

On the Isotopic Composition of Hailstones

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ABSTRACT

Theoretical considerations show that isotopic fractionation can occur during the freezing of supercooled droplets accreted by a hailstone. This is due to evaporation from the liquid during the freezing process with consequent enrichment of the deuterium and O¹⁸ content of the accreted ice. The enrichment is greatest when the temperature of the hailstone is near 0C. Calculations, based on the Rayleigh distillation formula and allowing for diffusivity effects, indicate that the maximum increase is about 6‰ for deuterium and 1.5‰ for O¹⁸. Analyses of samples of accreted ice formed in an icing tunnel have confirmed these predictions. The effect is sufficiently large to affect the interpretation of isotopic analyses of hailstones.

1. Introduction

As condensation of water vapor takes place within a cloud, the liquid phase acquires a greater concentration of HDO molecules than the vapor phase. The reason for this is that each molecular species has a different equilibrium vapor pressure (see Friedman *et al.*, 1964). The relative enrichment of the droplets is determined by the value of the separation factor α_s , which for a liquid-vapor system in isotopic equilibrium is given by

$$\alpha_s = R(\text{vapor})/R(\text{liquid}),$$

where $R = N^{\text{HDO}}/N^{\text{H}_2\text{O}}$ and is the ratio of the mole fractions of HDO and H₂O (hereafter called the D/H ratio). A similar effect occurs with the H₂O¹⁸ molecules.

A method of studying the formation of hailstones by determining the isotopic ratios of deuterium to protium in the various hailstone layers has been introduced by Facy *et al.* (1963). The method has been used subsequently by Merlivat *et al.* (1963), Ehhalt⁵ and Majzoub *et al.* (1968). In addition to making D/H measurements, Ehhalt determined the relative tritium content and Majzoub *et al.* the O¹⁸ content.

The basic assumptions underlying the interpretation of hailstone structure using this method is that the isotopic ratios in the supercooled cloud droplets can be calculated as a function of height (by assuming, for example, that the updraft rises adiabatically) and that this ratio remains unchanged during the accretion process. These then permit the growth history of the

hailstone to be traced. Because certain anomalies arise in computing the updraft profiles from such data, Bailey and Macklin (1965) suggested that there is in fact a change in the isotopic ratio of an accreted droplet during the time it takes to freeze. However, they did not give any quantitative assessment of the possible change.

In this paper we show theoretically that such a change is to be expected and we present experimental confirmation of this.

2. The freezing and isotopic exchange of accreted droplets

The temperature of a growing hailstone is raised above that of its environment because of the release of heat of fusion by the accreted droplets (Schumann 1938; Ludlam 1950, 1958). The temperature attained by a stone is determined by a balance between the rate at which the heat is liberated and the rate at which heat can be dissipated to the environment by forced convection. Since the hailstone temperature cannot rise above 0C, there is, for a given hailstone at a certain level in the cloud, a critical liquid water concentration for which all the accreted water may be just frozen. If the actual liquid water concentration is lower than the critical value, all of the droplets freeze and the hailstone temperature is <0C; if the liquid water concentration is above the critical value the excess water is incorporated into the ice structure giving a spongy deposit (List, 1960; Macklin, 1961). Ludlam (1958) refers to these as the dry and wet growth regimes.

The freezing of supercooled droplets accreted by a hailstone has been treated theoretically by Macklin and Payne (1967). The heat of fusion may be dissipated in four main ways, i.e., absorption by the droplet due to the fact that it is supercooled, conduction into the hailstone, and conduction and evaporation by forced convection through the air boundary layer at the hail

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⁵ Ehhalt, D. H., 1967: Deuterium and tritium content of hailstones: Additional information on their growth. Paper presented at the American Geophysical Union, Washington, D. C., April.

stone surface. The part of the freezing process due to the supercooling of the droplet occurs extremely rapidly. A fraction of the droplet solidifies at the expense of the remainder which is warmed to a temperature near 0C. The fraction frozen in this manner is given by $c_w(T_m - T_a)/L_f$, where c_w is the average value of the specific heat of water over the temperature range, T_m the melting point of ice, T_a the ambient temperature, and L_f the latent heat of fusion of water. The relative contributions of the latter three processes to the remainder of the freezing, which is generally much less rapid, is a rather complicated function of the droplet size and hailstone temperature.

