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CHEMICAL ENERGY IN COLD-CLOUD AGGREGATES: THE ORIGIN OF METEORITIC CHONDRULES

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ABSTRACT

If interstellar particles and molecules accumulate into larger particles during the collapse of a cold cloud, the resulting aggregates contain a large store of internal chemical energy. It is here proposed that subsequent warming of these accumulates leads to a thermal runaway when exothermic chemical reactions begin within the aggregate. These, after cooling, are the crystalline chondrules found so abundantly within chondritic meteorites. Chemical energy can also heat meteoritic parent bodies of any size, and both thermal metamorphism and certain molten meteorites are proposed to have occurred in this way. If this new theory is correct, (1) the model of chemical condensation in a hot gaseous solar system is eliminated, and (2) a new way of studying the chemical evolution of the interstellar medium has been found. A simple dust experiment on a comet flyby is proposed to test some features of this controversy.

Subject headings: comets — interstellar: matter — meteors and meteorites —
 solar system: general

I. INTRODUCTION

I present here a new connection between the chemistry of the interstellar medium and the chemistry of meteorites. My major argument is that meteoritic chondrules derive the energy for their crystallization from their own supply of internal chemical energy. If this idea is correct, it would solve a very old problem about the existence of chondrules as an abundant component of the early solar system, and it would enable a study of the history of the interstellar medium and its processes of accumulation. It would also contradict the idea favored by meteoritic chemists (e.g., Larimer and Anders 1967; Grossman and Larimer 1974) that the chemistry of the early solar system was dominated by thermal condensation from a hot gaseous state, a condition that would be of central importance to dynamic models of the formation of the solar system. Finally, it would open new opportunities for understanding the melting of some meteoritic parent bodies without the need of radioactive or gravitational heating, which require large bodies in order to retain the heat.

It is curious that this idea appears to have been overlooked in the recent literature, even though Urey and Donn (1956) advanced some aspects of it long ago. This neglect may have occurred because of the widespread meteoritic dogma that the solar system began as a hot gas, whose cooling sequentially would have condensed elements according to their volatilities rather than according to other chemical properties (Larimer and Anders 1967). During thermal condensation in a slowly cooling gas, the condensed forms, assumed to be equilibrated, would not contain substantial free energy,

already being in the lowest free-energy state. This meteoritic literature has envisioned the accumulation into larger bodies of small crystalline particles, olivine pyroxene, and metal. To produce from them a molten droplet of a radius of a few millimeters (typical of chondrules) has therefore seemed to require an input of external heat sufficient to melt chondrules so that they can then crystallize. This imagined requirement has stimulated many exotic mechanisms for the origin of chondrules. A summary of these, along with photographs and properties of chondrules, can be found in textbooks (e.g., Wasson 1974). None of these suggestions has ever seemed totally credible in light of the prolific abundance of chondrules (as much as 70% of some meteorites) and their very subtle textural and mineralogical properties.

II. INTERNAL CHEMICAL ENERGY

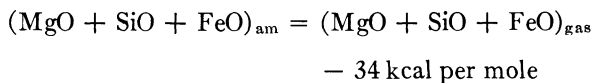
The new idea suggested here is both plausible and common: internal chemical energy is released when chemically unequilibrated aggregates are warmed to the point where rapid exothermic chemical reactions can begin. A more than ample supply of energy should be available in a collection of interstellar particles and molecules that begins and remains cold (~ 50 K as befits a dense molecular cloud), and the major question will remain whether it can be liberated fast enough to leave behind the appearance of once-molten textures.

To first focus on the bizarre chemical state, imagine that a cold cloud of pure MgO molecules accretes into a low-density "dust particle" consisting of randomly oriented MgO molecules frozen at 10–50 K. This state resembles a liquid in the sense of possessing no long-range order, although it would not be fluid owing to its immobility and it would still retain a close correlation of each Mg ion with only a single O ion. When heated

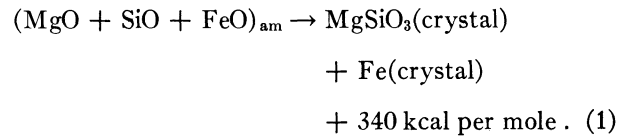
¹ Fulbright Fellow on leave from Rice University, 1979 August–1980 August.

