

CARBONYL TRANSPORT OF METAL
IN METEORITE PARENT BODIES

by

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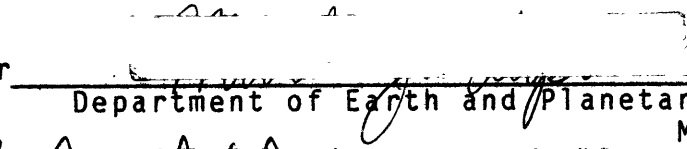
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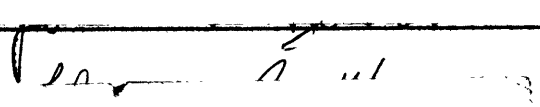
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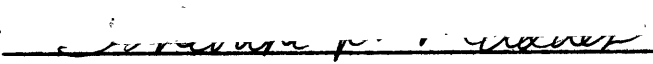
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MARK JOSEPH LUPO

Submitted to the Department of Earth and Planetary Sciences
on May 8, 1981 in partial fulfillment of the
requirements for the Degree of Master of Science in
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ABSTRACT

A new model for the formation of iron meteorites has been tested thermodynamically and has been found possible within the confines of our present knowledge of the kinetics of the breakdown of carbonyls. The model entails the production of carbonyls in parent body asteroids from the interaction of metals and CO. The gaseous carbonyls flow upward and condense in the low temperature upper meters of the asteroid. When the CO gas has diffused away, the carbonyls, which maintain a vapor pressure with a large liquid sink, begin to slowly deposit the metals and release CO. Metal is deposited at low temperature, which unlike the igneous model, is consistent with the occurrence of chondritic matter and silicate fragments with sharp edges that have been found in iron meteorites. Three sizes of hypothetical spherical asteroids were modeled with two different compositions.

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Carbonyl Transport of Metal
in Meteorite Parent Bodies

Introduction

The presently accepted model for the formation of most iron meteorites is a high temperature process involving the downward transport of liquid metal by gravity in a parent body of at least 50 km in radius. The differentiated body is later disrupted, and pieces of the core or shell become the iron meteorites. Studies of the Fe-Ni phase diagram and the cooling of metal from high temperatures have given a satisfactory explanation of the observed crystal structure of certain iron meteorites, such as type II A,B (Goldstein and Ogilvie, 1965; Wood, 1964)

Not all iron meteorites, however, are compatible with this igneous process. Chondritic matter and crystals of lawrencite (FeCl_2) enveloped in the iron phase, and silicate fragments with sharp broken corners are inconsistent with the high temperatures necessary to melt iron. In particular, the group I AB irons are very rich in silicate inclusions (Wasson, 1974), sometimes up to 15% by weight, as in Woodbine (Mason, 1967). This led Bloch and Müller (1971) to propose a low temperature model: carbonyls in comets decompose to form metals and CO gas during a perihelion passage enveloping silicates and iron chlorides at temperatures of 100°C rather than at iron's melting point. This model also has difficulties. The disseminating material of the comet is hydrous;

water readily attacks iron pentacarbonyl to produce magnetite, hydrogen and carbon monoxide. It also reacts with iron to produce iron oxides and hydrogen. Further, it is doubtful that the time of perihelion passage is long enough to sublimate enough of the comet to produce significant amounts of iron. In the deposition of iron, nucleation sites are important and these seem to be lacking in space.

Although strings of "swaddling kamacite" were obtained in the lab (Bloch and Wirth, 1980) when an $\text{Fe}(\text{CO})_5$ - $\text{Ni}(\text{CO})_4$ gas mixture at 180°C was passed between the poles of a permanent magnet, the absence of water vapor makes this experiment less than realistic for a cometary environment. The rate of deposition of iron is retarded severely by low carbonyl pressures so that even at 180°C and 1 dyne cm^{-2} pressure, the rate of deposition is $10^{-4} \text{ g day}^{-1}$ per square centimeter of metal.

It can easily be shown that carbonyl transport was not important in the solar nebula. The pressure - temperature profile was assumed to be an adiabat

$$\left(\frac{P}{P_0}\right) = \left(\frac{T}{T_0}\right)^{C_p(T)/R} \quad (1)$$

where T and P were taken to be the pressure and temperature at 1AU, 600K and 10^{-4} bars respectively (Lewis, 1972). R is the gas constant and $C_p(T)$ is the heat capacity of a mixture of 90% H_2 and 10% He, which is a weak function of temperature. The CO pressure, fixed by cosmic abundances, is one thousandth the total pressure everywhere in this range in

temperature. Then, since



we obtain

$$P_{\text{Fe}(\text{CO})_5} = K_{\text{eq}}(P_{\text{CO}})^5 a_{\text{Fe}} \quad (3)$$

where a_{Fe} is the activity of iron, which approaches 0.94 by 600K and K_{eq} is the equilibrium constant of the reaction here. Using data from the JANAF table supplement (1978), we see that

$$\log K_{\text{eq}} = \frac{8961.5}{T} - 29.177 \quad (4)$$

We assume, following Lewis and Prinn (1980), that most of the carbon in the solar nebula at all temperatures and pressures was CO. Figure 1 demonstrates that the carbonyl pressure is so far below that of CO as to be insignificant. This argument should not only lay to rest the idea of iron transport by carbonyls in the nebula, but of the accretion of carbonyls into comets. Even with an increase in CO abundance, it would be hard to imagine bare elemental iron available to react with CO in a cometary environment.

In this paper, the upward transport of iron and nickel by carbonyls in asteroid parent bodies will be investigated. Carbon monoxide is released from the center of a young asteroid. As it flows past the level of the most favorable kinetics and thermodynamics, carbonyls form. The gas continues to rise. At a higher level, the carbonyl dissociates and

iron and nickle are deposited. An impact or any other disruption liberates iron-rich chunks, or even metal chunks into space and these fall to earth as meteorites.

Assumptions

Two compositions will be modeled, ordinary chondritic (H) and C3 carbonaceous chondritic. The H group was chosen to represent the ordinary chondrites, and the C3's were chosen since other carbonaceous chondrites have a prohibitively high water content and lack metal, making iron transport impossible. These compositions bracket the ordinary chondrites. H group ordinary chondrites have a mean iron weight percent of 27.61 (Mason, 1971) and a mean nickel weight percent of 1.63 (Mason, 1965). About half the iron is metal, about half is in FeO (as silicates) and in FeS. We will use a 13 wt. percent metallic iron abundance. The median value for the concentration of carbon in ordinary chondrites is 1000 ppm (Moore and Lewis, 1965, 1967; Otting and Zahringer, 1967). The water abundance is \leq 0.1% by mass on average (Kaplan, 1971; Boato, 1954) and its source is presumably amphiboles, which have never been observed in meteorites, but are suspected on theoretical grounds to reside in the matrices at these low abundances. Type 3 carbonaceous chondrites are, on the average, 25.15 wt. % iron (Mason, 1971) almost all of which is found in olivine and clinopyroxene as FeO. For this work, it will be assumed that the C3 parent body is 4.02% iron metal by mass, as in Warrenton, an Ornan group chondrite (C03). Since the nickel, which is 1.43 wt. % (Wiik, 1956) is mostly found as metal, the metal phase is 26% nickel and 74% iron. The carbon abundance is 0.19% (Wiik, 1956) and H₂O is set at 0.1% (Wiik, 1956).

Two surface temperatures have been modeled, 175K and 150K. An object at the inner edge of the belt (2.3AU) with an albedo of 0.17 would have a surface temperature of 175K. At the outer edge of the main belt (3.3AU) a body with an albedo of 0.07 would have a temperature of 150K.

A central temperature of 1500K was chosen so that there would be a substantial core of material above the Fe-FeO-FeS eutectic melt temperature, which is 1200K. The source of heat is to be short-lived radio-active nuclides, such as ^{26}Al , for the purpose of generating the CO gas for the production of carbonyls. It would not be expected that temperatures much exceeded this value since convection in the liquid phase would tend to flatten the temperature gradient, and cool the asteroid interior.

As for the body above the level of incipient melting, conduction is assumed to be the mechanism of heat transport, so the steady state temperature profile is

$$T(z) = \frac{s\rho}{3K} \left(\frac{1}{2} z^2 \right) + T_c . \quad (5)$$

T_c is the central temperature, s is the heat production rate in $\text{erg g}^{-1} \text{sec}^{-1}$, ρ is the density of the material, (taken as 4g cm^{-3} for the ordinary chondritic body and 3.5 for the C3), and K is the thermal conductivity, which is $\approx 4 \times 10^5 \text{ erg K}^{-1} \text{sec}^{-1} \text{cm}^{-1}$. The heat production is chosen to give the proper surface temperature at the surface of the body and a central temperature ($z = 0$) of 1500K. Clearly s must be larger for

small bodies and for bodies with carbonaceous composition. To maintain the temperature profile for a 30km body with a 175K surface temperature and an ordinary chondritic composition, $s = 8.83 \times 10^{-5} \text{ erg g}^{-1} \text{ sec}^{-1}$, a value more than three orders of magnitude greater than the modern value (Kaula, 1968, p 111), but nonetheless easily attainable by the decay of ^{26}Al alone if only 10ppm of the ^{26}Mg observed in chondrites today is radiogenic.

Three different size bodies have been modeled for each surface temperature and composition, a 10km, a 30km and a 100km radius body. The bodies were assumed to be spherical and incompressible, with all of the constituents initially homogeneously distributed.

The lithostatic pressure at any level is given by

$$P_{\text{lith}} = \frac{2}{3} G \rho^2 r (R^2 - z^2) \quad (6)$$

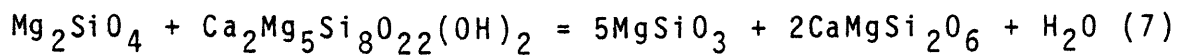
where P_{lith} is in dynes cm^{-2} , G is the gravitational constant, R is the total radius of the body (cm), and z is the distance from the center. The gas pressure in our models cannot exceed the lithostatic pressure at any level. The central pressure of the 100km body with an ordinary chondritic composition is 223.5 bars. Given that the crushing strength of ordinary chondrites is often kilobars (Wasson 1974) the assumption of a constant density in the parent bodies is quite satisfactory.

Metal will be found in grains having a radius of $0.1\mu\text{m}$

to 100 μ m. The grains are assumed to be spheres, with a homogeneous mixture of iron, nickel and traces of other metals. The H-group metal grains are 94% iron, 6% nickel. The C3-group parent body is assumed to have taenite grains that are 74% iron, and 26% nickel, as in the Warrenton chondrite.