Macklin and Payne estimate that the freezing of droplets 20–40 μ in diameter, the size that may reasonably be expected in cumulonimbus updrafts (Macklin and Bailey, 1966), is almost completely governed by the hailstone temperature when it is lower than a few degrees below zero. Under these conditions, the droplet is rapidly frozen by conduction into the stone, and the subsequent dissipation of this latent heat to the environment through the air boundary layer takes place from the frozen ice surface. As the hailstone temperature approaches 0C, the contribution of the heat conduction into the stone to the freezing process is reduced until, at 0C, the freezing is controlled entirely by the two forced convection processes. At this stage, the freezing is similar to a liquid film (Macklin, 1962).

Fractionation of the isotopes of hydrogen and oxygen invariably occurs when liquid water evaporates at the temperatures being considered here. For evaporation under conditions where the vapor is immediately removed, the Rayleigh distillation formula may be applied, Friedman *et al.* (1964) giving the relation

$$R/R_0 = \theta^{\alpha-1}, \quad (1)$$

where R_0 is the initial D/H (O^{18}/O^{16}) value of the liquid before the fraction $1-\theta$ of the liquid has evaporated. The assumption underlying Eq. (1) is that the mixing and diffusion processes within the liquid and its vapor are sufficient to prevent the build-up of large concentration gradients of HDO and H_2O^{18} molecules near the surface. For temperatures applicable to hailstone growth, values for α_e for deuterium have been given by Merlivat and Nief (1967) and those for O^{18} can be extrapolated from the data of Szapiro and Steckel (1967). Because $\alpha_e < 1$, evaporation results in a deuterium enrichment of the remaining liquid.

In the case of the phase change from ice to water, Friedman *et al.* (1964) point out that there can be no fractionation since each molecular layer of ice melts in its entirety, and the self-diffusion coefficient of ice molecules is very small [about 10^{-5} times that for liquid water according to Kuhn and Thürkauf (1958)]. Similarly, no fractionation occurs during evaporation from an ice surface. This means that when the hailstone temperature is sufficiently low for the heat of fusion to be conducted rapidly into the hailstone and then

dissipated to the environment from an ice surface, there is virtually no fractionation because the droplet freezing time is so short. The isotopic ratio in the deposit is then the same as that of the droplets from which it is formed. On the other hand, when the hailstone temperature is 0C, the evaporation takes place from a liquid surface, fractionation occurs, and the isotopic ratio is higher in the deposit than that initially in the droplets.

It is possible to estimate the fraction of the droplets evaporated during freezing in the following way. The rate of heat transfer per unit area by forced convection from a hailstone is given by (see Macklin, 1963)

$$h = \frac{XRe^{1/2}}{2a} (Pr^{1/3}k\Delta T + Sc^{1/3}L_v D\Delta\rho), \quad (2)$$

where X is a numerical factor, Re the Reynolds number, a the hailstone radius, Pr the Prandtl number, k the thermal conductivity of air, ΔT the difference in temperature between the hailstone surface and the environment, Sc the Schmidt number, L_v the latent heat of vaporization of water, D the diffusivity of water vapor in air, and $\Delta\rho$ the difference between the water vapor density at the hailstone surface and in the environment. The two terms represent the contribution by thermal conduction transfer and evaporative transfer, respectively. The fraction of the total transfer which takes place by evaporation is therefore

$$\frac{h_e}{h} = \frac{Sc^{1/3}L_v D\Delta\rho}{Pr^{1/3}k\Delta T + Sc^{1/3}L_v D\Delta\rho}. \quad (3)$$

For the reasons given above the maximum contribution of evaporation to the freezing process occurs when the hailstone temperature is 0C since then there is no conduction into the stone. The quantity of heat to be dissipated from a droplet of mass m at an initial temperature T_a in freezing to ice at T_m (0C) is $m[L_f + c_w(T_a - T_m)]$. The fraction evaporated is therefore

$$1 - \theta = \frac{h_e [L_f + c_w(T_a - T_m)]}{h L_v}. \quad (4)$$

In the case of a droplet freezing on the surface of a hailstone there are two further possible contributions to the fractionation process which must be considered. These arise because the vapor has to be diffused away through the air boundary layer at the hailstone surface. Since the heavier molecules have a slightly smaller diffusivity, the fractionation is consequently, correspondingly increased. On the other hand, the evaporation takes place because there is a density difference between the vapor at the surface and in the environment. The latter value is that corresponding to the saturated vapor pressure at the ambient temperature. Because the value of α_e falls with temperature, the isotopic ratio in the vapor at the (warmer) surface of the hailstone is higher than that in the vapor in the

(colder) environment. The HDO and H₂O¹⁸ gradients are therefore relatively higher than the H₂O gradient, promoting the diffusion of the former. This tends to offset the effect of the lower diffusivity.

