Table 2. Atomic formula of garnet calculated to 12 oxygens.

Site	Atom	Assuming divalent Fe		Assuming trivalent Fe	
X	Si	3.00		3.00	
Y	Si	0.78	2.06	0.62	1.84
	Al	0.23		0.22	
	Fe	1.02		0.97	
	Cr	0.03		0.03	
Z	Mg	2.98	3.08	2.86	2.96
	Na	0.10		0.10	

composition. The name *majorite* has been approved for the garnet by the International Mineralogical Association Commission on New Minerals. The name honors Alan Major, who assisted Ringwood (*2*) in high-pressure synthesis of garnet from pyroxene composition.

The spinel has an olivine composition that overlaps the composition of the spinel in the Tenham meteorite (*3*). Binns, Davis, and Reed assigned the name ringwoodite to the spinel phase. The ringwoodite of the Coorara meteorite has a variable composition, which overlaps the composition of the Tenham ringwoodite (Table 1). The Coorara specimen contains 0.2 percent by weight of Mn, whereas no Mn was listed (but might have been overlooked) for the Tenham material. The composition range of the olivine in the main body of the Coorara meteorite overlaps that of the ringwoodite.

The Coorara ringwoodite, like the Tenham ringwoodite, has an eye-catching purple color in thin section and consists of discrete grains, often coarsely interwoven with a pyroxene. The majorite is fine-grained (several micrometers across) and forms a brownpinkish matrix with goethite and kamacite surrounding the coarse spinel and pyroxene crystals.

A small sliver of the matrix from the veinlet yielded a Debye-Scherrer pattern (*4*) whose lines could be indexed in accordance with the reference patterns for pyrope garnet, goethite, and α iron in the Powder Diffraction File. The extrapolated cell dimension for the majorite was 11.524 ± 0.002 Å consistent with the value 11.51_5 Å obtained by Mason *et al.* (*1*). The line intensities are quite similar to those for pyrope reference card 15-742 of the Powder Diffraction File.

The majorite of the Coorara meteorite is so fine-grained that microprobe analysis was very difficult. The compositions (*5*) reported in Table 1 were obtained from a polished thin section by rejecting some data with a high Fe and low Si content, which were thought to result from overlapped goethite and other Fe-rich minerals. The oxidation state of the Fe is unknown, and the analysis has been calculated to 12 oxygen atoms on the two extremes of all divalent and all trivalent Fe (Table 2). Whatever the assumption, some Si must be in nontetrahedral coordination, almost certainly in octahedral coordination. The major elements Mg, Fe, and Si have concentrations similar to those of the orthopyroxene that occurs as a major constituent of the main body of the meteorite, but the minor elements are quite different. The garnet is brownish, but the color may result from iron oxides rather than being inherent. The garnet of the Tenham meteorite has x-ray and chemical properties (*2*) similar to the properties reported here.

Also in the polished thin section of the vein are rare crystals of an optically isotropic material of orthopyroxene composition. These crystals are probably majorite, but an x-ray validation has not yet been obtained.

The ringwoodite and majorite were undoubtedly formed from olivine, pyroxene, and other minerals in the meteorite as a result of extraterrestrial high-pressure transformations. The overlap of the composition ranges of the ringwoodite and olivine indicates an isochemical transformation. The major elements of the majorite and pyroxene are fairly similar when account is taken of substitution of Si by Al (see Table 2). However the minor element concentrations are quite different. The Na and Al of the majorite probably come from plagioclase. The Cr probably comes in part from chromite. Presumably original pyroxene with lesser amounts of plagioclase, olivine, and chromite were converted into the fine-grained mixture of majorite with lesser amounts of iron-rich phases. Subsequently, terrestrial weathering caused considerable changes in the hydration and oxidation states of the iron.

On the basis of incompatibility of the cell dimension of majorite with the cell dimension expected theoretically for a garnet with an Mg-rich olivine composition, McConnell (*6*) proposed that the garnet has the composition of khoharite, whereas Geller (*7*) suggested that its composition is a mixture of pyroxene and olivine. The new chemical data yield an estimated cell dimension that is consistent with the observed cell dimension.

The great similarity between the chemical and textural data for the Tenham and Coorara meteorites strongly suggests a common extraterrestrial origin. However, Tenham is an observed fall (1879), whereas the weathered condition of Coorara (found in 1967) indicates that it probably fell hundreds or even thousands of years ago.