Gas production

The three most important elements to consider in determining the gas composition are hydrogen, carbon and oxygen because of their abundance. The water in the parent bodies would be from water bearing silicates, such as tremolite. Below is a reaction which should account for much of the water in an ordinary chondrite:



the transformation of tremolite to diopside at high temperature. Using available thermodynamic data (Robie, et al., 1979) we find that

$$\log K_{\text{eq}} = - \frac{5820.8}{T} + 7.580 \quad (8)$$

If the activities of the minerals are unity, then the pressure of water at 1200K would be 536 bars, swamping the CO pressure. But this equilibrium could never be achieved since H₂O is only 1000ppm in our parent body. In a cubic centimeter ($\rho=4 \text{ g cm}^{-3}$, pore volume = 0.15 cm^3), there are only 2.22×10^{-4} moles of water. Even if all of it were liberated into the gas at 1200K, the pressure would only be 148 bars. (At 900K, $P_{\text{H}_2\text{O}} = 111$ bars; equilibrium would be possible). Even so, 148 bars is substantial as shall be shown below. To obtain the hydrogen to water ratio, the reaction



is studied. It has ΔG^0 of $-3367 \text{ cal mole}^{-1}$ at 1200K (JANAF, 1971), that is, an equilibrium constant of 4.103.

$$K = \frac{a_{\text{FeO}} P_{\text{H}_2}}{a_{\text{Fe}} P_{\text{H}_2\text{O}}} \quad (10)$$

At the Fe-FeO boundary $a_{\text{Fe}} = 10a_{\text{FeO}}$, so $X_{\text{H}_2\text{O}}/X_{\text{H}_2} = 0.0259$. Invoking mass balance and the limit to moles of H_2 , $P_{\text{H}_2} = 144.3$ and $P_{\text{H}_2\text{O}} = 3.7$ bars. It is assumed that the carbon bearing gas in the asteroids was released at the Fe-FeO-FeS ternary eutectic temperature, 1200K, since the iron must melt and permit the carbon in it to contact the gas. This high temperature is not a necessary condition for the release of H_2 and H_2O however.

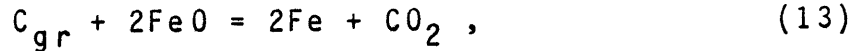
To obtain the carbon monoxide pressure, the reaction



is considered. The JANAF tables (1971) give the equilibrium constant at 1200K, 10.359.

$$K = \frac{a_{\text{Fe}} P_{\text{CO}}}{a_{\text{FeO}} a_{\text{gr}}} \quad (12)$$

The activities of iron and FeO are 0.94 and 0.1 respectively in an H chondrite. A mole fraction of 0.06 of nickel in the iron nickel alloy and a carbon concentration of 1000ppm lead to an activity of 0.0623 for graphite (Lewis, Barshay and Noyes, 1979). The CO pressure is therefore 0.0687 bars. The same procedure is used with the reaction

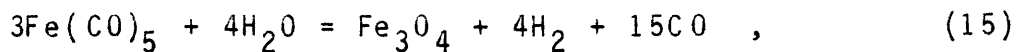


which has an equilibrium constant of 2.068 at 1200K, to get the CO_2 pressure of 0.00146. The CO/CO_2 ratio is then 47.09. Turning these pressures into mole fractions, the composition of the gas is 0.05% CO , 10ppm CO_2 , 2.50% H_2O and 97.45% H_2 .

A gas with the above composition would not transport metal. The CO would be rapidly converted to CH_4 via the reaction



X_{CH_4}/X_{CO} would be 461 at 1200K and it increases as temperature decreases. Secondly, water destroys iron pentacarbonyl.



although the hydrogen abundance may restrict the loss of carbonyls. The presence of water does not destroy the metallic iron since H_2O is only one thousandth of the mass and iron metal is fully one eighth. Nonetheless, this gas is definitely hostile to the transport model proposed.

However, outgassing experiments with meteorites and terrestrial rocks show that H_2 and H_2O will be outgassed at temperatures significantly below 1200K. Shepard (1938) experimented with two obsidians. The first outgassed 7% of its water in 3 months at $400^{\circ}C$ (673K), the second 70% of its water in one hour at $300^{\circ}C$ (573K). As powder, at 573K, the first lost 10% of its water in 30 minutes (30% after 9 hours) and the second lost 70% (87% after 9 hours). Emmons (1964) ob-

tained his gas from greenstone within 24 hours at only 473K and obtained water from biotite, granite and diorite at 773K in 3 hours. MacKenzie and Milne (1953) obtained the greatest moisture loss from 373K to 673K. At 773K much hydrogen was also liberated. Boato (1954) worked with carbonaceous chondrites and found that already at 453K anywhere from 17% to 47% of the water was released, and, nearly all of it was out by 1073K, but the water he got at $T < 180K$ was terrestrial water that had been adsorbed by the meteorite (he checked this by measuring the D/H ratio).

Clearly H_2 and H_2O outgassed before temperatures reached the Fe-FeO-FeS ternary eutectic. Diffusion of H_2 and H_2O , however, is also much faster than that of CO or of a carbonyl. To answer the question of whether or not these gases were totally gone by the time CO began to stream upward is a complex matter involving the time it took for the central temperature to rise, the time it took for these gases to form, the average particle size in the asteroid and the porosity of the asteroid. For an average internal temperature of 500K, and a pore radius of 0.5 μm , the diffusivity of hydrogen is $7.7 \text{ cm}^2 \text{ sec}^{-1}$, and 94% of it would be lost in 1000 years. The diffusivity of water is $2.6 \text{ cm}^2 \text{ sec}^{-1}$ and in 1000 years 72% of it would be gone. But in an asteroid only 10km in radius, lithostatic pressures range from 0 to 2.2 bars. This means that only 1.3×10^{-5} to 1.7×10^{-5} moles of gas can be in the gas phase at a time, per cubic centimeter. If 10^{-5} of it is hydrogen, and $H_2 + H_2O$ is 1000ppm, (0.004 g

cm⁻³), then only one percent of the gas could be in the gas phase at a time. Even if it takes thousands of years for these gases to come out, the half life of ²⁶Al is 740,000 years. Tens of thousands of years could elapse between the time that 600K was attained and when the ternary eutectic temperature was reached. It will be assumed here that hydrogen and water were no longer present by the time CO began to outgas. Small quantities of residual hydrogen will turn some of our precious CO into CH₄, which is innocuous. Traces of H₂O will not damage the carbonyls since at the levels carbonyls are abundant, water is beginning to condense and it probably would have reacted with an Fe to produce FeO and H₂ before reaching such a level.

For an asteroid of C3 composition, the metal phase is clearly taenite. From a composition of carbon of 1900 ppm and a nickel activity of 0.26, we get an activity of 0.29 for graphite (Lewis, Barshay and Noyes 1979). The activity of iron is 0.74. The activity of FeO is obtained from



(Mueller, 1965). $\Delta G^0 = -46.474$ at 1200K (JANAF, 1971).

Since type 3 carbonaceous chondrites (which used to be called olivine-pigeonite chondrites) have their iron in olivine and pyroxene, and since some metal is present (though not much), the oxygen fugacity is chosen to be on the FeO-Fe boundary, 10⁻¹⁷. This leads to a value of a_{FeO} of 0.80. Using the method above, $P_{\text{CO}} = 3.248$ bars. $P_{\text{CO}_2} = 0.701$ bars. The War-

Warrenton chondrite has a water content of 1000 ppm so the total of the H_2O and H_2 pressures will be similar to above.

$P_{H_2}/P_{H_2O} = 3.795$, but the total pressure due to these gases cannot exceed 129.33 bars ($\rho = 3.5 \text{ g cm}^{-3}$). If a different C3 had been chosen, its water content could have been 2% and nearly the full 563 bars of this gas would be possible. The gas composition for our Warrenton parent body is $X_{CO} = 2.4\%$, $X_{CO_2} = 0.5\%$, $X_{H_2O} = 20.2\%$, $X_{H_2} = 76.9\%$ and for a more water rich C3, it could well have been $X_{CO} = 0.1\%$, $X_{CO_2} = 271 \text{ ppm}$, $X_{H_2O} = 20.8\%$, $X_{H_2} = 79.0\%$. We will assume here that the hydrogen and water escaped before the CO gas began to be released.

Time factor

In the ordinary chondritic parent bodies, under the above assumptions, the gas is 97.9% CO and 2.1% CO₂. It has a pressure of 0.070 bars until lithostatic pressure drops to 0.070 bars (at $r = 9.84$ km in a 10km asteroid). It is of interest to determine the rate of flow of this gas, and also to determine the length of time that outgassing would be occurring.

In the ten kilometer asteroid, the average flow rate can be deduced from the equations for Knudsen diffusion since throughout the asteroid, the mean free path of the CO molecules exceeds the tube diameter. The velocity of a gas in a packed column in free molecular flow is given by

$$v = \frac{\dot{\phi}}{\rho} = D \frac{dx}{dz} \quad (17)$$

where $\dot{\phi}$ is the flux, ρ is the mass density, D is the Knudsen diffusivity of the gas and dx/dz is the gas concentration gradient.

$$D = \frac{2}{3} \bar{v} r \quad (18)$$

where \bar{v} is the average speed of the gas and r is the diameter of the pore. Since

$$\rho = \frac{NM}{V} = \frac{MP}{RT} \quad (19)$$

where V is volume, N is the number of molecules and M is the molecular weight, and since

$$D = 9700 r \sqrt{T/M} \quad (20)$$

and

$$\phi = \frac{D}{L} \frac{\Delta P}{RT} \quad (21)$$

the convenient relationship

$$v = 9700 r \sqrt{T M^{-3}} \frac{\Delta P}{L \bar{P}} \quad (22)$$

is obtained, with L defined as the length over which the pressure changes by ΔP and \bar{P} being the average pressure over that length. The velocity of the gas was found to be 3.4×10^{-7} cm sec⁻¹ in the region where the temperature was between 1000 - 1200K. It increased as a function of radius and is 1.9×10^{-6} cm sec⁻¹ at the 300K level. The velocity at the surface (T=175K) is 4.4×10^{-5} cm sec⁻¹. Integrating the velocity over position, we see that it took 29,000 years for a parcel of gas at the 1200K level (z = 4.76 km) to reach the surface.

To answer the second question of how long outgassing occurred, there are two aspects to be dealt with: the supply of the volatile and the cooling rate of the asteroid. If the asteroid has a carbon concentration of 1000 ppm (wt) then a cubic centimeter will contain ($\rho=4$) 0.004 grams or 1.4×10^{-4}

moles. The ideal gas law is used, with $P = 0.0687$ bars, $V = 0.15 \text{ cm}^3$ (the pore space) and $T = 1200\text{K}$. We see that the amount of carbon removed by having that CO gas flow upwards is equivalent to 0.3 ppm. It is the same if the CO_2 gas is included. With the carbon concentration down the activity of graphite falls a little, so does pressure of CO_2 and CO and the next drop is less severe. If the core is defined as the region in the asteroid where the temperature is over the eutectic melt temperature of the Fe-FeO-FeS system, the core of the 10km asteroid contains $4.5 \times 10^{17} \text{ cm}^3$, each with 10^{-7} moles of CO gas. To fill the whole pore volume of the asteroid according to the above pressure scheme, the number of moles of CO gas necessary is 7.8×10^{11} moles, so that each core cubic centimeter must discharge its gas seventeen times to fill the asteroid. Each time the gas flows out of a cube's pores it is replaced by a gas whose pressure is slightly lower. Each seventeen outflows constitutes an "iteration" of a gas, that is, a period of 29,000 years for the gas to completely come out and be replaced. Since the gas in a cube can replace itself several thousand times, and since seventeen of these is an iteration, there is enough carbon in the asteroid for 430 iterations with the pressure over 0.006 bars, and 860 iterations over 0.0006 bars.

Having shown that there is enough volatile component to have outgassing several millions of years, the question of cooling becomes important. If the heat capacity is taken as $10^7 \text{ erg gm}^{-1} \text{ deg}^{-1}$, the temperature gradient discussed above

implies a heat content of 1.18×10^{29} ergs. After the asteroid cooled, the heat content would be 2.93×10^{28} ergs (it would be 175K to the center), so 8.88×10^{28} ergs must be dissipated.