An estimate of the magnitude of these effects can be obtained from the work of Ehhalt and Knott (1965) who used Sverdrup's (1951) model in which the transport of water vapor is carried out by pockets of air which linger at the surface in passing. The molecular water vapor then diffuses into this pocket of air during the short period of contact. From Eq. (10) of Ehhalt and Knott's paper for the evaporation of limited quantities of water, we obtain,

$$\alpha_k = \left(\frac{D'}{D}\right)^{\frac{1}{2}} \left[\frac{1 - h'Ra/\alpha_d Rd}{1 - h'} \right] = \left(\frac{D'}{D}\right)^{\frac{1}{2}} \left[1 + \left(\frac{h'}{1 - h'}\right) \left(1 - \frac{1}{\alpha_d} \frac{Ra}{Rd}\right) \right], \quad (5)$$

where α_k is the kinetic separation factor. The overall fractionation factor is then

$$\alpha = \alpha_d \cdot \alpha_k, \quad (6)$$

where α_d is the equilibrium separation factor at the droplet temperature, Ra and Rd the D/H ratios of the water vapor in the atmosphere and the water in the droplet, respectively, h' the humidity of the air measured relative to the droplet temperature, and D' and D the diffusivities of HDO (H₂O¹⁸) and H₂O molecules in air. Ehhalt and Knott give the values of D'/D for the two molecular species as 0.984 and 0.971, respectively.

During hailstone formation under adiabatic conditions (i.e., no mixing with outside air) Ra/Rd will be α_e at the air temperature; consequently, Ra/Rd α_d < 1. For a hailstone whose temperature is 0C at an ambient temperature of -20C, the difference in the HDO isotopic gradient compensates for the difference in diffusivities and calculations show that the overall fractionation is reduced by only 1%. However, the diffusion effects are pronounced in H₂O¹⁸ evaporation because α_e is closer to unity and the overall fractionation is increased by a factor of 2.0 in this case.

The maximum values of R/R_0 , which occur when the hailstone temperature is 0C, have been calculated for a typical hail cloud from (1) and (4), taking into account diffusivity effects using (5) and (6). These values are given in Table 1. The deuterium enrichment ranges from 3.6-6.4‰ and the O¹⁸ from 0.9-1.5‰.

3. Experimental

a. Icing tunnel experiments

As a check on the above theoretical predictions of the isotopic enrichment taking place during the accretion process, isotopic analyses were made of a number of ice samples formed in the icing tunnel described by Bailey and Macklin (1968). The ice samples were accreted on

TABLE 1. Isotopic fractionation of a freezing droplet due to evaporation. (Maximum values of the ratio R/R_0 for a typical hail cloud are shown as a function of temperature. Diffusivity effects have been taken into account.)

	T_a (°C)			
	-5	-10	-20	-30
h_e/h	0.52	0.51	0.49	0.46
$1-\theta$	0.066	0.060	0.048	0.038
$(R/R_0)_D$	1.0064	1.0058	1.0046	1.0036
$(R/R_0)_{O^{18}}$	1.0015	1.0013	1.0011	1.0009

perspex rods 7 mm in diameter rotating at 30 rpm. The air speed and ambient temperature were held approximately constant at 20 ± 2 m sec⁻¹ and -20 ± 3 C, respectively. Tap water was used for the experiments and the median volume diameter of the droplet distribution was 29 μ with a maximum diameter at 60 μ . The liquid water concentration was varied by varying the number of droplet sprays in operation and the liquid water concentrations used ranged between about 1 and 5 gm m⁻³.

