(*4*), I found that the mature larvae weighed 62 percent more than the provisions bearing eggs. The increase could be accounted for as water uptake by the larvae, not the provisions. The relative water content of the provisions remained constant (43 ± 2 percent) throughout larval development, while the growing larvae contain about 70 percent water. Pollen balls by themselves did not gain weight. The greatest increase in amount of water in the larva takes place when the provisions are almost consumed. Many insects are known to take up water as vapor through the cuticle (*5*), and halictids are probably no exception.

Malyshev's (*6*) statements on the hygroscopic nature of provisions were apparently without experimental support. If the provisions were as hygroscopic as Batra and Bohart (*1*) believe, there would be no need to postulate progressive feeding, and no need for Batra (*7*) to have added a honey supplement to provisions in the laboratory.

The nature of cell construction of halictids, particularly the waterproof nature of the cell lining (*3*), preserves high humidity inside the cells. If the cells are opened, however, as is apparently the case for *Evylaeus malachurus* (*2*), it may be necessary for the adults to moisten the provisions to compensate for water loss.

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References

1. S. W. T. Batra and G. E. Bohart, *Science* **168**, 875 (1970).
2. G. Knerer, *ibid.* **164**, 429 (1969).
3. D. G. K. May, thesis, University of Kansas (1970).
4. K. A. Stockhammer, *J. Kans. Entomol. Soc.* **39**, 157 (1966).
5. J. W. L. Beament, *Advan. Insect Physiol.* **2**, 67 (1964).
6. S. I. Malyshev, *EOS* **11**, 249 (1935).
7. S. W. T. Batra, *Insectes Soc.* **11**, 159 (1964).

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May (*1*) has supported our conclusion (*2*) that the excess weight gain of halictid cell contents cannot be used, as it was by Knerer (*3*), as evidence of progressive provisioning by these bees.

The peripheral question as to how the cell contents gain weight (water) remains unresolved. Some water absorption through the spiracles or the cuticle of the larva is possible. Healthy larvae should be maintained in a humid atmosphere without provisions in order to test this hypothesis adequately. Halictid provisions, consisting of a mixture of honey and pollen, are probably hygroscopic. Extracted honey, when kept at high humidity, gains up to 33 percent in weight because of hygroscopicity (*4*).

The provisions are stored in cells having a porous cap or no cap. Cells typically are in soil that is moist enough to support vegetation. Air spaces in such soil remain at 100 percent relative humidity (*5*), thus the nest (except perhaps near the entrance) and the cells would be at or near 100 percent relative humidity.

Young halictid larvae initially feed at one area on the surface of the spheroidal provisions, creating a small, moist-appearing indentation beneath the mouthparts. This concavity evidently lowers the vapor pressure at that point, so that water from the saturated cell atmosphere condenses there. It is thus continually ingested by the young larva. Unlike *Augochlora* (*1*), an exceptional halictid that nests in wood, the greatest increase in water content of *Nomia* occurs during the early larval instars (*2*). The provisions with brood of the solitary soil-nesting andrenid bee *Calliopsis* dried out at 93 percent relative humidity but appeared normal when kept at 100 percent relative humidity (*6*). The high humidity requirement of halictine provisions, among other factors, may account for my need to add diluted honey to provisions kept at high, but evidently not 100 percent, relative humidity (*1, 7*).

General condensation in the cell may also be an important source of water. It regularly forms on the cell lining, provisions, and brood of halictid bees when the soil temperature decreases. Condensation forming on the larvae and provisions of *Pseudopanurgus* is swallowed (*8*), and the larvae of this solitary, soil-dwelling panurgine bee, like halictid larvae (*2*), grow rapidly before much provision is consumed.

Progressive provisioning in halictine bees was tentatively postulated (*7*) because females of *Dialictus zephyrus* were seen opening sealed cells and touching, with their glossae, provisions bearing brood. Radioactive tracers and dyes (*7*) should be used to determine if this behavior represents progressive provisioning, the addition of secretions, or the removal of substances from the provisions. It remains significant to the study of the evolution of insect social behavior that halictine bees *may* progressively provision when contacting the developing brood, whether in sealed (*7, 9*) or in open (*3, 9*) cells.

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References

1. D. G. K. May, *Science*, this issue.
2. S. W. T. Batra and G. E. Bohart, *ibid.* **168**, 875 (1970).
3. G. Knerer, *ibid.* **164**, 429 (1969).
4. F. W. Fabian and R. I. Quinet, *Mich. State Coll. Agr. Exp. Sta. Tech. Bull.* No. 92 (1928), pp. 1–41.
5. H. O. Buckmann and N. C. Brady, *The Nature and Properties of Soils* (Macmillan, New York, 1963).
6. A. F. Shinn, *Univ. Kans. Sci. Bull.* **46**, 753 (1967).
7. S. W. T. Batra, *Insectes Soc.* **11**, 159 (1964); *Univ. Kansas Sci. Bull.* **46**, 359 (1966).
8. J. G. Rozen, Jr., *Amer. Mus. Novitates* No. 2297 (1967), pp. 1–43.
9. S. W. T. Batra, *J. Kans. Entomol. Soc.* **41**, 120 (1968).