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Orientation Order of Dipole Molecules in the Surface of Embryonic Droplets

Abstract. *During the growth of embryonic droplets in an imperfect vapor the surface polar molecules pass from a disordered orientation state to an ordered orientation state, the transition size being on the order of 100 molecules. This transition poses an interesting model problem in the study of order-disorder transitions in the thermodynamics of small systems.*

Until 1962 the classical nucleation theory for water condensation, as given by Becker and Döring (*1*), had been regarded as well founded and substantially verified by experiment. In 1962 Lothe and Pound (*2*) pointed out that, according to this treatment, the embryonic droplets are considered to be at rest in the vapor whereas, in reality, they form a macromolecular gas so that their translation and rotation must be considered. This correction increases the concentration of droplets of critical size by a factor of $\sim 10^{20}$ and destroys the previous good agreement between theory and experiment for the much tested case of water vapor (*2*). Since 1962 several vapors have been studied experimentally, and neither the Becker-Döring theory nor the Lothe-Pound theory is reliable for use in accurately predicting condensation in supersaturated vapors. For example, the critical supersaturations for the homogeneous nucleation of water, ethanol, and methanol are consistent with the Becker-Döring theory; critical supersaturations for hexane lie between the predictions of the Lothe-Pound theory and those of the Becker-Döring theory; and critical supersaturations for ammonia and benzene are consistent with the Lothe-Pound theory (*3*).

Recently a relation between the homogeneous nucleation of a liquid and the molar surface entropy of the planar liquid surface has been discovered (*4*). The molar surface entropies of liquids whose critical supersaturations for homogeneous nucleation are consistent with the Becker-Döring theory are $\sim$ 10 joule/deg, in contradistinction to $\sim$ 22 joule/deg for those liquids whose critical supersaturations are consistent with the Lothe-Pound nucleation theory. Orientation in the surface of the molecules will lead to a lower entropy than that which prevails in the state where surface molecules are disordered. Therefore, assuming that the "normal" surface entropy of disordered surface molecules equals $\sim$22 joule/deg, we may attribute the entropy deficit of $\sim$12 joule/deg to surface orientation (*4*).

Recent attempts to resolve the disagreement between the present theories of vapor condensation and experimental results have centered around suggested models for the surface structure of embryonic droplets which differ from models which postulate the flat-plane surface structure exhibited by liquids that obey the Becker-Döring theory (*4–6*). In particular, two models for the orientation order of the surface dipole molecules were assumed: in model 1 there is no preferential orientation of the molecules defining the surface (*4, 5*); in model 2 the surface dipole molecules remain oriented for embryonic sizes, and the surface free energy of such droplets is greater than that given by the capillarity approximation if the dipole-dipole interaction energy of the oriented surface molecules is corrected for surface curvature (*6*).

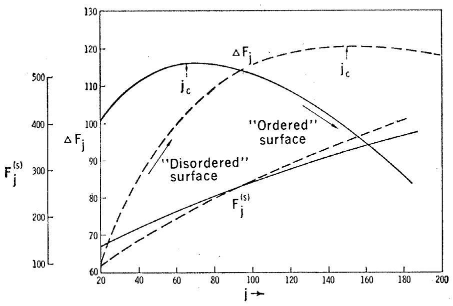

Fig. 1. Values of ΔF_j and $F_j^{(s)}$ (in units of kT) plotted as a function of droplet size j for the disordered surface model (model 1, dashed lines) and the ordered surface model (model 2, solid lines) with $T = 263.2$°K and $S = 5.0$. The critical size of the droplet j_c for the two models is indicated.

The important feature of the two models is that the surface tension of embryonic droplets in vapors described by the Becker-Döring theory is greater than the surface tension of the bulk liquid, whereas the surface tension of embryonic droplets in vapors described by the Lothe-Pound theory is equal to the surface tension of the bulk liquid (*6*). It has been concluded that the failure of the Lothe-Pound theory to explain the nucleation of polar liquids is due to its failure to account for the deviation of embryonic surface properties from bulk liquid surface properties (*6*). The apparent success of the Becker-Döring theory to explain the nucleation of polar liquids is believed to be fortuitous (*6*).

Within the framework of these two models, I argue that there exists a droplet size j_t (j denotes the number of molecules of the cluster) such that for $j < j_t$, the surface molecules exist in the disordered state (model 1), and for $j > j_t$, the surface molecules "prefer" the ordered state (model 2). The argument is based on a fundamental thermodynamic principle, namely, that at equilibrium the free energy of the surface of a droplet of j molecules will be a minimum.