The following procedure was adopted. Three runs were carried out in each experiment. In the first the liquid water concentration in the tunnel was maintained at approximately 1 gm m⁻³ for ~20 min. This ensured that, as far as possible, the initial conditions for the second run were consistent. The second run was carried out at a higher liquid water concentration and provided the experimental samples for analysis. In the third run the same liquid water concentration as in the first was used and the samples formed were also analyzed to provide a comparison with the values obtained for the experimental samples. By rotating a thermometer in the airstream it was found that deposits formed in liquid water concentrations of about 1 gm m⁻³ had a mean temperature < -12C. No fractionation is expected to occur at such a low temperature because of the extremely short freezing time of the droplets (see Macklin and Payne, 1967).

Because the air speed in the tunnel dropped to zero near the walls, the ends of the deposits were tapered. The nonuniform portions were cut away and only the central uniform portions (about 15 cm in length) were used to obtain the samples for analysis. The ice was broken up and placed in airtight polythene bottles before it was allowed to melt.

The effective liquid water concentration for each sample (i.e., the product of the actual liquid water concentration and the average collection efficiency) was obtained from the mass and length of the cylindrical deposit. The total mass M of the deposit is given by

$$M = \pi(a^2 - a_0^2)\rho_i L, \quad (7)$$

where L and a are the length and radius, respectively, of the deposit and a_0 the radius of the perspex rod. The mass accreted on a cylinder of radius a per unit time is given by $2aLVEW$. If this mass is spread uniformly

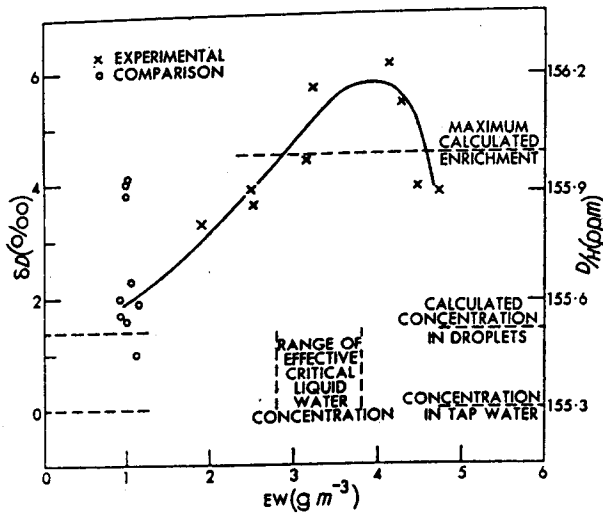


FIG. 1. The deuterium enrichment of the accreted ice samples above that of the tap water used for the experiments as a function of the effective liquid water concentration. The scale on the right-hand side represents the absolute D/H ratio based on Craig's (1961) estimate for Standard Mean Ocean Water (SMOW).

over the surface of the cylinder and freezes into ice of density ρ_i , then

$$EW = \frac{\pi \rho_i (a - a_0)}{Vt}, \quad (8)$$

where t is the time of the run; a may be eliminated from (7) and (8) giving

$$EW = \frac{[\pi \rho_i (M/L) + (\pi \rho_i a_0)^2]^{1/2} - \pi \rho_i a_0}{Vt}. \quad (9)$$

Because of the high air speed used in the present experiments the deposits had a high density of approximately 0.90 gm cm^{-3} (Macklin, 1962). This value was used in calculating the effective liquid water concentrations.

b. Method of isotopic analysis

The ice samples were isotopically analysed at the New Zealand Institute of Nuclear Sciences. The D/H analysis was performed by converting the water to hydrogen gas over hot zinc using the technique of Friedman (1953). The D/H ratio of the H₂ was then determined on a double collection mass spectrometer of the "Nier II" type (Kirschenbaum, 1951). To obtain the accuracy required, the experimental and comparison samples were compared with the tap water used for the appropriate experiment, using the sample switching technique of McKinney *et al.* (1950). The samples were also analysed for their O¹⁸ content by the technique of Epstein and Mayeda (1953). As the isotope differences found in the samples were not large, all samples were prepared in triplicate in order to give as much significance as possible to the results. By this means the standard error has been reduced to 0.3‰ for the deu-

terium samples and 0.1‰ for the oxygen samples. Using a 2 σ criterion the error limits are then $\pm 0.6‰$ for D and $\pm 0.2‰$ for O¹⁸.