It was implied earlier that in a 10 km asteroid,

$$T(r) = 1500 - 13.25 r^2 \quad (23)$$

where r is in kilometers. With some differential equation solving, the actual equation as a function of time, is

$$T(r,t) = 175 + (1325 - 13.25 r^2) e^{-\alpha^2 b^2 t} \quad (24)$$

where 175K is the steady state term, $\alpha^2 = K/C_p \rho = 1.0 \times 10^{-2}$ $\text{cm}^2 \text{sec}^{-1}$ and $b^2 = 7.5/R^2$ where R is 10 km (10^6 cm). It can be shown that once cooling has begun, after 108,000 years, no part of this asteroid is at 1200K and that after 422,000 years the whole excess heat content has dropped by a factor of e . Therefore, these models can go through at least two iterations, with just over 100,000 years for the process of cooling take place. See table I.

In the 30 km asteroid, the flow rate can be determined from equations for continuum diffusion, since only the uppermost 570 meters had the mean free path of the gas molecules exceeding the tube diameter. There, the flow is modeled as it was above, by Knudsen diffusion. To get the velocity of the gas we use the Blake-Kozeny equation

$$v = \frac{\Delta P}{L} \cdot \frac{D_p^2}{150\mu} \frac{\epsilon^3}{(1-\epsilon)^2} \quad (25)$$

where D_p is the diameter of a particle, which was taken to be two microns; μ is the viscosity which was assumed to be 10^{-4} poise, and ϵ is the porosity, which was taken as 0.15 (Wasson, 1974, p176). The results of the repeated use of this formula are in table I. It would take a parcel of gas at $z = 14.27$ km ($T = 1200K$) 413,764 years to get to the surface of the asteroid. Since the cores's pore volume can contain 1.2×10^{12} moles of CO gas and 1.54×10^{13} moles are needed to fill the pore volume with the above pressure gradient, the pores in the core must produce gas 13 times to fill the asteroid and itself with the correct amount of CO gas. This will be called one iteration, and it will last 414,000 years. Since it will take this asteroid at least 3.08×10^{13} sec = 976,000 years to cool to the point that gas production will be impossible, there is time for at least two iterations. CO gas would be largely gone by the time 1.5×10^5 years have elapsed. It will, however take 3.80 million years for the excess heat to be dissipated by a factor of e.

In the case of the 100 km asteroid, the gas can be treated as a continuum all the way through. Its velocity is shown in table I. The time it takes for a parcel of a gas to travel from the "core" to the surface is 420,208 years. To fill the asteroid with gas would require the pores in the "core" to empty themselves 13.6 times. This would be an "iteration." Since gas production could go on for 10,800,000 years after cooling began (before no place in the asteroid

was melted) 26 iterations could occur and the pores would have to replenish themselves 350 times. It is clear that, near the end, the CO and CO₂ pressures would be down by a factor of 1.1. After 42,250,000 years, the excess heat of 8.88×10^{31} ergs will be reduced by a factor of e, and the steady state solution will not be isothermal, but long lived radioactive nuclides will hold the central temperature no less than eight degrees above the average surface temperature!

Perhaps 5×10^7 years may elapse between the time the steady state temperature gradient is established and the time cooling begins. For C3 chondrites, the pore gas pressure drops by an order of magnitude after 240 refillings, or every 25 iterations. The carbon concentration would be only 19 ppm after 2×10^7 years in the slowest (100km) asteroid, leaving plenty of time for deposition. In the 30 and 100 km ordinary chondrites, however, 430 iterations or 1.7×10^8 years are needed to reduce the carbon content of the "core" by an order of magnitude. If after 5×10^7 years cooling has set in to the point that no part of the core is melted, then 600 ppm carbon remain in the core and all of the deposition results must be multiplied by 0.4 and the deposition will occur at a somewhat greater depth.

It is of note that the time in seconds given in table I is a time limit for equilibration in each "zone" of the asteroid. As the subject of kinetics is addressed, table I should be consulted to judge whether or not a reaction went

to completion. Reaction rates are usually given in grams $\text{hr}^{-1} \text{ cm}^{-2}$. Given that in each cubic centimeter of material there is about 0.5 grams of metal upon which to nucleate or react, and given our chosen grain radius of one micron, there are 1.5×10^{10} grains or 1875 cm^2 of metal surface per cm^3 of material. Further, there are 3600 seconds per hour, so a rule of thumb is that these numbers can be divided by 2 and they would be in convenient units of $\text{g sec}^{-1} (\text{cm}^3 \text{ of material})^{-1}$. For the C3 body, there are 0.2 grams of metal per cm^3 of material, so the "rule of thumb" would be to divide by six.

The rates of formation of carbonyls and deposition of metals are highly pressure-dependent. Five (or four for $\text{Ni}(\text{CO})_4$) moles of gas are reacting to form one mole of gas. Iron pentacarbonyl and nickel carbonyl are both ideal gases, so this reaction brings in a significant loss of volume.

Kim, et al. (1973) prepared iron tailings which were 53.96% iron by weight, and 26.54% metallic iron. The iron grains were of the size 44 μm . Rhee, et al. (1973) took the material and exposed it to CO gas after first having reduced the iron. They found that 394 K was the optimum temperature for forming iron pentacarbonyl and that the reaction went 35% to completion in only two hours, when the CO pressure was 21 atm. As temperature increased, the carbonyl was inclined to decompose and deposit the metal. As temperature decreased, the carbonyl was more stable but the reaction rate was reduced. At 366 K however, it was still quite rapid. Based on

a scanty set of data points, Rhee et al. were so bold as to propose the following formula for computing the rate:

$$r_s = \frac{K_s a_{Fe}}{(RT)^5} \left(\frac{RT}{P_{CO}} \right)^n (P_{CO}^5 - P_{Fe(CO)_5}/K_e) \quad (26)$$

where K_s is the reaction rate constant and K_e is the equilibrium constant, and r_s is the rate per unit area free iron surface. The variable n is the number of CO molecules adsorbed on non-reacting iron sites and involved in forming an $Fe(CO)_5$ molecule. They found n to be about 3. Thus, holding all else constant, the rate increases as T^{-2} .

Similarly, the rate of $Ni(CO)_4$ formation decreases with an increase in temperature (Sykes and Townshend, 1955). The carbonyl is more stable at lower temperatures. At 409 K, 0.06 grams of nickel were converted per hour. At 323 K, 1.60 g hr^{-1} were converted. It should be pointed out, however, that the equilibrium values demand less conversion at 409 K than at 323 K and the authors felt that equilibrium was most quickly achieved at temperatures of 398 to 409 K. Data below room temperature do not exist, but given the enormous lengths of time available on the asteroid and the laboratory time scale of the reaction even down to room temperature, it will be assumed here that the carbonyl forming reaction will attain equilibrium even at temperatures as low as 225 K.

At sufficiently low pressures, the deposition reaction, that is, the breakdown of the carbonyl and the deposition of metals, will still proceed at a laboratory pace at room tem-

perature. The actual quantitative expression for the rate of decomposition and deposition of iron pentacarbonyl is

$$r = \frac{c_1 c_2 \exp(-E_0/RT) \exp(E_a/RT) (P_a - P_{CO}^5/K_{eq})}{(1 + c_2 \exp(E_a/RT) \times P_a + c_3 \exp(E_r/RT) P_{CO})^{1.8}} \quad (27)$$

Where c_1 , c_2 , and c_3 are known constants, E_a , E_0 and E_r are known energies, P_a is the carbonyl pressure in Torr and r is the rate of deposition in $\text{g hr}^{-1} \text{ cm}^{-2}$ free iron surface (Carlton and Oxley, 1965). K_{eq} here is the equilibrium constant of deposition, and is given by

$$K_{eq} = 3.34 \times 10^{11} \exp(24850/T + 16.06 \log T - 1.76 \times 10^{-3} T - 3.032 \times 10^5/T^2) \quad (28)$$

If the temperature were 300 K, with $P_a = 29$ Torr and $P_{CO} = 285$ Torr, $r = 9.09 \times 10^{-16} \text{ g hr}^{-1} \text{ cm}^{-2}$, or 1.6×10^{-3} grams per 100,000 years given the iron content and 1 μm grain size. On the other hand, if all the CO gas were gone, $r = 1.28 \times 10^{-6} \text{ g hr}^{-1} \text{ cm}^{-2}$ or 1.4 g year^{-1} at room temperature.

Clearly, the rate is dependent on free iron surface area available for deposition. Chemical kinetics is the limiting factor in deposition below 473 K. The rate limiting step is the decomposition of adsorbed iron carbonyl on the deposition surface and the activation energy of the decomposition reaction is about $20 \text{ Kcal g}^{-1} \text{ mole}^{-1}$ (Carlton and Oxley, 1965).

Nickel carbonyl deposition and nickel deposition is handled in Carlton and Oxley (1967). It is described by a similar equation

$$r = \frac{c_1 c_2^2 \exp(-E_o/RT) \exp(2E_a/RT) (P_a^2 - P_{CO}^8/K_d^2)}{(1 + c_2 \exp(E_a/RT) \times P_a + c_3 \exp(E_r/RT) \times P_{CO})^2} \quad (29)$$

where P_a is now the nickel carbonyl pressure in Torrs,

$$K_d = \exp(64.2 - 10500/T). \quad (30)$$

This reaction rate is also dependent upon area of iron grains. It deposits upon nickel, iron or stainless steel. The rate of nickel deposition is generally orders of magnitude faster than iron at similar temperature pressure and CO pressure. If the CO pressure is low enough, nickel will be deposited at 273 K on a convenient laboratory time scale. But the reaction is strongly inhibited by carbon monoxide pressure (Garratt and Thompson, 1934a). Extrapolating to a temperature of 225 K, given a nickel carbonyl pressure of 5 Torr (the vapor pressure) and a CO pressure of 0.1 Torr, we see that $r = 2.36 \times 10^{-11} \text{ g hr}^{-1} \text{ cm}^{-2}$, so that even at these extreme conditions a gram of nickel could still be deposited in a cubic centimeter in less than 3000 years. If P_{CO} is zero it deposits at twice the rate.

It should be pointed out that if the asteroid (in particular the 30 km and 100 km H type) cooled before it could use up its carbon, there is still plenty of time to deposit the metals before the whole asteroid cools to the point where kinetics prevent the decomposition of carbonyls and the deposition of metals.

Having determined the composition of the gas that will

be flowing upwards in the asteroids, having disposed of harmful H_2O , having established that the reactions forming carbonyls are not kinetically inhibited, having addressed the flow rates of gas and the kinetic deposition and having established that at bare minimum several iterations can occur in each asteroid, the actual transport of iron can be investigated.

The Results

A computer program was run to depict the equilibrium conditions in each of the twelve parent bodies described above. Figures 2-7 show the equilibrium gas pressure for each of the gases CO; Fe(CO)₅ and Ni(CO)₄ and lithostatic pressure all as a function of temperature which is a function of depth. Presented here are the 10 km, 30 km and 100 km asteroids both of C3 and H composition, but only at 175 K. The six asteroids whose surface temperature was 150 K so resembled their counterparts of 175 K that to treat them here would be redundant.