enough for the density to increase and for the MgO molecules to rearrange themselves, a spontaneous phase transition will occur, accompanied by at least the 18.5 kcal per mole of heat normally required to melt crystalline MgO. Taking $C_p = 0.2 \text{ cal gm}^{-1} \text{ K}^{-1}$ for MgO, this heat would have the potential, if it could be adiabatically contained within the accumulate, of raising the temperature by 2300 K, leaving a hot crystal. Even more heat would be liberated if the initially frozen MgO molecules are arranged in a snowflake density less than that of MgO liquid, in which case much of the vaporization energy of MgO would also be liberated. The crystallization would proceed as a thermal diffusion, leaving a hot crystal behind as it propagates into the initially immobile structure. This propagation of the crystallization front probably accounts for the barred and radiating textures so common in the chondrules, which appear in many ways to have once been molten. The example above need never have been molten in the common meaning of the word. This example of energy arises from contraction (partial condensation) and from crystallization (not recrystallization), and is derived from an increase in ionic coordination and from long-range ordering.

A considerably larger energy is obtainable via chemical reactions (formation of chemical bonds), with crystallization being only the final transformation. Without doubt, chemical energy should exist to some degree in interstellar grains. Donn and Urey (1956) and Greenberg (1976) have suggested that a high concentration of free radicals can be expected in icy mantles, and that these may liberate so much energy when they become mobile as to explode the grain mantle (Greenberg 1976) or as to later cause cometary outbursts (Donn and Urey 1956). Within a large aggregate of grains, this energy and that from other low- T reactions may be thermally trapped in the aggregate, raising its temperature. Clearly calculations along this line will require a reasonably complete description of the chemical state of an accumulate of interstellar particles, a large challenge to astrophysics. Concentrating for a moment on the abundant refractory elements that are the major constituents of the chondrules (ferromagnesian silicates) it seems relatively nonbiased to first consider a frozen collection of equal numbers of MgO, SiO, and FeO molecules. These molecules are probably rapidly formed on grain mantles (when Mg, e.g., finds an O atom) and ejected by recoil. Ultimately, they are accreted as molecules in the cold cloud. This picture has some similarity to that proposed in more detail by Duley, Millar, and Williams (1979), except that their metallic monoxides are already arranged in a (metastable) cubic crystal lattice, at least locally. I will regard them as an amorphous paste, with each monoxide molecule bound by 0.5 eV to the accumulate by polarization forces. This binding is comparable to that required to boil water, and is a key physical assumption. Then the energy difference between gas and snowflake is



which leaves an energy difference for crystal formation that is much greater:



This energy comes largely from the formation of new ionic bonds (creation of Si^{+4}) and is a full order of magnitude greater than the heat released by crystallization of the meltdowns of the right-hand side of equation (1). The heat released, if it were sudden enough, would be adequate to vaporize a substantial part of the mixture. The more difficult chemical question is: how hot must the mix be before equation (1) proceeds at an adequate rate for the heat release to exceed the radiative and evaporative cooling of the particle? At lower temperatures the reaction will die out, whereas at higher temperatures a thermal runaway ensues. I enjoy thinking of this thermal runaway in terms of fireworks, where common experience shows that if a portion (the fuse) is heated to luminous temperatures, the total energy content is released in a time $\tau_\epsilon = \epsilon/\dot{\epsilon} = 10^{-2}$ s, whereas if it is only warmed nothing happens. This energy-release time scale is also crucial to the problem under discussion. The cooling rate, on the other hand, can be estimated much more quantitatively. Assuming round blackbodies, the radiative power is

$$L = 4\pi a^2 \sigma T^4 = 7.125 a^2 (\mu\text{m}) (T/1000 \text{ K})^4 \text{ ergs s}^{-1}, \quad (2)$$

whereas the total chemical energy content estimated from equation (1) is $Q = M\epsilon$, where $\epsilon = 340 \text{ kcal per mole} = 9.12 \times 10^{10} \text{ ergs g}^{-1}$. The cooling time scale is derived from the ratio of these two quantities:

$$\tau_c = Q/L = 0.054 a (\mu\text{m}) \rho (T/1000 \text{ K})^{-4} \text{ s}, \quad (3)$$

which, at 10^3 K , where the reactions and crystallization should proceed swiftly, has the contrasting values $\tau_c = 0.05 \text{ s}$ for $a = 1 \mu\text{m}$ and $\tau_c = 500 \text{ s}$ for $a = 1 \text{ cm}$. This dependence on particle size leads us to expect that the thermal runaway occurs only for aggregates larger than a minimum size, say a few millimeters, as befits the observed chondrules. Whether the particle can ever reach that reactive temperature once heating has begun depends upon the sign of dT/dt :

$$dU/dt = C_p dT/dt = M\dot{\epsilon} - L = Q \left(\frac{1}{\tau_\epsilon} - \frac{1}{\tau_c} \right), \quad (4)$$

where the reaction time scale $\tau_\epsilon = \epsilon/\dot{\epsilon}$ and the cooling time scale $\tau_c = Q/L$ are both evaluated at the instantaneous temperature. If $\tau_\epsilon < \tau_c$, the aggregate rises in temperature. It is unfortunately not possible to go further in a quantitative way, because τ_ϵ depends in detail upon the hierarchy of chemical reactions available and upon their temperature sensitivities. Greenberg's (1976) estimate of 0.025 eV per molecule suddenly released by free-radical combination near 50 K, if

equated to $k\Delta T$, yields $\Delta T = 290$ K in that sudden event, which may in turn allow the density of the snowflake to collapse, releasing a significant fraction of the heat of vaporization, which in turn enables equation (1) to occur. A very much more detailed description will be required to calculate τ_e at each temperature.

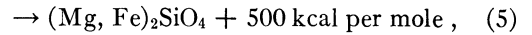
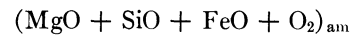
If the initial configuration of monoxides is the cubic crystal arrangement proposed by Duley, Millar, and Williams (1979), the final products are the same as equation (1) but the energy released, though much less (40 kcal per mole), is still more than adequate to produce high temperatures.

The final composition in equation (1) is commonly called "reduced" in the meteoritic literature because it is the composition of the least oxidized of the meteorites, the enstatite meteorites (e.g., Wasson 1974). Many cosmogonical models of the solar system are forced to think of this as an actual reduction process, because equilibrium with a hot gas down to temperatures as low as 600 K produces initially more oxidized condensates. To circumvent this, proponents of solar condensation have postulated carbon-rich portions of a hot gaseous nebula (Larimer 1975). In the model proposed here, no reduction ever actually occurs. I propose equation (1), or something similar, to be the origin of the enstatite chondrules and meteorites, as well as of the Earth, which also has free iron. The result is not more oxidized because there is no more oxygen in the bulk mixture of equation (1). The common occurrence of FeS, CaS, and other sulfides in these meteorites occurs because the initial collection of grains is expected to be rich in these sulfides (Clayton and Ramadurai 1977). In many models of cosmogony, the sulfides must be later introduced by allowing H_2S to attack the previous condensates (Larimer and Anders 1967), an awkward sequence of events. This problem of sulfides is also traceable to the assumption of a hot thermal condensation sequence in the solar system.

Because the heating and cooling are expected to be so rapid (seconds), the chondrules cannot exchange oxygen with the low-density gaseous surroundings. Their reduction-oxidation balance is determined by the bulk composition. This may even vary locally, so that redox variations may persist within a single chondrule, as Leitch and Smith (1980) have found in differing enstatite minerals within a single chondrule of the enstatite meteorite Indarch. The bulk chemical composition of each chondrule is also determined by the bulk mixture of the aggregate, excepting only that volatile species may be evaporated as part of the cooling mechanism.