The results have been expressed in the standard notation

$$\delta D (\text{‰}) = \frac{(D/H) \text{ sample} - (D/H) \text{ reference}}{(D/H) \text{ reference}} \times 1000,$$

and similarly for δO^{18} . The reference sample used in each case was the tap water used to form the droplets. The results have been expressed also as D/H and O¹⁸/O¹⁶ ratios using Craig's (1961) estimate of D/H = 158 ± 2 ppm and O¹⁸/O¹⁶ = 1993.4 ± 2.5 ppm for Standard Mean Ocean Water (SMOW).

4. Results and discussion

The results of the experiments are shown in Figs. 1 and 2. From Fig. 1, which shows the deuterium content of the ice plotted as a function of the effective liquid water concentration, and Fig. 2, which shows the corresponding results for O¹⁸, it is seen that although there is an obvious scatter the results generally follow the average curves shown in which there is a steady enrichment of the deuterium and O¹⁸ isotopes as the EW value is increased towards the critical concentration for which the temperature of the deposit reaches 0C; above this concentration the enrichment decreases. The range of critical values shown in the figures was calculated using the heat transfer relation for smooth cylinders given by Douglas and Churchill (1955). Because accreting ice surfaces are rough the critical liquid water concentrations are somewhat underestimated which explains the slight displacement of the maxima to the right. However, the deposits grown at the higher liquid water concentrations were definitely spongy. The reason for the fall in enrichment in the wet growth regime is that now the average fraction of each droplet frozen is less than unity. There is less evaporation per droplet and consequently less enrichment.

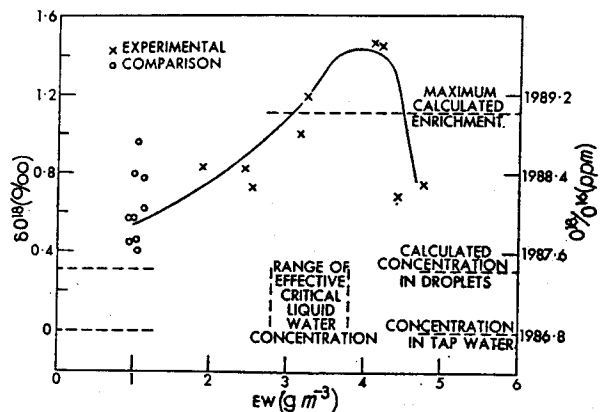


FIG. 2. Same as Fig. 1 except for O¹⁸ enrichment. In this case, the scale on the right-hand side represents the absolute O¹⁸/O¹⁶ ratio based on Craig's (1961) estimate for SMOW.

Figs. 1 and 2 show that there is a definite relationship between the deuterium and O^{18} enrichments. To illustrate this more clearly, Fig. 3 shows the δD values plotted against those for δO^{18} . The slope of approximately 4 obtained for the average line is much less than the slope of 8–10 expected for processes involving equilibrium evaporation only and indicates that diffusion effects are partly responsible for the enrichments obtained.

In interpreting the results quantitatively, allowance must be made for two effects present in the icing tunnel which differ from conditions in a hail cloud. The first of these is the introduction of the water droplets at about 5C. While cooling to the ambient temperature ($-20C$), the droplets evaporate and this results in a small isotopic enrichment. Using calculations similar to those used to obtain the R/R_0 values in Table 1, it was estimated that the enrichment would be about 1.4‰ for deuterium and 0.3‰ for O^{18} . It should be noted that these values are approximate since the temperature of the droplets is changing in this case and in making these calculations the value of α_e for $-10C$ has been used. From Figs. 1 and 2 it is seen that the isotopic ratios of the comparison samples are enriched above those of the tap water by somewhat more than these amounts. It should be noted also that the evaporation which occurred during the cooling of the droplets obviously did not take place under equilibrium conditions so that the low slope of the line in Fig. 3 is not entirely due to diffusion effects during the actual freezing of the droplets on the cylinder.