In the carbonaceous asteroids, the CO pressure is 3.248 bars until the lithostatic pressure drops to below 3.949 bars. Below this, the CO pressure is maintained at 82.2% of the lithostatic pressure. In the ordinary chondritic asteroid, the CO pressure would be 0.0687 bars until the lithostatic pressure dropped to 0.070 and would be maintained below this at 97.9% lithostatic pressure. The iron pentacarbonyl pressure was determined by the following relationship

$$P_{\text{Fe}(\text{CO})_5} = K_{\text{eq}} a_{\text{Fe}} (P_{\text{CO}})^5 \quad (31)$$

and the nickel carbonyl pressure by

$$P_{\text{Ni}(\text{CO})_4} = K_{\text{eq}} a_{\text{Ni}} (P_{\text{CO}})^4. \quad (32)$$

For the nickel reaction,

$$\log K_{\text{eq}} = 8.148.3/T - 20.550 \quad (33)$$

(JANAF, 1971, 1978). Mass balance was invoked so that the total pressure of these two carbonyls and of CO would not exceed lithostatic pressure. It was found that nickel carbonyl was five orders of magnitude more abundant than iron pentacarbonyl, simply based upon equilibrium considerations and the assumption that nickel is readily available as is iron. But that assumption is not realistic. Nickel is not found in independent grains, but in iron nickel alloy. In carbonaceous chondrites, where the iron is taenite, only 26% of the metal atoms on the surface of a grain are nickel. Once the nickel is used up, no new nickel carbonyl molecules can form until the iron atoms on that layer react with CO to form iron pentacarbonyl, thus exposing new nickel atoms to the gas. In an iron nickel alloy, the diffusivity of nickel is given as

$$D = 2.11 \exp(-73 \pm 2.0 \text{ Kcal mole}^{-1}/RT) \quad (34)$$

for an alloy that is 5.79% nickel (McEwan, et al., 1959), and by

$$D = 0.497 \exp(-66.40 \pm 1.52 \text{ Kcal mole}^{-1}/RT) \quad (35)$$

for an alloy that is 9.21% nickel (Hancock and Leak, 1967). For the first alloy, typical of the kamacite found in ordinary chondrites, the diffusivity of nickel at 400 K is $10^{-40} \text{ cm}^2 \text{ sec}^{-1}$. For the other alloy, $D = 10^{-37} \text{ cm}^2 \text{ sec}^{-1}$. Given 40 million years ($1.3 \times 10^{15} \text{ sec}$) a nickel atom in the first alloy would be expected to move $3.6 \times 10^{-13} \text{ cm}$ and $1.1 \times 10^{-11} \text{ cm}$

in the other (interatomic spacing is on the order of 10^{-8} cm). In a spherical grain one micron in radius, the amount of nickel diffused would be $3.38 \times 10^{-6}\%$ given 317 million years in the first alloy, and $1.07 \times 10^{-4}\%$ in the second. Carbonyls were most abundant at temperatures colder than 400 K. Clearly, the number of moles of nickel carbonyl that could form is constrained by diffusion of nickel in iron-nickel alloys to be 26% of the total number of moles of carbonyl gas. This would be 6% in the ordinary chondritic case. Mass balance for the gas is worked out in the following way. All three gases, CO, $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ are ideal, so

$$P_i V = n_i RT, \quad (36)$$

where n_i is the number of moles of the particular gas. It has been shown that, in the ordinary chondrite case,

$$n_{\text{Ni}} = 6n_{\text{Fe}}/94. \quad (37)$$

The subscript Ni will stand for $\text{Ni}(\text{CO})_4$ and Fe for $\text{Fe}(\text{CO})_5$, and T for total. Mass balance is given as

$$n_T = n_{\text{CO}} + 5n_{\text{Fe}} + 4n_{\text{Ni}} \quad (38)$$

where n_T is the total number of moles of CO available and n_{CO} is the number that remain as CO gas. Since

$$P_{\text{Fe}(\text{CO})_5} = a_{\text{Fe}} K_{\text{eq}} (P_{\text{CO}})^5 \quad (39)$$

and

$$n_{\text{Fe}} = P_{\text{Fe}(\text{CO})_5} V / RT, \quad (40)$$

we substitute 37 into 38, then 40 into 38, and yield

$$n_T = n_{CO} + 5 \frac{P_{Fe(CO)_5}^V}{RT} + 4 \frac{6}{94} \frac{P_{Fe(CO)_5}^V}{RT} \quad (41)$$

The values of n_T and n_{CO} are given by 36 and V/RT is cancelled out to give

$$P_T = P_{CO} + B a_{Fe} K_{eq} (P_{CO})^5 \quad (42)$$

where $B = 5.255$ for an ordinary chondritic composition and 6.405 for the C3 composition.

The above equation is valid only until iron pentacarbonyl begins to condense. The carbonyl forms a liquid at less than 350 K, and its exact temperature of condensation is a function of pressure. Its pressure is henceforth given by the vapor pressure equation

$$\log P = \frac{-1966}{T} + 5.212 \quad (43)$$

where P is pressure in bars. At this point, equilibrium must be re-established by equation 39 and much CO is converted to $Fe(CO)_5$, which would condense. Of course, at the same time, $Ni(CO)_4$ is being produced, but its pressure can increase. Eventually its vapor pressure is reached and $Ni(CO)_4$ liquid begins to form. Its vapor pressure is given by

$$\log P = \frac{-1517.7}{T} + 4.809 \quad (44)$$

until the temperature drops to the freezing point, 248 K.

Then

$$\log P = \frac{-2078}{T} + 7.060 \quad (45)$$

(Anderson, 1930). After many iterations, much liquid carbonyl will build up. It was shown above that there was plenty of time before cooling in the 100 km H asteroid to deposit most of the carbonyl that could be made even if cooling began before the completion of CO outgassing. That cooling would set in at this time is by no means necessary. In the smaller asteroids many iterations could occur before cooling began. There are 14 iterations in every ^{26}Al half life. The T-Tauri effect on the interior could last tens of millions of years. It is assumed here that all the asteroids stayed warm long enough to outgas all of the CO, so that the mechanism for iron transport can be fully explored, an assumption that is not unrealistic. Although the C3 asteroids contain a greater concentration of carbon than H chondrites, the carbon is depleted at 30 times the rate. Should cooling cause the melted region to disappear so that $T_c < 1200$ K, deposition would begin 420,000 years later when the last of the CO produced vacated the asteroid.

When the CO gas is gone, the carbonyls will begin to decompose and deposit metals at a healthy rate. See table II. The liquid or solid carbonyls form a sink that will maintain the carbonyls at their vapor pressures. CO gas exits the asteroid at a rate that is 16 times that of the carbonyl gases since Knudsen diffusion flow is proportional to the mass of the molecule to the 3/2 power. The carbonyl speed is actually down by more than a factor of 16 when its

condensation is accounted for. Carbonyl solids are not mobile, but liquids could drip downward, but upon crossing the vaporization line, they would become a gas and diffuse back upwards, so the deposition should be most prevalent in the upper meters of the asteroid, where condensation occurred. Therefore, in quantitatively assessing the mass transport, the asteroids can be divided into four zones. The innermost 85% of each asteroid is divided into an unaltered zone (the bulk of the 85%) and a depleted zone, where carbonyl pressures were sufficient to deplete this region of metals. The outer two zones are depicted in table II. The region above each dashed line is depleted in nickel, whose carbonyl has not condensed yet at this level, but enriched in iron, which has. The uppermost zone has both iron and nickel deposition going on. These zones will henceforth be referred to as zones 1, 2, 3, and 4 in ascending order. Since much of the carbonyl deposited will have been formed in the upper zone from whence it originated, it is of interest to determine the state of the gas as it crossed zonal boundary lines. This is done in table III. We are interested only in the carbonyl groups that entered this region bonded to metal. The others produce a null net effect.

The volume of the "core" tells us the mass of carbon present. The percentage of CO_2 tells us how much carbon we can discount to this process. By determining the amount of CO that remained CO at the zone 2 - zone 3 boundary we can get an idea of how much CO did not form a carbonyl until it en-

tered the region where deposition would eventually occur, as well as the total production of iron pentacarbonyl. To quantify the extra nickel production of zone 3, the loss amount of CO needed to bring that gas into equilibrium with the vapor pressure of $\text{Fe}(\text{CO})_5$ is computed and knowing that 6 moles of $\text{Ni}(\text{CO})_4$ should form for every 94 moles of $\text{Fe}(\text{CO})_5$ (or 26 for every 74 in a C3 body), we get the nickel transport across the 3 - 4 boundary.

Table III illustrates the net transport effects well. To place the metal deposits in a more detailed way than the zone system will require further assumptions. Note that the zone boundary lines could be one kilometer lower in the case of an ordinary chondritic asteroid which cooled before the onset of deposition. For the deposition inhibiting CO to be out of the way, the central temperature must be below 1200 K. Thus the whole transient term in equation 24 must be down by a factor of 1.3 so that where the temperature was 300 K, it is now 272 K, etc. This puts the zone boundaries about one kilometer deeper in a 100 km asteroid, and 300 meters deeper in the 30 km asteroid.

To notice that enrichments were on the order of a percent and discard this model as a small effect would be a mistake. It is too much to demand a perfectly even distribution of metal deposit throughout the entire volume of each zone. It is entirely possible that the metals were deposited in discrete sites, perhaps where a small amount of metal was present already as a nucleation site, or under favorable con-

ditions. This process is autocatalytic. Local enrichments in metal could be 100% or more.

One scenario for "clumping" of iron would be for the liquid carbonyls to flow downward to a point just above the zone boundary. If it were to flow below this point, it would become a gas and return to the condensation zone. The part of the zone just above the boundary has several advantages that make it a preferential place for deposition. First, it is at a lower gravitational potential, the liquids would flow there. Second, the higher temperatures permit the highest vapor pressures. It is from the gas phase that decomposition and deposition occur. Third, the deposition rates are eight orders of magnitude more favorable at the bottom than at the top of a deposition zone. Fourth, the upflow of liberated CO gas from the rapid deposition below could inhibit the rate of deposition above.

The numbers of moles of carbonyls given in table III are the net gain for a deposition zone, but the total carbonyl inventory is higher. It is entirely possible for carbonyls that formed higher up in the zone to flow downward, exaggerating the deposition below and depleting the upper parts of the metal with respect to its original abundance. This could account for the apparent trend in L-chondrites for a slight increase in nickel abundance with petrologic grade.

Some of the gas is sure to make its way to the surface. Escape velocity on the 100 km asteroid of ordinary chondritic composition is the greatest, yet it is only $14,900 \text{ cm sec}^{-1}$.

The peak velocity of a Maxwell velocity distribution of the heaviest gas ($\text{Fe}(\text{CO})_5$ whose weight is 196) at 100 K, which is well below the surface temperature of the asteroid, is 9200 cm sec^{-1} . Since this is better than 60% of the escape velocity, there are millions of escapes per second and the life time of this "atmosphere" is nil. If nickel carbonyl could linger, it could photodissociate to leave nickel, with CO escaping (Garratt and Thompson, 1934b).

Finally, after metal has been deposited, the gases have departed and the asteroid has cooled, a violent event such as an impact can occur, and metal-rich material or even metal chunks will be liberated into space, some of which eventually fall as meteorites to earth.

