocks for periods long enough to create minerals that are formed at high pressure. The escape of water from regions of tectonic overpressure would have to be correspondingly slow to explain kyanite veins and pegmatites. Another serious difficulty was in the preservation of kyanite, for any metamorphic pressure-temperature cycle of rocks must make a considerable excursion through the sillimanite field at elevated temperatures in order for the rock to return to the surface.

The present determination removes both difficulties. The kyanite field now dominates the geologic portion of the pressure-temperature plane, which fact is intuitively more satisfactory in explaining the predominance in nature of the kyanite polymorph. Reasonable pressures of deep metamorphism (3 to 5 kbar) require that the temperature be no higher than 450° to 550°C to prevent inversion to sillimanite. If a temperature of 500°C is reached in the aureole of a granite body intruded at a depth of 8 km, for instance, kyanite will change to sillimanite. If temperatures remain fairly high until the rock has risen by natural causes so that it is closer to the earth's surface, the kyanite-sillimanite line would not be recrossed at temperatures higher than 200° to 300°C when cooling occurs. The very slow sillimanite-andalusite inversion, especially where water is absent, might prevent inversion to andalusite. Hence the sillimanite could be preserved. The occurrence of kyanite in metamorphic rocks is easier to explain, in that a geothermal gradient of 30°C/km lies entirely within the kyanite field until a temperature of 600°C is reached. Kyanite, once created, might remain ever after in its own field of stability.

ROBERT C. NEWTON

*Department of the Geophysical
Sciences, University of Chicago,
Chicago, Illinois*

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13. I thank Drs. P. M. Bell, F. R. Boyd, J. R. Goldsmith, and D. Green for helpful conversations. The microprobe analyses were provided by Dr. Mabel Corlett. Supported by NSF grant GP 1445.

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## Gonadotropin-Induced Anomalies of the Zona Pellucida of the Baboon Ovum

Abstract. *Vesiculation and other anomalies were observed in the zona pellucida about the ovum of female baboons* (Papio anubis) *that had received treatment with Pergonal and human chorionic gonadotropin; and in some instances the zona pellucida was absent.*

The mature ovum is surrounded by a thick homogeneous membrane, the zona pellucida, which is believed to be a secretion product of adjacent follicular cells (*1*). The function of the zona is protective, and during the course of fertilization it is a barrier that must be penetrated by the spermatozoa.

Formation and constitution of the zone pellucida in maturing follicles of the baboon (*Papio anubis*) appear to encounter interference in animals that have been treated with Pergonal (*2*) (trade name for human postmenopausal gonadotropin) and human chorionic gonadotropin. These gonadotropins are currently finding wide usage in the treatment of infertile women and produce a condition of superovulation that has led to a high incidence of multiple births (*3*).

We studied ovarian sections of seven untreated animals and compared the data with that of ovaries obtained from five animals, in two groups, whose regimen of treatment was as follows.

Group 1: Starting on the 5th day of the menstrual cycle, we administered 75 international units of Pergonal intramuscularly to three animals for 8 days. Human chorionic gonadotropin (2000 units) was also administered intramuscularly on each of days 6 and 7, and 2000 units were injected intravenously on the 8th day in order to produce a sudden surge of ovarian stimulation (*4*).

Group 2: The two animals in this group received 150 international units of Pergonal intramuscularly, the treatment being started on the 5th day of the menstrual cycle and continued for 5 days. A reduced dose of 75 units per day was given for an additional 3 days. This was complemented by a dose of 2000 units of human chorionic gonadotropin administered intramuscularly on days 6 and 7 and intravenously on day 8. Ovariectomy was performed after various periods of time following intiation of treatment. Histologic preparations were stained with hematoxylin and eosin, and the first 25 follicles (secondary and tertiary) that were viewed and found to contain ova were examined for the presence and condition of the zona pellucida. Findings are given in Table 1.

Ovaries of 80 percent of the treated animals showed a high incidence of defective development of the zona pellucida. This was indicated by a variety of anomalies that included vesiculation, hypotrophy, and absence of this structure. The effect was particularly marked in the tertiary follicles. Slides of the

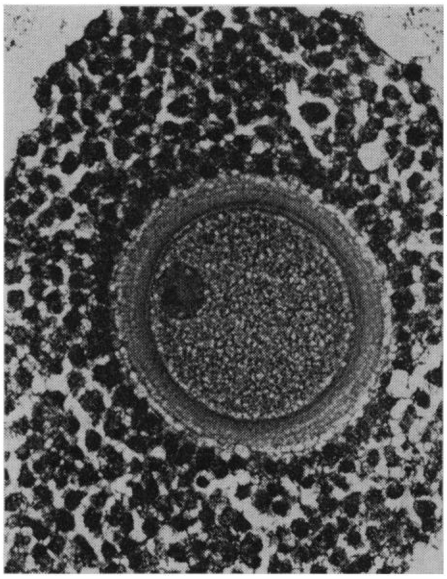

Fig. 1. Ovum of untreated animal with normal zona pellucida.

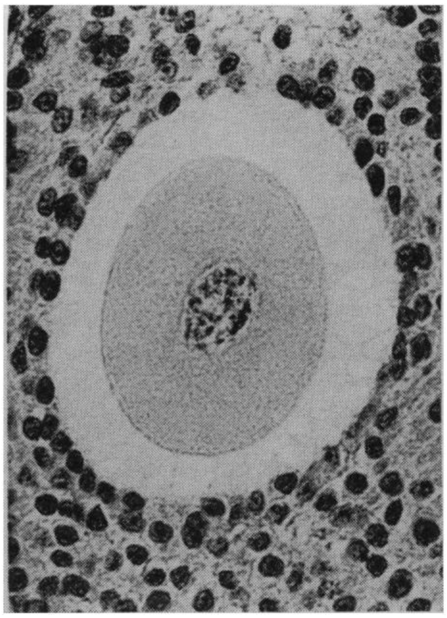

Fig. 2. Ovum of treated animal showing vesiculation of the zona pellucida.