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Density of Low Temperature Ice

Delsemme and Wenger (*1*) present results showing a very large density, 2.32 g cm^{-3}, for water ice formed below 100°K at pressures of 6 to 8 × 10^{-3} mm-Hg. We have measured both the density and refractive index of ice formed under similar temperature and pressure conditions without observing abnormally high densities or a high refractive index.

We determined the density of low temperature ice by uniformly condensing water vapor over a very well-defined, cryogenically cooled, flat surface at a known constant mass deposition rate, $\dot{m}$. As the ice formed, its constant thickness deposition rate, $\dot{\tau}$, was measured, which allowed the ice density, ρ, to be calculated from

$$\rho = \frac{\dot{m}}{A\dot{\tau}} \qquad (1)$$

where A is the deposition area. In order to measure the thickness deposition rate as accurately as possible, we used optical thin-film interference techniques (*2*) with monochromatic light. By using these techniques we obtained both the thickness deposition rate and the refractive index of the ice as it was deposited.

In our experiments water vapor was condensed under vacuum on the outside of a hollow copper cryosurface which was cooled internally by flowing liquid nitrogen through it. Both this cryosurface and the liquid nitrogen addition lines to it were completely surrounded by a vacuum jacket except for one flush, planar surface, the cryoplate, on which the water vapor was condensed. This metal vacuum jacket prevented condensation of water vapor anywhere except on the cryoplate whose area, A, was accurately known. Before the experiments, the cryoplate was polished to a root-mean-square surface roughness of approximately 0.01 μm and was then cleaned with acetone and alcohol. Moreover, particular care was taken throughout the experiments to insure that the surface remained clean to eliminate the possibility of impurities affecting the formation of the ice.

Temperatures of both the vacuum jacket and the cryoplate were monitored with thermocouples throughout each run, and the temperature of the vacuum jacket was never below 283°K (10°C). The entire cryosurface and vacuum jacket assembly was enclosed in a vacuum chamber and prior to each test the chamber was evacuated to about 1×10^{-6} mm-Hg. Then the cryoplate surface was cooled to 82.2°K. During deposition this temperature never increased more than 3°K. Before the water vapor was introduced, the chamber was valved off from the pumping system.

For these measurements distilled water in a reservoir was outgassed by boiling the water while pumping out the space above it with a vacuum pump. After outgassing, water was vaporized under vacuum in the reservoir and then conducted into the vacuum chamber at a constant, known mass-flow rate. A baffle was placed over the gas inlet to insure that the gas had no direct path to the cryoplate. The water vapor condensed on the cryoplate at a rate of 3×10^{-6} g cm^{-2} sec^{-1}. This mass-deposition rate was further verified as being constant by the invariant fringe period of the observed interference patterns and the fact that the pressure in the chamber remained constant at 4×10^{-4} mm-Hg during the ice deposition. After the flow of water vapor was stopped, the final equilibrium pressure in the vacuum chamber never exceeded 2×10^{-4} mm-Hg. The ice layer never exceeded 25 μm in thickness so there was not an appreciable temperature difference across it.

The average of ten independent measurements for this low temperature ice gave a density of 0.81 ± 0.02 g cm^{-3}, where the uncertainty is the combined uncertainty of each factor in Eq. 1. Each of the individual measurements was within this uncertainty of the average density.

Many investigators (*3*) have shown that amorphous ice is formed by condensing water vapor at temperatures below approximately 112°K and that this ice transforms irreversibly to cubic ice when it is warmed to about 150°K. Upon warming our ice deposits, we simultaneously observed, when the temperature reaches 150°K, a large and very abrupt increase in both temperature and visible-infrared spectral reflectances. These irreversible changes are the result of the transition from amorphous to cubic ice. It is therefore concluded that we have measured the density of an amorphous ice deposit.