Iron meteorites formed in this way would show definite evidence of the carbonyl process. In industry, efforts are made to keep the carbon impurity down to a percent (Oxley, 1966). The IAB group is well known to contain cohenite (Fe_3C), as well as graphite nodules (Wasson, 1974). This class has nickel abundances that average about 7.55 wt %, which may tell us something about the oxidation state of iron in the parent body. It is also this class which could contain up to 15% silicates by weight. The IA iron El Taco has some silicate inclusions that are $9 \times 10 \text{ cm}$ and contains cracks (Buchwald, 1975). There is a definite limit to the amount of silicates and troilite that can be found in an iron meteorite, which in no way reflects upon its environment, but rather on its structural integrity since in a breakup of an iron,

the exposed silicates would disperse. Evidence of this is seen in the hemispherical pits centimeters in diameter which can be seen on the surface of some iron meteorites, which on occasion contain traces of troilite (Lewis, 1968; Read, et al., 1967). This is evidence that these pits could represent cavities left behind by nodules of material inherent in the parent body at the deposition level other than iron and removes the requirement that this region be at least 85% metal by mass.

It is interesting to note that the famous siderophile elements almost all form carbonyls. There are $\text{Ir}(\text{CO})_8$ and $\text{Ir}_4(\text{CO})_{12}$, $\text{Re}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$, for example. Cobalt (see table IV) forms complex carbonyl molecules, as does platinum. Osmium and rhodium form carbonyl chlorides, as does platinum. If these carbonyls were also formed and deposited these elements in I AB irons, it would make an interesting and worthwhile research project to determine the fate of the chlorine, and whether or not lawrencite $(\text{Fe}, \text{Ni})\text{Cl}_2$ will form. I AB irons have a lower iridium content than other irons. Perhaps iridium octacarbonyl is not as effective a transporter of iridium as iron and nickel carbonyls, so that the full iridium content is not imparted into them. Of elements noted for carbonyl behavior, it is interesting that molybdenum is enriched in Canyon Diablo (Mason, 1971), a noted IA, and that bromine, which is a trace element in meteorites, is seen in Odessa. Bromine is often in complex carbonyls, such as platinum carbonyl bromide. However, it is also true that

chromium and tungsten which form carbonyls are not particularly prevailing in I AB's compared to other irons, although a thorough kinetic and thermodynamic investigation might lead to the reason. It is hoped that some of the points raised here are investigated.

Work has been done with reacting carbonyls in the presence of CS_2 and H_2S . Iron, nickel, troilite and pentlandite form, and the kamacite-taenite phases are enveloped by the sulfides much as observed in meteorites (Bloch and Wirth, 1980). If only H_2S and $Fe(CO)_5$ are used, then the products obtained were iron and troilite.

In carbonaceous chondrites, metal is not common, needless to say. If any were found, particularly iron, in any large quantity, it would be safer to suspect carbonyl vapor deposition than the survival of iron at unfavorable oxygen fugacities. That meteorite would be due further investigation.

In ordinary chondrites, there are two trends of interest. There is an overall increase in metal content with petrologic grade (Schmitt, et al., 1972), and there is a slight decrease in nickel in L4's. If ordinary chondrites come from the top kilometers of a parent body (say one H parent, one L parent and one LL parent), and petrologic grade is assumed to represent temperature, so that the highest grades with the less-distinct chondrules were subjected to higher temperatures during formation, it is possible that they all came from a deposition zone whose lower parts were

enriched in metal. In any case, higher temperatures, to which higher petrologic grade has been attributed, promote deposition of metals from carbonyls, as shown above. On the negative side, no clear trend could be observed in LL's. Further, the amount of iron oxides in H's decreases with petrologic grade. This is an effect that could be attributed to different conditions, such as temperature of condensation, or oxidation state of iron, and would take away from a deposition depth argument.

The second trend is that in the L chondrites, the L4's have one nickel abundance, and the L5 and L6 chondrites have another. The L4 chondrites, presumably formed at lesser depth, have a lower nickel content (Greenland and Loverling, 1965). This does not support the idea of nickel deposition in "zone 4" of their parent body, unless it was a 10 kilometer object, in which case the lower nickel abundances are expected (table III), or unless the L4 chondrites formed very near the surface, well above the zone 3 - zone 4 boundary.

In the formation of large bodies of iron, it is easy to imagine the entrapping of silicate fragments and chondritic matter. Sharp edges in this material would remain, unlike in high temperature igneous models where the melting point of iron is reached.

Industrial Applications

If the events described in this thesis have actually occurred, it would be expected that the upper layers of asteroids would contain more iron, especially if their original carbon content is higher than 0.1 wt %. Vigarano type composition will give it a 1% carbon content.

If, in the future, it becomes more economically (or politically) feasible to exploit the resources in space, a process for mining asteroids of metal could be devised using carbonyls.

A space vehicle would park near a metal-rich asteroid surface. (Metal-rich material could have been pre-mined or extracted from shallow depth by an advance crew, if necessary.) CO is then reacted with the ore at kinetically optimum conditions (about 400 K and 20 atm) if possible. Iron pentacarbonyl gas is then heated to 600 K on board the vessel, in a plating chamber. The liberated CO gas is pumped back out to be reused until the sufficient metal quantity has been taken aboard or the asteroid has been exhausted. The vessel could then travel to earth, or more conveniently to a space station, where metals could be sorted. Nickel, iron, chromium and tungsten would be easily obtainable, as well as molybdenum, if it is available. If platinum is abundant, more complicated techniques can be employed to form its carbonyl halides. These sorted metals could then be sent to earth, or be used in space. If space industrialization becomes a reality, it could well be cheaper to obtain raw ma-

terials from asteroids than to blast dense metals off the surface of the earth, with its vastly larger escape velocity and potential well.

Conclusion

In conclusion, a new model for the formation of iron meteorites involving the production of carbonyls at 300-400 K in an asteroid, their upward transport as a gas, and their dissociation at low pressure after carbon monoxide has diffused out, has been tested thermodynamically, and has been found possible within the confines of our present knowledge of the kinetics of the breakdown of carbonyls at low temperatures. The iron nickel ratio in I AB irons tell us that the parent body was an ordinary chondrite or they would be on the order of 26% nickel by weight. "Iron asteroids" must not be considered to be iron based on observations of their surfaces, until their bulk densities are known. The possibility cannot be overlooked that they are merely iron coated. If iron is preferentially deposited at a depth of 290 meters in a 10 km asteroid, it is possible that the upper layer was stripped away leaving an iron surface.

The chemical questions brought up concerning other carbonyls depositing siderophiles, bromine traces and chlorine, as well as the question of the appearance of lawrencite, should be investigated. Further, the deposition rates at zero CO pressure were extrapolated below the experimental data to below room temperature. Although very low rates were reported, this could be tested by considering a sample at 250 K for one year with sufficient deposition area to obtain a detectable amount of iron.

This work is by no means intended to be the last word on

the subject of carbonyl transport of metal in asteroids.

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Table I

<u>Temperature range (K)</u>	<u>Location (km)</u>	<u>Velocity cm sec⁻¹</u>	<u>Time (sec)</u>
10 km asteroid:			
1000-1200	6.14-4.76	3.4×10^{-7}	4.1×10^{11}
800-1000	7.27-6.14	4.8×10^{-7}	2.4×10^{11}
700- 800	7.77-7.27	6.2×10^{-7}	8.1×10^{10}
600- 700	8.24-7.77	7.4×10^{-7}	6.4×10^{10}
500- 600	8.69-8.24	9.2×10^{-7}	4.9×10^{10}
400- 500	9.11-8.69	1.2×10^{-6}	3.5×10^{10}
350- 400	9.32-9.11	1.5×10^{-6}	1.4×10^{10}
300- 350	9.52-9.32	1.9×10^{-6}	1.1×10^{10}
275- 300	9.62-9.52	2.4×10^{-6}	4.2×10^9
250- 275	9.71-9.62	3.4×10^{-6}	2.6×10^9
225- 250	9.81-9.71	4.2×10^{-6}	2.4×10^9
200- 225	9.91-9.81	7.4×10^{-6}	1.4×10^9
185- 200	9.96-9.91	1.4×10^{-5}	3.6×10^8
175- 185	10.00-9.96	4.4×10^{-5}	9.1×10^7
30 km asteroid:			
1000-1200	18.43-14.27	9.1×10^{-8}	4.6×10^{12}
800-1000	21.81-18.43	1.1×10^{-7}	3.0×10^{12}
700- 800	23.31-21.81	1.3×10^{-7}	1.2×10^{12}
600- 700	24.72-23.31	1.3×10^{-7}	1.1×10^{12}
500- 600	26.06-24.72	1.4×10^{-7}	9.5×10^{11}
400- 500	27.33-26.06	1.5×10^{-7}	8.5×10^{11}
350- 400	27.95-27.33	1.5×10^{-7}	4.1×10^{11}
300- 350	28.55-27.95	1.6×10^{-7}	3.8×10^{11}
275- 300	28.85-28.55	1.6×10^{-7}	1.9×10^{11}
250- 275	29.14-28.85	1.6×10^{-7}	1.8×10^{11}
225- 250	29.43-29.14	1.6×10^{-7}	1.8×10^{11}

200- 225	29.72-29.43	2.2×10^{-6}	1.3×10^{10}
185- 200	29.89-29.72	4.6×10^{-6}	3.7×10^9
175- 185	30.00-29.89	1.6×10^{-5}	6.9×10^8

100 km asteroid:

1000-1200	61.43-47.58	3.0×10^{-7}	4.7×10^{12}
800-1000	72.68-61.43	3.8×10^{-7}	2.9×10^{12}
700- 800	77.70 -72.68	4.2×10^{-7}	1.2×10^{12}
600- 700	82.42-77.70	4.5×10^{-7}	1.1×10^{12}
500- 600	86.87-82.42	4.7×10^{-7}	9.6×10^{11}
400- 500	91.11-86.87	5.0×10^{-7}	8.4×10^{11}
350- 400	93.16-91.11	5.1×10^{-7}	4.0×10^{11}
300- 350	95.17-93.16	5.3×10^{-7}	3.8×10^{11}
275- 300	96.15-95.17	5.4×10^{-7}	1.8×10^{11}
250- 275	97.13-96.15	5.4×10^{-7}	1.8×10^{11}
225- 250	98.10-97.13	5.4×10^{-7}	1.8×10^{11}
200- 225	99.05-98.10	5.5×10^{-7}	1.7×10^{11}
185- 200	99.62-99.05	5.5×10^{-7}	1.0×10^{11}
175- 185	100.00-99.62	5.6×10^{-7}	6.8×10^{10}

The 10 km asteroid had its velocities determined by the equation for Knudsen diffusion (22). The 30 km asteroid had its mean free path exceeding the diameter of the tube for the last 570 meters. The rest of this asteroid and the whole 100 km asteroid underwent continuum diffusion (equation 25).