The total surface free energy of a droplet of spherical surface area A is

$$F_j^{(s)} = \sigma_j A = 4\pi\sigma_j \left(\frac{3v_l}{4\pi}\right)^{2/3} j^{2/3} \quad (1)$$

where σ_j is the surface tension for a liquid cluster of j molecules, with each molecule occupying a volume v_l in the liquid state. For the state with a disordered surface (model 1), it has been suggested that the surface tension of the randomly oriented water surface should be approximated by the surface tension of ice (*5*), that is, $\sigma_j = \sigma(\text{i})$. For the state with an ordered surface (model 2), it has been argued that the correction for dipole-dipole interaction due to curvature yields a surface tension dependence of the form (*6*)

$$\sigma_j = \sigma_\infty + U_s/A \quad (2)$$

where σ_∞ is the surface tension for the flat plane surface of water and $U_s \cong 2.2 \times 10^{-12}$ erg.

The elevation of the total Helmholtz free energy of the system as the transition is made from vapor only to a droplet of j molecules plus vapor is given by

$$\Delta F_j = -J\, kT \ln S + F_j^{(s)} \quad (3)$$

where k is the Boltzmann constant, T is the temperature, and S is the supersaturation ratio (*9*). I have evaluated $F_j^{(s)}$ and ΔF_j (Eqs. 1 and 3) for models 1 and 2 for $20 \leqq j \leqq 200$, assuming a supersaturated vapor at $T = 263.2$°K and $S = 5.0$. For this temperature $\sigma(\text{i}) = 100.2$ dyne/cm and $\sigma_\infty = 77.4$ dyne/cm (*7*). The results are presented in Fig. 1. The surface free energy of the disordered surface (model 1) is less than that of the ordered surface (model 2) when j is less than 94 molecules; the surface free energy of the ordered surface is less than that of the disordered surface when j is greater than 94 molecules. The same conclusion is, of course, true for ΔF_j.

In general, this transition size j_t for the "crossover" of free energies may be determined by equating Eq. 2 with the surface tension of ice, $\sigma(\text{i})$. The quantity j_t is dependent only on temperature, the temperature dependence originating from the surface tension. If we invoke the principle that the free energy of a droplet of j molecules will be a minimum (for equilibrium), the dipole molecules in the surface of an embryonic droplet will be randomly oriented for $j < j_t$ and they will be ordered for $j > j_t$.

For the disordered surface (model 1) nucleation occurs when an embryonic droplet grows beyond the critical size, that is, $j > j_c = 150$ for the particular example in Fig. 1. However, within the framework of the thermodynamic equilibrium argument for the surface structure of droplets given above, the orientation of the surface molecules does not remain random up to $j = 150$ but becomes ordered at $j_t = 94$. Since the critical size of the droplet in model 2 is 70 molecules, the transition at $j = 94$ leaves the ordered droplet on the "far side" of the "ordered surface" free energy peak, and spontaneous growth of the droplet occurs. In effect, the transition size becomes the critical size for nucleation, and the free energy peak is ΔF_j $(j = j_t)$, which is less than ΔF_j $(j = j_c)$ for both models. This lower free energy peak results in an increase of 0.33×10^3 in the steady-state nucleation rate with respect to the rate for the state with a disordered surface (model 1) (*8*).

The features of the ΔF_j curves (Fig. 1) are dependent on the choice of T and S. For my choice of parameters, j_t is less than j_c. However, it is possible to choose the environmental conditions such that the converse is true (for example, $T = 232.2°\text{K}$, $S = 10$, $j_c = 79$ for the model with a disordered surface, and $j_t = 118$ or $j_t > j_c$).

Thus far in the discussion I have assumed that, when a droplet reaches the transition size j_t, it instantaneously relaxes to the state with an ordered surface. The orientation relaxation frequencies of polar molecules in the bulk liquid or in the solid state vary over a wide range and are strongly temperature-dependent. For water at room temperature, the relaxation frequency is about 3×10^{10} cycle sec^{-1} (*9*). In ice at $-20°\text{C}$ the relaxation frequency is of the order of 10^3 cycle sec^{-1} (*9*). A comparison of this orientation relaxation time with the mean time needed for a droplet of j_t molecules to grow until it reaches j_c size will give an indication of whether the equilibrium argument is justified. White (*10*) has recently studied the kinetics of steady-state "random walks" on the positive integers and has applied the theory to nucleation phenomena. He finds that the mean time τ_{j_t} it takes a droplet of size j_t to traverse the range of sizes to the critical size is given by