Our measured value for the density of ice formed at low temperatures can be corroborated by using it and the measured refractive index to compute the specific refraction from the Lorentz-Lorenz equation and noting the agreement between the result and known specific refraction values. The Lorentz-Lorenz approximation relates the density and refractive index of a substance by

$$\frac{n^2 - 1}{n^2 + 2}\ \frac{1}{\rho} = P(\lambda) \qquad (2)$$

where n is the refractive index of the substance at a particular wavelength λ of light and $P(\lambda)$ is the specific refraction at the same wavelength. Within the uncertainties of our measured density and refractive index, the specific refraction is constant (*4*) and independent of the temperature, pressure, and phase of the substance. At a wavelength of 0.589 μm we have found that the refractive index of these deposits is 1.264 ± 0.013. Our values of density and refractive index give a specific refraction of 0.205 cm^3 g^{-1}. This value of specific refraction agrees very well with those given by Dorsey (*5*) for the same wavelength: 0.210 cm^3 g^{-1} for ice at -3°C, 0.206 cm^3 g^{-1} for liquid water at 20°C, and 0.209 cm^3 g^{-1} for water vapor at 1 atm and 110°C.

It is difficult to explain the difference between the density results from our study and those of Delsemme and Wenger because of the vague description of their experimental apparatus and techniques. At first one might suppose that the disagreement is due to differences in the impurities present in the two systems. However, it should be noted that any impurities present in our chamber (base pressure of 10^{-6} mm-Hg) were substantially less than the amounts of impurity that can be deduced as present in the experiments of Delsemme and Wenger (base pressure of 10^{-4} mm-Hg). It would be of interest to have more specific values for the minimum amounts of impurity that prevented formation of the superdense ice observed by them.

It is possible that unequal mass deposition over the surface and inherent inaccuracies in photographic thickness measurements account for the high densities of low temperature ice obtained by Delsemme and Wenger. In all gas condensation studies there is a problem of insuring a uniform deposition of mass over the entire substrate. This problem can be particularly severe for a nonplanar substrate such as a cone. As one example, more gas could condense on that part of the surface which has a direct view of the gas inlet than would condense elsewhere on the surface. Moreover, it would be difficult to visually observe the uniformity of a thin transparent deposit over an entire three-dimensional surface. In addition, measurements of small thicknesses by photographic techniques are inherently less accurate than optical interference measurements. For a "compact snow" formed by high rates of introduction above 200°K, Delsemme and Wenger do obtain a density near that found by other investigators for ice I_h. This might be fortuitous when compared with their lower temperature results, as the high flow rate could lead to a more uniform deposit over the surface and, further, the thickness of an opaque deposit should be easier to measure photographically than that of a transparent deposit.

Finally, with the Lorentz-Lorenz equation, the density obtained by Delsemme and Wenger gives a refractive index of 1.958 at a wavelength of 0.589 μm. This value is indeed large compared with what is usually expected for ice deposits. A refractive index measurement of their ice which satisfied the Lorentz-Lorenz equation would help corroborate their density value.

In conclusion, we have measured the density and refractive index of uniformly thick amorphous ice deposits formed over a well-known area. These deposits were formed under conditions of temperature, pressure, and, as near as can be deduced, purity similar to those used by Delsemme and Wenger. We did not measure unusually high values of either density or refractive index for these ice deposits.

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References and Notes

1. A. H. Delsemme and A. Wenger, *Science* **167**, 44 (1969).
2. K. E. Tempelmeyer and D. W. Mills, Jr., *J. Appl. Phys.* **39**, 2968 (1968); P. R. Müller, thesis, Univ. of Tennessee (1969).
3. B. J. Luyet, *Phys. Rev.* **56**, 1244 (1937); J. A. Pryde and G. O. Jones, *Nature* **170**, 685 (1952); work and review M. Blackman and N. D. Lisgarten, *Proc. Roy. Soc. Ser. A* **239**, 93 (1957); J. A. McMillan and S. C. Los, *Nature* **206**, 806 (1965); J. A. Ghormley, *J. Chem. Phys.* **48**, 503 (1968); D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford, London, 1969), pp. 89–90.
4. S. Glasstone, *Physical Chemistry* (Van Nostrand, Princeton, N.J., 1946), pp. 528–529; A. Weissberger, E. Proskauer, J. Riddick, E. Toops, Jr., *Organic Solvents* (Interscience, New York, 1955), p. 21; M. Born and E. Wolf, *Principles of Optics* (Pergamon, Oxford, 1965), pp. 84–90; D. Eisenberg and W. Kauzmann, *ibid.*, p. 115.
5. N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold, New York, 1940), p. 484.
6. Sponsored by the Arnold Engineering Development Center, Air Force Systems Command, under contract F40600-69-C-0001 with ARO, Inc.

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Seiber *et al.* (*1*) give evidence of the existence of a low temperature ice whose density is near 0.81 g cm^{-3}. It is however not obvious that they have observed the same allotropic form as ours (*2*). Three differences are conspicuous between the description of their measurements and ours; they concern the temperature, the rate of condensation, and the impurities.