Table II

Asteroid	Depth (km)	Time (yr)	Temp (K)	Rate of deposition, $P_{CO=0}$	
				$g\ cm^{-3}\ \text{millenium}^{-1}$ Fe	Ni
C3-100 km	4.83	5700	300	6934	115165
	3.85	5700	275	528	4144
	2.87	5700	250	23	****69**
	1.90	5400	225	0.49	0.27
	0.95	3200	200	5.3×10^{-3}	3.05×10^{-5}
	0.38	2200	185	1.66×10^{-6}	1.30×10^{-8}
C3- 30 km	1.45	6000	300	6934	102941
	1.15	5700	275	528	3751
	0.86	5700	250	23	****68**
	0.57	6700	225	0.49	0.27
	0.28	1900	200	5.3×10^{-3}	3.05×10^{-5}
	0.11	360	185	1.66×10^{-6}	1.30×10^{-8}
C3- 10 km	0.29	1250	250	23	24
	0.19	700	225	0.49	9.45×10^{-2}
	0.09	200	200	5.3×10^{-3}	*****
	0.04	47	185	1.66×10^{-6}	1.30×10^{-8}
H-100 km	2.87	5700	250	65.9	15.9
	1.90	5400	225	1.4	0.20
	0.95	3200	200	1.5×10^{-2}	*****
	0.38	2200	185	4.75×10^{-6}	3.72×10^{-8}
H- 30 km	0.86	5700	250	65.9	6.9
	0.57	6700	225	1.4	9.23×10^{-2}
	0.28	1900	200	1.5×10^{-2}	*****
	0.11	360	185	4.75×10^{-6}	3.72×10^{-8}
H- 10 km	0.29	1250	250	65.9	5.7
	0.19	700	225	1.4	8.59×10^{-2}
	0.09	2200	200	1.5×10^{-2}	*****
	0.04	47	185	4.75×10^{-6}	3.72×10^{-8}

Table III

<u>Asteroid Layer</u>		<u>Location (km)</u>	<u>Moles of CO exiting total</u>	<u>zone carrying Fe</u>	<u>carrying Ni</u>
100 km	1	0.00-91.11	2.06×10^{17}	-	-
C3	2	91.11-95.17	4.08×10^{16}	1.30×10^{17}	3.54×10^{16}
	3	95.17-97.13	3.13×10^{16}	-	4.49×10^{16}
	4	97.13-100.	-	-	-
30 km	1	0.00-27.33	5.54×10^{15}	-	-
C3	2	27.33-28.55	2.00×10^{15}	2.79×10^{15}	3.82×10^{14}
	3	28.55-29.43	1.99×10^{15}	-	3.90×10^{14}
	4	29.43-30.00	-	-	-
10 km	1	0.00-9.52	2.06×10^{14}	-	-
C3	2	9.52-9.71	5.07×10^{13}	1.51×10^{14}	3.91×10^{12}
	3	9.71-9.91	5.04×10^{13}	-	4.16×10^{12}
	4	9.91-10.00	-	-	-
100 km	1	0.00-95.17	1.47×10^{17}	-	-
H	2	95.17-97.13	2.51×10^{16}	1.16×10^{17}	6.17×10^{15}
	3	97.13-99.05	2.51×10^{16}	-	7.08×10^{15}
	4	99.05-100.	-	-	-
30 km	1	0.00-28.55	3.97×10^{15}	-	-
H	2	28.55-29.14	9.16×10^{14}	2.91×10^{15}	1.47×10^{14}
	3	29.14-29.72	9.15×10^{14}	-	1.93×10^{14}
	4	29.72-30.00	-	-	-
10 km	1	0.00-9.52	1.47×10^{14}	-	-
H	2	9.52-9.71	3.64×10^{13}	1.06×10^{14}	5.39×10^{12}
	3	9.71-9.91	3.64×10^{13}	-	7.09×10^{12}
	4	9.91-10.00	-	-	-

Iron			Nickel		
moles entering	moles already present	enrichment %	moles entering	moles already present	enrichment %
-	-	-	-	-	-
-2.60x10 ¹⁶	1.11x10 ¹⁸	-2.34%	-8.86x10 ¹⁵	3.76x10 ¹⁷	-2.36%
2.60x10 ¹⁶	1.45x10 ¹⁸	+1.79%	-2.43x10 ¹⁵	1.93x10 ¹⁷	-1.26%
-	-	-	1.12x10 ¹⁶	2.97x10 ¹⁷	+3.77%
-	-	-	-	-	-
-5.57x10 ¹⁴	3.01x10 ¹⁶	-1.85%	-9.56x10 ¹³	1.01x10 ¹⁶	-0.95%
5.57x10 ¹⁴	2.54x10 ¹⁷	+0.23%	-2.09x10 ¹²	7.88x10 ¹⁵	-0.03%
-	-	-	9.77x10 ¹³	5.57x10 ¹⁵	+1.75%
-	-	-	-	-	-
-3.03x10 ¹³	5.54x10 ¹⁴	-5.47%	-9.79x10 ¹¹	1.87x10 ¹⁴	-0.53%
3.03x10 ¹³	8.89x10 ¹⁴	+3.41%	-6.29x10 ¹⁰	2.05x10 ¹⁴	-0.03%
-	-	-	1.04x10 ¹²	9.51x10 ¹³	+1.10% ¹
-	-	-	-	-	-
-2.32x10 ¹⁶	2.11x10 ¹⁸	-1.10%	-1.54x10 ¹⁵	1.28x10 ¹⁷	-1.20%
2.32x10 ¹⁶	3.25x10 ¹⁸	+0.71%	-2.28x10 ¹⁴	1.31x10 ¹⁷	-0.17%
-	-	-	1.77x10 ¹⁵	6.65x10 ¹⁶	+2.66% ²
-	-	-	-	-	-
-5.82x10 ¹⁴	5.73x10 ¹⁶	-1.02%	-3.68x10 ¹³	3.47x10 ¹⁵	-1.06%
5.82x10 ¹⁴	8.78x10 ¹⁶	+0.66%	-1.15x10 ¹³	3.55x10 ¹⁵	-0.32%
-	-	-	4.83x10 ¹⁴	1.77x10 ¹⁵	+2.73% ³
-	-	-	-	-	-
-2.12x10 ¹³	2.05x10 ¹⁵	-1.03%	-1.35x10 ¹²	1.24x10 ¹⁴	-1.09%
2.12x10 ¹³	3.29x10 ¹⁵	+0.65%	-4.25x10 ¹¹	1.36x10 ¹⁴	-0.31%
-	-	-	1.77x10 ¹²	6.31x10 ¹³	+2.81% ⁴

¹Only 0.01% enrichments are kinetically possible.

²Only 0.43% enrichments are kinetically possible.

³Only 0.26% enrichments are kinetically possible.

⁴Only 0.03% enrichments are kinetically possible.

(See table II.)

Table IV

The Siderophiles and their Carbonyls

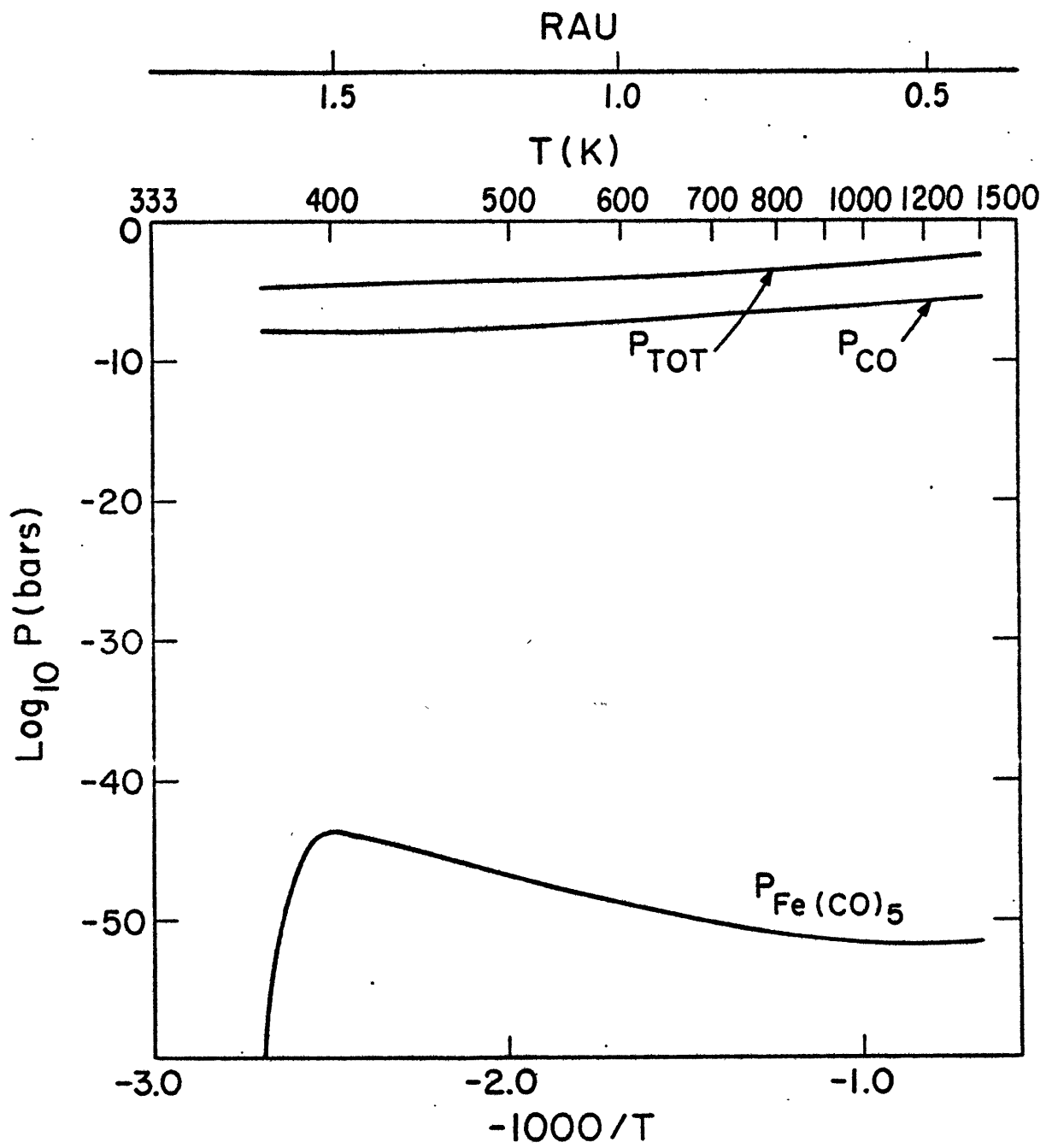
Pt	Forms only carbonyl halides	$\text{Pt}(\text{CO})_2\text{Cl}_2$, etc.
Os		$\text{Os}(\text{CO})_5$, $\text{Os}_2(\text{CO})_9$
Ir		$\text{Ir}_2(\text{CO})_8$, $\text{Ir}_4(\text{CO})_{12}$
Pd	Forms only carbonyl halides	$[\text{Pd}(\text{CO})\text{Cl}_2]_n$, etc.
Ru		$\text{Ru}(\text{CO})_5$, $\text{Ru}_2(\text{CO})_9$, $\text{Ru}_3(\text{CO})_{12}$
Rh		$\text{Rh}_2(\text{CO})_8$, $[\text{Rh}(\text{CO})_3]_n$, $\text{Rh}_4(\text{CO})_{11}$
Ni		$\text{Ni}(\text{CO})_4$
Co		$\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$
Ge	No known carbonyls	