The existence of more oxidized chondrules can be traced to the surface deposition of free oxygen during accumulation. At temperatures of 50 K and less it can be expected that O_2 can to some degree freeze out onto the surfaces of the accumulating grains. Free oxygen is expected, because only H_2O and CO_2 can lock up the solar oxygen supply in molecules, and that transition will not have reached completion. In accumulations

that occur below about 50 K, therefore, the basic thermal runaway is



the ferromagnesian olivine prominent in oxidized chondrules. The bulk composition determines the amount $f = FeO/(MgO + FeO)$ of oxidized iron in the olivine and pyroxene $[(MgO, FeO)SiO_2]$ silicates. The spectrum of chondrule compositions will be determined by the ratios $MgO:SiO:FeO:O_2$ within separate aggregates. Different chondrules within unequilibrated chondrites show wide ranges in the value of f (Van Schmus 1969). They represent varying oxidations of the basic enstatite mixture.

It would, of course, be possible to regard the enstatite mixtures as reduced versions of a basically more oxidized aggregate, although I do not subscribe to such a view. This could arise if the temperatures are such that the coldest aggregates freeze out an abundant reducing agent (C, CH, C_2H_2 , CN, etc.) on the surfaces of the grains, so that the cold macroscopic aggregates are loaded with exothermic reducing agents. Considerable CO , CO_2 , and H_2O would then have to be released from the chondrules. I find this clumsier and less reconcilable with oxygen isotopic compositions. Hydrides (e.g., MgH) may to some degree replace oxides in the initial mix, thereby lowering the oxygen supply and increasing the energy release.

III. DYNAMIC SETTING

If this chemical idea is to be correct, it must couple in a natural way to the dynamics of the accumulation processes to explain the sizes of chondrules and their almost bimodal distribution between enstatite chondrules ($f \approx 0$) and more-oxidized chondrules ($f \approx 0.2 \rightarrow 0.3$), with a gap in between. The characteristic sizes (a few mm) seem to fit to order of magnitude with studies of the accumulation processes (Cameron 1975; Völk *et al.* 1978). For the most part, atoms and molecules accrete from the gas onto grains before the grains can accumulate to larger bodies, whose final sizes are $\sim 10^{0\pm 1}$ cm. Near the end of this growth, particles can decouple from gaseous turbulence (if present) and settle gravitationally to a disk. This entire procedure occurs under conditions that are quite cold (~ 10 K). But because the viscous accretion disk should have an ambient temperature of perhaps 400 K (Cameron 1978), the particles must eventually be warmed to that temperature. Chemical reactions begin, leading eventually to equations (1) and (5). The finer dust will be heated more gradually as it settles, not having the thermal blanket necessary to achieve high internal temperatures during chemical alterations. The fine particles are also able to reaccrete the volatiles. This scenario roughly explains the sizes of the chondrules and their difference from the finer dust (matrix).

The bimodal distribution between enstatite and oxidized forms may be sought in the temperature of accumulation. I have suggested that if it is above 50 K,

the O₂ coating the individual grains is evaporated before they accumulate to parents of chondrules, so that the enstatite mixture results. The fact that enstatite chondrules are found only within enstatite meteorites suggests that the matrix accumulated from similar though smaller dust. Some accumulations, however, will have occurred while the ambient temperature is still cold (<50 K), in which case the grains are coated with O₂ while they accumulate into larger bodies. These are probably earlier aggregates than the enstatite aggregates, since the ambient temperature probably increased with time. Alternatively, the enstatite and oxidized accumulations may have occurred in different spatial regions, in which case their accumulation temperatures would differ in a very natural way. This kind of spatial difference is far more plausible than the chemical inhomogeneity required in the thermal condensation models: C/O ≈ 1 in the enstatite-forming gas and C/O < 1 in the remainder of the hot gaseous solar system (Larimer 1975).

The suggestion of O₂ as the oxidizing agent for cold accumulation need not be taken too seriously. Other possibilities can be found. For example, one could return to an old idea of Wood's (1963) for the carrier of the oxidizing agent. Noting that metallic Fe is oxidized to Fe₃O₄ near 400 K, he argued that the oxidized chondrules accreted below this temperature whereas the enstatite meteorites accumulated above it. (But see Larimer and Anders 1967 for criticism of this idea *in a cooling nebula*.) Other oxidizing agents (e.g., H₂O₂) would have yet other temperature thresholds for inclusion. I have here suggested O₂ on the assumption that the accumulation was very cold and that the temperature rise in the large (cm-sized) accumulates was too sudden to allow the trapped O₂ to evaporate before reacting.