$$\tau_{j_t} = \sum_{i = j_t}^{j_c} N_i/I \sim N_{j_t}^{\,\mathrm{e}} I^{-1}$$

where N_i is the steady-state concentration of droplets of i molecules, I is the steady-state current, and $N_{j_t}^{\mathrm{e}}$ is the equilibrium concentration of droplets of transition size j_t. For the example presented here, τ_{j_t} is $\sim 10^{-5}$ second. Depending on whether we picture the surface dipoles as relaxing like dipoles in room-temperature water or like dipoles in ice, we may conclude that the droplet grows in the state with an ordered surface for $j > j_t$ or that it follows the path of the free energy curve for the disordered surface to nucleation at $j_c = 150$. Since most experiments are performed under conditions in which the embryonic droplets are in the supercooled water state, a state that is nearly approximated by the structure of ice, one would be tempted to conclude that droplets follow the path of the free energy curve for the disordered surface.

Although it is of fundamental physical interest to resolve this question, the difference of 10^3 in the steady-state current for the two models is not significant in a determination of the critical supersaturation. However, it is clear that a knowledge of absolute nucleation parameters must await a better knowledge of the fine structure of macromolecular systems (that is, $j \simeq 100$ molecules).

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Palmoxylon simperi and Palmoxylon pristina: Two Pre-Cretaceous Angiosperms from Utah

Abstract. *Petrified palm stems* (Palmoxylon simperi *and* Palmoxylon pristina) *from the Middle Jurassic Arapien Shale Formation near Redmond, Sevier County, Utah, are the first unequivocal angiosperms reported from pre-Cretaceous strata.*

The search for pre-Cretaceous angiosperms is an old one, and although many authors have proclaimed such a discovery, none of their claims has survived the critical investigations of subsequent researchers. The point of origin for the angiosperms is considered by some authors to be a sharp one (*1*) with the Lower Cretaceous being the boundary. It is estimated that

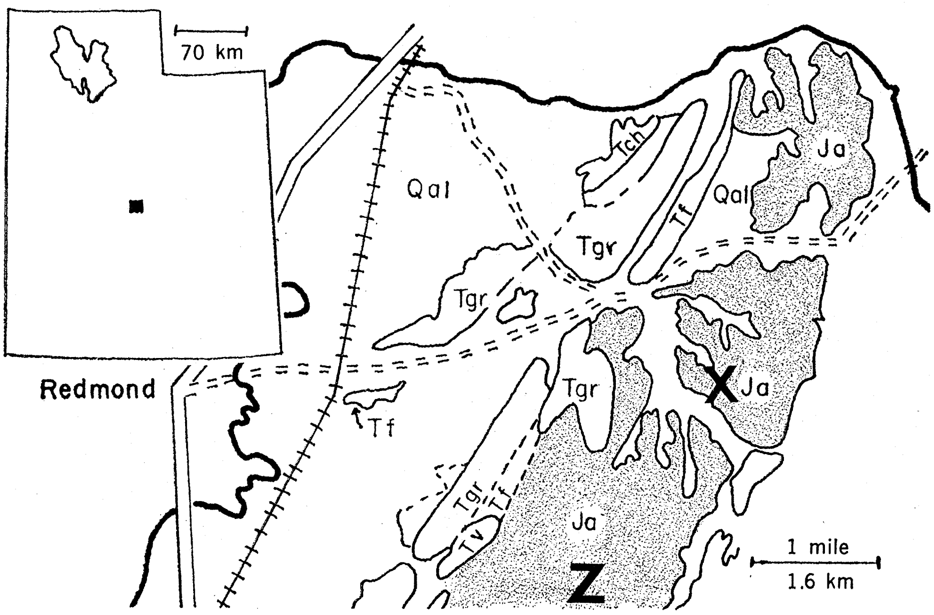

Fig. 1. Index and geologic map showing sites from which the petrified logs of *Palmoxylon pristina* (*X*) and *P. simperi* (*Z*) were collected. *Qal* = Quaternary sediments; *Tv* = Tertiary volcanics; *Tch* = Tertiary Crazy Hollow Formation; *Tgr* = Tertiary Green River Formation; *Tf* = Tertiary Flagstaff Formation; *Ja* = Jurassic Arapien Shale (restricted) [modified after Hardy (*13*)].