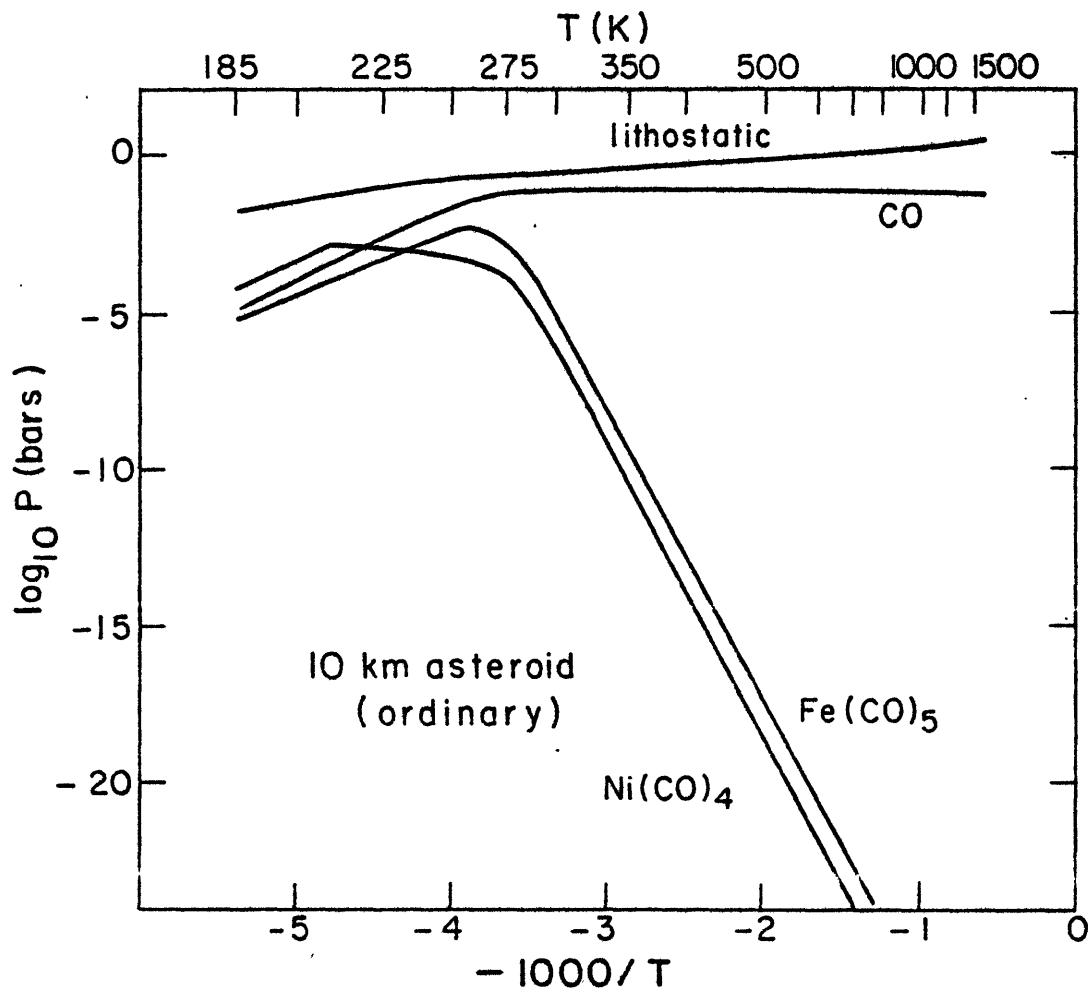
(Emeléus and Anderson, 1938)

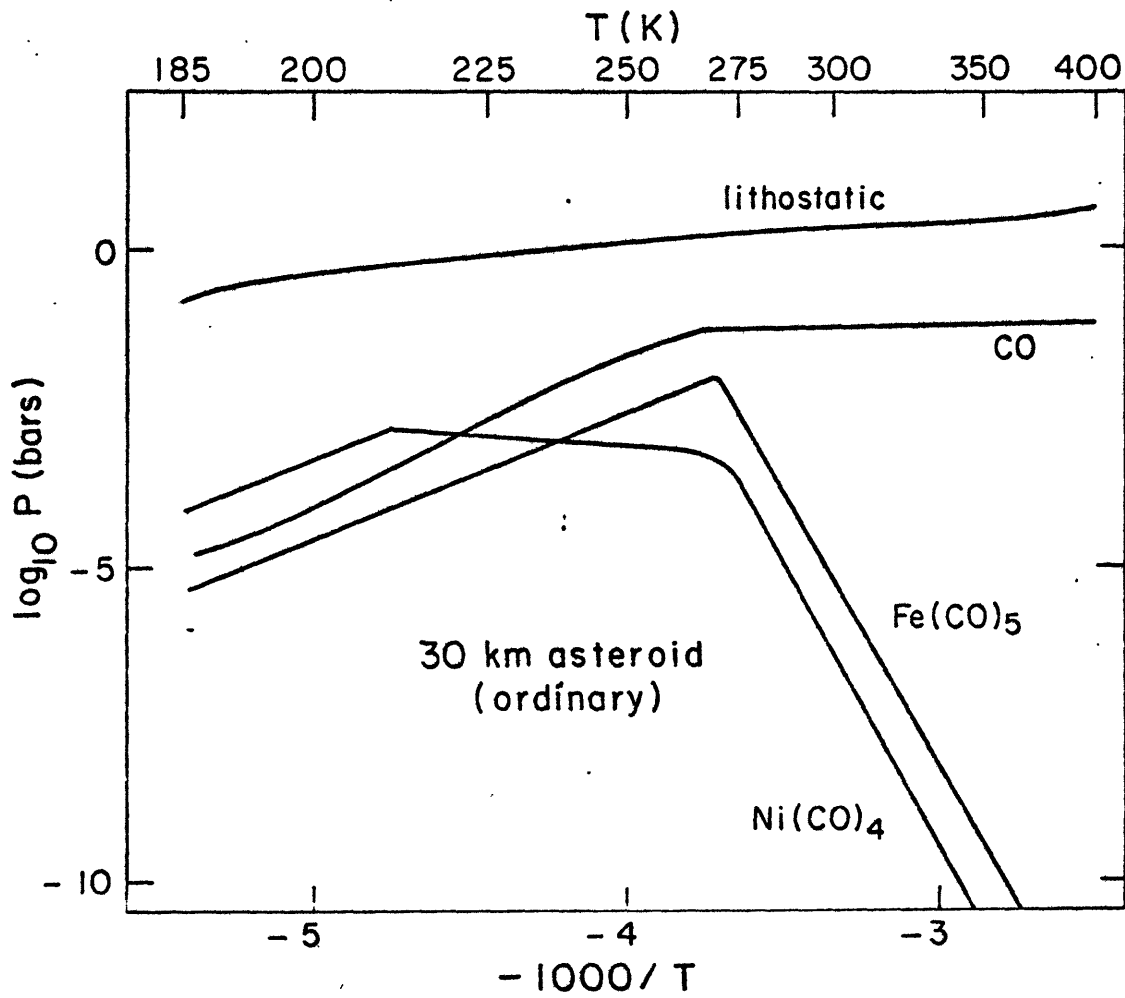
Figure Captions

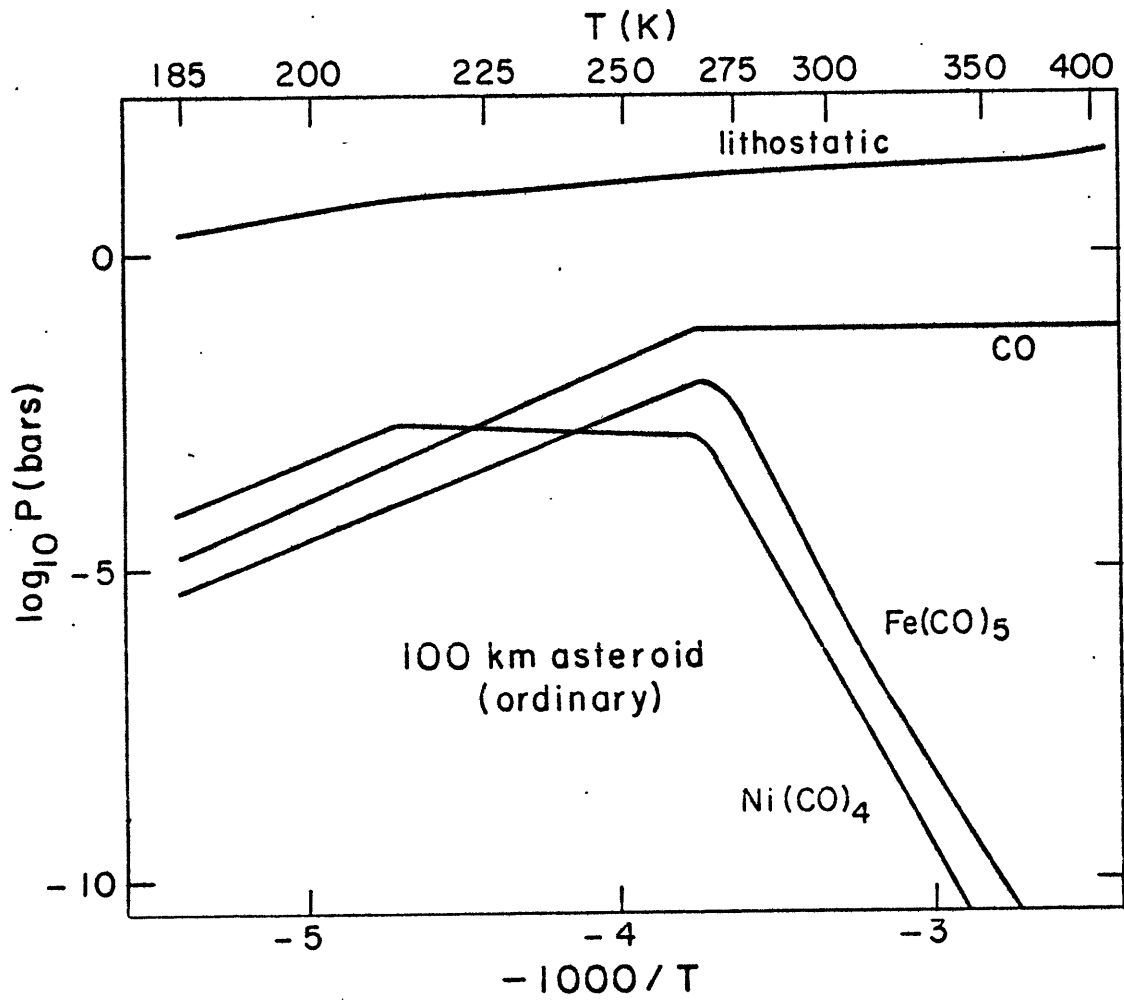
Figure 1: The pressure of iron pentacarbonyl is at least 35 orders of magnitude less than CO. At 600 K, the activity of iron begins to drop as magnetite appears. At 373 K, iron disappears and the activity of magnetite is one.