Probably the most significant astrophysical result of the correctness of this chemical-energy model for the origin of the chondrules would be the elimination of the model of the early solar system as a hot gas, whose thermal condensation fractionates the chemical elements according to volatility (Larimer and Anders 1967). The necessity of a vaporization epoch as distant from the Sun as the region of meteorite formation would, if it actually occurred, provide a severe dynamical constraint on models of solar formation. If not, the solid bodies may accrete from unvaporized presolar condensates. A broader implication for astrophysics would be the establishment of ways of studying the interstellar medium and its accumulation history in laboratory stones! This quest has occupied the writer for some years (Clayton 1978, and references therein; Clayton 1980*a, b*), with chemical energy being only the newest thread.

IV. CaAl-RICH INCLUSIONS

In many respects the CaAl-rich inclusions (CAI) of the C2 and C3 meteorites are similar to chondrules. They are composed primarily of very refractory mineral forms within a less extreme matrix. The major chemical difference is that CAI are very rich in Ca and Al, these

elements being comparable to Mg and Si in abundance, whereas chondrules are dominated by magnesium silicates. Clayton (1977*a, b*, 1980*b*) has created a model in which dust collections rich in Ca and Al SUNOCONs later have these SUNOCONs fused into new mineral fields by a sudden heating event (initially suggested to be high-speed collisions). The ideas of this *Letter* suggest the possibility that rapid exothermic chemical heating could be the agent for fusing the SUNOCON-rich mixture, which Clayton (1980*b*) argued could be prepared by accumulation of the largest grains from a distribution of grain sizes. The quick fusion of these CaAl-rich minerals is attested to by the inclusion of *Fremdlinge* (El Goresy, Nagel, and Ramdohr 1978) completely within these minerals and by the very inhomogeneous distribution of trace Na and Mg within a single anorthite (CaAl₂Si₂O₈) crystal (El Goresy *et al.*). The way in which the initial collection of grains was very ¹⁶O-rich was clearly described by Clayton (1977*a*, p. 262). What is now being suggested is that the chemically very reactive mantles surrounding the SUNOCONs provide the initial heating that joins CaAl-rich SUNOCONs into minerals apparently molten, yet decidedly unequilibrated. A review of how isotopic anomalies persist in these same inclusions has been provided by Clayton (1979), and a theory relating isotopically fractionated O, Mg, and Si within them to a history of sputtering of interstellar dust has been advanced by Clayton (1980*a*).

V. COMETARY DUST

The existence of CAI, of olivine chondrules, and even of free metal has been explained by advocates of a hot gaseous solar system as being due to thermal condensation during cooling of that gas (e.g., Grossman and Larimer 1974). Because vaporization of interstellar dust by external heating would surely be restricted to regions within a few AU of the Sun if it occurs at all, and because the comets probably formed at distances greater than 10³ AU, the comets should not in that cosmogony contain those refractory minerals attributed to the solar condensation sequence. I suspect, on the other hand, that comets will contain their own version of refractory minerals, probably resulting from the internal heating advanced in this work. A great opportunity exists for subjecting early-solar-system models to this test with a flyby of comet Halley, for which such a dust particle analyzer has been designed (Dalmann *et al.* 1978). If small refractory inclusions exist there, the solar condensation sequence will no longer be viable. This argument appears to have been overlooked in the literature in spite of the fact that burned-out comets, scattered into Apollo orbits, have been advanced as the origin of carbonaceous chondrites (Wetherill 1976). An analogous conclusion can be drawn if dust particles collected in the stratosphere (Brownlee 1978) can be shown to be cometary dust.

Discussions of these ideas with F. Begemann, R. J. Borg, E. Ferguson, A. El Goresy, E. Jessberger, J.

Jordan, T. Kirsten, H. Völk, and H. Wänke have been very helpful. I thank P. Eberhardt for pointing out that the initial version of this work had overlooked Donn and Urey's papers on chemical heating. First public disclosure of these ideas was in the meeting of

the Division of Extraterrestrial Physics of the Deutsche Physikalische Gesellschaft in Mainz, 1980 March 6. Research was supported by NASA grant NSG-7361, by the Max-Planck Gesellschaft, and by Rice University.

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