The second effect arises because the physical limitation of the size of the icing tunnel prevents adequate isolation from its surroundings. The icing tunnel is housed in a cold room and in practice we are attempting to control the isotopic composition of the water vapor in the room [which is important because of its influence through the R_a/R_d term in Eq. (5) and because of the possible exchange with the droplets before they are accreted] by the water sprayed into the room below the tunnel. In the experiments at higher EW values the vapor evaporating from the droplets while cooling will tend to swamp out the effects of water vapor from other sources such as the leakage into the room of the outside air during the entry of the operator and the evaporation of ice accumulated on the walls and floor during previous experiments. In the comparison runs, which were carried out with EW values around 1 gm m^{-3} , this contamination appears to have had a greater influence. This is considered to be the reason for the scatter in these results.

Nevertheless, the results are consistent with the theory outlined above. The enrichment of the samples increases with liquid water concentration reaching a maximum near the critical value. From the Rayleigh distillation formula [Eq. (11)] and using the value of α obtained from (6), the maximum enrichment of the water droplets during freezing was estimated to be 3.1‰

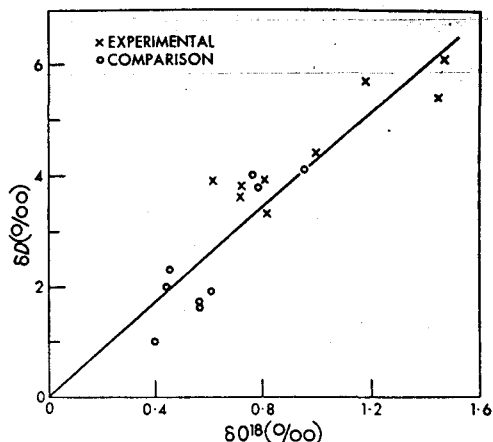


FIG. 3. The deuterium enrichment of the accreted ice samples as a function of the O^{18} enrichment.

for deuterium and 0.8‰ for O^{18} . These are in agreement with the measured values.

5. Application to hailstone growth

Analyses of hailstones carried out to date show variations in D/H and O^{18}/O^{16} ratios of about 20‰ and 2‰, respectively. The above considerations show that an analysis of the growth history of a hailstone as proposed by Facy *et al.* (1963) is feasible provided due allowance is made for deuterium and O^{18} enrichment due to evaporation during the freezing of the droplets. If the growth is close to the wet limit during the entire history of the stone as suggested by Mossop and Kidder (1962), Browning *et al.* (1963) and Browning (1966), then a constant correction only need be added. However, if the growth of the stones varies between the wet and dry regimes then the analysis becomes more complicated.

Majzoub *et al.* (1968) have found that, except in the case of opaque cores, the opaque layers in hailstones have lower D/H and O^{18}/O^{16} values than clear layers. They infer from this that the opaque cores are formed at low altitudes and that during the remainder of its growth the hailstone oscillates between two altitudes. The opaque layers are formed at higher altitudes (i.e., at colder temperatures). On the basis of the present experiments, it is possible that the difference in the isotopic ratios of opaque and clear layers may be at least partly due to isotopic fractionation during the freezing of the droplets. Clear layers are formed near the wet growth limit while opaque layers are formed either in the dry or wet growth regimes (see Macklin, 1962; List, 1963). Clear layers, therefore, have higher D/H or O^{18}/O^{16} ratios than opaque layers, particularly if the latter were formed in the dry regime.

From Figs. 1 and 2 the differences in δD and δO^{18} values of an ice deposit grown in a liquid water concentration half the critical value and one grown near

the wet growth limit is about 2‰ and 0.4‰, respectively. For hailstones these differences have to be increased by about 50‰ because evaporation contributes more to the overall rate of heat transfer in this case than in the present experiments. The difference is further enhanced if the average droplet size in the cloud is smaller, or the droplet distribution narrower, than that used in the present experiments. The freezing times would then be more strongly dependent on the hailstone temperature and the maxima corresponding to those in Figs. 1 and 2 sharper. Thus, changes in the liquid water concentration can produce variations in the isotopic composition of the growth layers even at the same ambient temperature. Browning *et al.* (1963) suggest that such changes could be produced by variations in the water vapor content of the air feeding the updraft while List and Lozowski (1968) suggest that variations in the liquid water concentration could be produced by changes in the level of the accumulation zones of hailstones due to a fluctuating updraft. The actual magnitude of the variations, however, are unknown.

Majzoub *et al.* (1968) find differences of about 10‰ and 1‰ for the δD and δO^{18} values between the clear and opaque ice layers of hailstones. Part of these differences may be accounted for by the mechanism discussed here.

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