First, the temperature range used for the condensation process does not overlap with ours. They report that their condensation took place between 82° and 85°K. We observed the condensation of the glassy superdense ice between 93° and 98°K only; between 98° and 103°K some anomalous density effects were still observed which disappeared higher than 103°K. It is unfortunate that while we could not explore the range lower than 93°K, Seiber *et al.* did not explore the range higher than 85°K.

The second difference concerns the condensing rate. We produced the high density ice with rates from 33 to 920×10^{-6} g cm^{-2} sec^{-1}, and we reported that the condensing rate does not seem very critical. Crystal forming is however usually rate-sensitive, and we have no information available on the possible production of the glassy superdense ice when the rate is 3×10^{-6} g cm^{-2} sec^{-1} as it is in the experiment of Seiber *et al.*, that is 11 times lower than the lowest of the rates we used.

The third difference might be the crucial one. We reported that methane or air, left in the vacuum chamber at an initial pressure of 10^{-4} mm-Hg, stops the apparition of a pure high density ice. This pressure corresponds to about 2×10^{-7} g of air or methane, and in a typical experiment we condense at least 2×10^{-1} g of water. Glassy high density ice can be produced only after the chamber has been purged with water vapor. In this instance, the dilution factor of the impurities is of the order of 10^{-5}, if we neglect other sources of impurities like water itself or desorption phenomena by the walls.

The observed amount of impurity limiting the production of high density ice lies therefore between 10^{-6} and 10^{-11} times the amount of water used. Seiber *et al.* do not give enough information to compute their amount of impurity, but with an ice layer more than one order of magnitude thinner than ours, we presume that a pressure of residual air of 10^{-6} mm-Hg would give an amount of impurity nearer 10^{-6} than 10^{-11}. Then we believe that the mixed clathrate hydrate of oxygen and nitrogen will form at the beginning of the condensation. It will develop a crystal lattice which might grow even when the impurities have been used up. In this respect, the clathrate lattice, with its gaps either empty or filled with the impurities, has densities of 0.798 and 0.896 g cm^{-3}, respectively (*3*). It may be significant that the density found by Seiber *et al.* is in between, which could mean that they have observed the (almost empty) clathrate lattice. Of course, it could also transform irreversibly to cubic ice near 150°K.

The concise description of our technique left indeed several questions unanswered. Our density is obtained as the ratio of the final mass of the ice to its final volume. The weight of the total amount of water is found back within 0.1 percent and the error (±6 percent) comes from the assessment of the volume only.

The volume is established by optically superpositioning the photographic enlargements of the cone with and without its ice layer. Fiducial marks and wires seen in the field are used to check the magnification and the positioning. The accuracy of the positioning is of the order of 10 μm, which is much better than the resolving power of the negatives. In particular, the misplacement of the second picture along the cone axis is definitely smaller than 10 μm, measured on the cone itself.

In a typical experiment, the thickness of the dense icy layer is around 300 μm near the top and the middle of the cone, and diminishes steadily to 200 μm, then quickly to zero, near the base of the cone. A numerical integration of rings around the cone takes into account the variation of ice thickness at different heights. Of course this implies the existence of an axial symmetry of the mass deposition over the surface. It happens that the profile of the cone which faces the gas inlet and the one directly opposite are the two that have been photographed, and they have never shown any asymmetry.

From the window, it is possible to change the angle of sight by some 45° and no asymmetry has ever been detected visually. The surface of the ice is clearly detectable by the bright reflection of light from an electric bulb inside the vacuum chamber. Pictures of the cone with different ice layers are published in (*4*). A heating system monitored by thermocouples and a metal vacuum jacket are also used to prevent condensation anywhere but on the cone. Uneven shrinkage of the photographic emulsion was found to be negligible by superimposing two pictures of the cone itself.

The technique described was developed for another purpose, namely the measurement of very low apparent densities of snows. Although this technique is not the best for high densities, it is however difficult to doubt the existence of a form of low temperature ice with an unusually high density.

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References

1. B. A. Seiber, B. E. Wood, A. M. Smith, P. R. Müller, *Science*, this issue.
2. A. H. Delsemme and A. Wenger, *ibid.* **167**, 44 (1970).
3. A. H. Delsemme, *13th Coll. Astrophys. Liege* **37**, 77 (196 M. von Stackelberg, *Naturwissenschaften* **36**, 327 (1949); *ibid.*, p. 3 M. von Stackelberg and H. R. Muller, *J. Chem. Phys.* **19**, 1319 (195 W. F. Claussen, *ibid.*, p. 259; *ibid.*, p. 632.
4. A. H. Delsemme and A. Wenger, *Planet. Space Sci.* **18**, 709 (1970).

15 June 1970