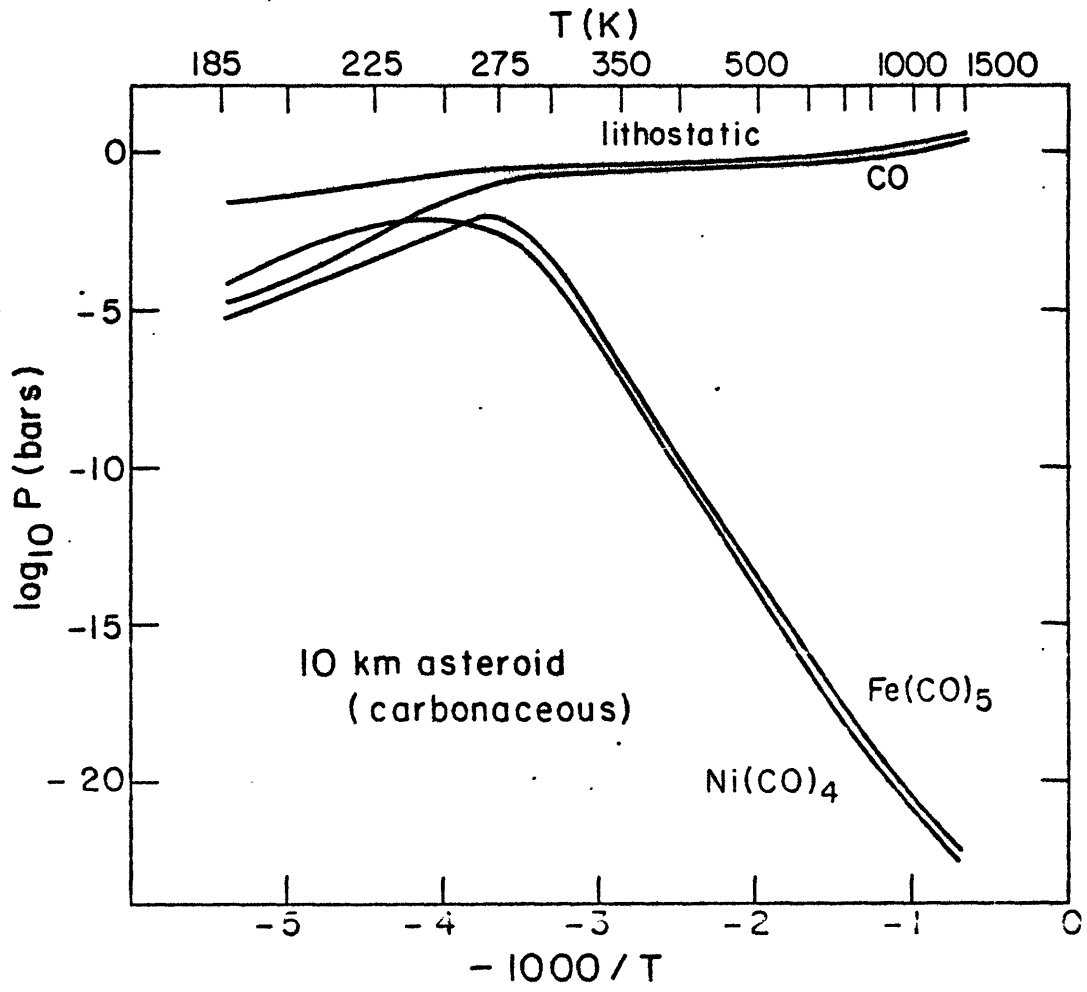
Figures 2 - 7: These figures show the equilibrium gas pressure for each of the gases CO, Fe(CO)₅, and Ni(CO)₄, and of lithostatic pressure which is a function of depth. These figures depict the situation before cooling has altered the temperature gradient given in equation 23 for the 10 km asteroid, and before outgassing has reduced the pressure of the gases.

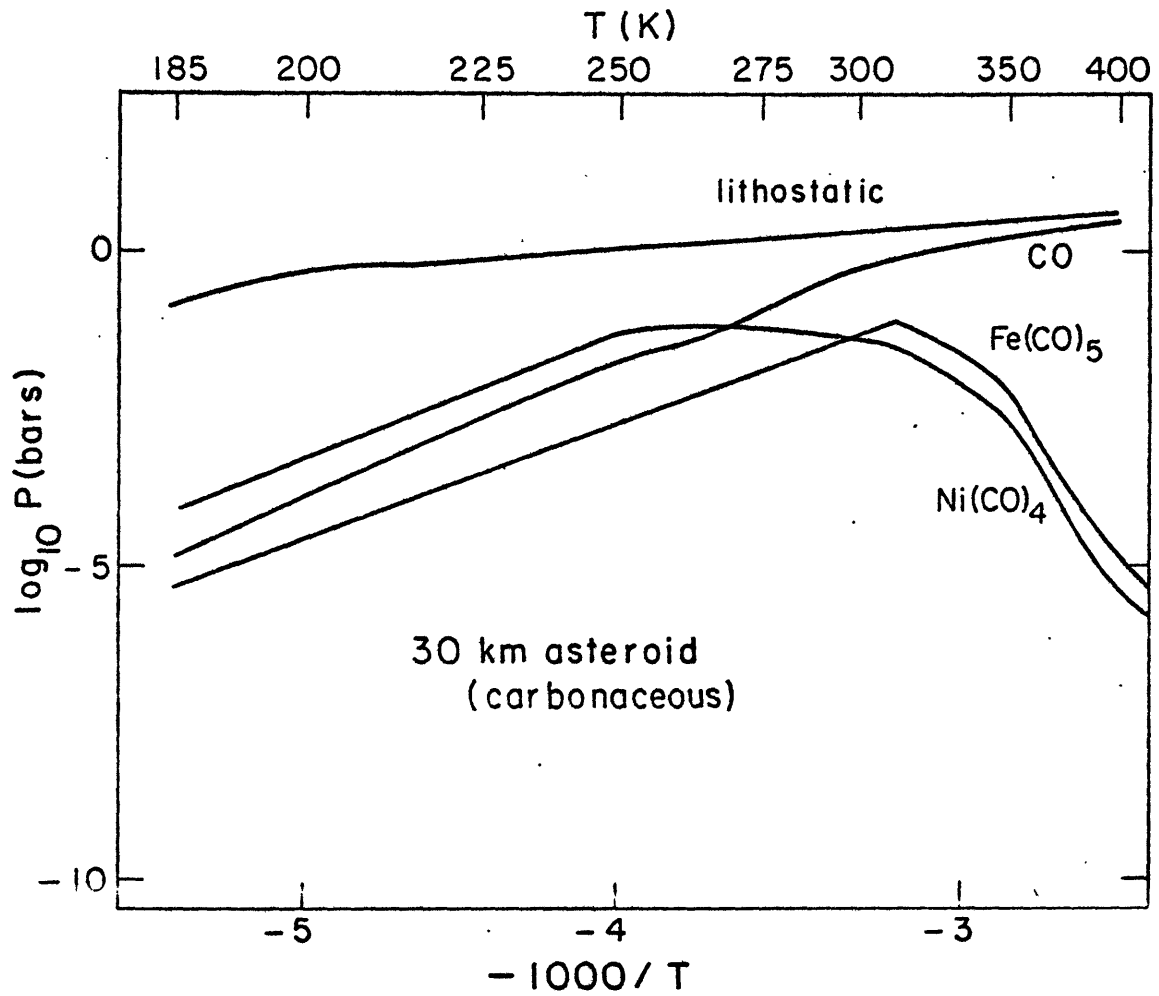


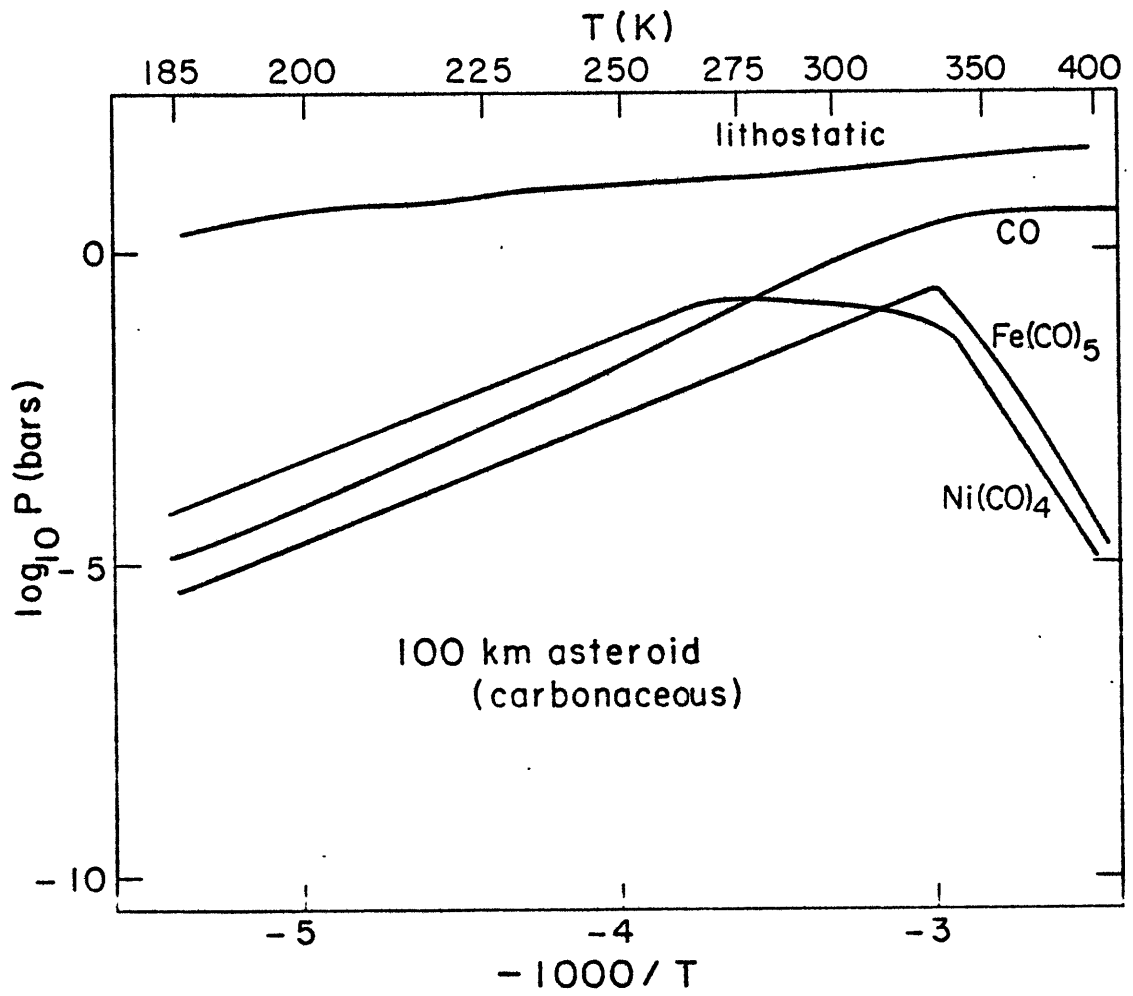












Biographical Note

Mark Lupo was born on March 28, 1957 in Huntington, New York and grew up in Northport. He is a graduate of Northport High School, which he attended from 1972 - 1975. Mark attended MIT from September 1975 to June 1979 as an undergraduate and earned two degrees: Bachelor of Science in Earth and Planetary Science, and Bachelor of Science in Applied Mathematics. Readmitted in 1979 as a graduate student, he has served as a teaching assistant and as a research assistant. His publications include

Lupo, M. J., and Lewis, J. S. (1979). Mass- radius relationships in icy satellites. Icarus 40, 157-170.

Lupo, M. J., and Lewis, J. S. (1980). Mass - radius relationships and constraints on the composition of Pluto. Icarus 42, 29-34.

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Lupo, M. J. (1981). Mass - radius relationships in icy satellites after Voyager. (In preparation).