

JUPITER FORMED WITH MORE TAR THAN ICE

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ABSTRACT

Elemental abundances in Jupiter determined from *Galileo* probe measurements are compared to recently revised solar system abundances. When normalized to the abundance of sulfur, the most abundant refractory rock-forming element reliably determined in Jupiter's atmosphere by the *Galileo* probe, abundances of argon, krypton, and xenon are 1 times solar, the observed oxygen is depleted by a factor of 4, and carbon is enriched 1.7 times. The fairly uncertain nitrogen abundance ranges from 1 to 3 times solar. The oxygen abundance in Jupiter derived from the observed atmospheric water abundance is only a lower limit to the total planetary oxygen because oxygen is also bound to rock-forming elements such as magnesium or silicon sequestered deep in the planet. The sulfur abundance constrains the amount of rock-forming elements on Jupiter. Considering the amount of oxygen bound to silicate rock, the total oxygen abundance on Jupiter of 0.47 times solar system indicates an overall oxygen depletion by about a factor of 2. The hydrogen and helium abundances in the Jovian atmosphere are depleted (0.48 and 0.39 times solar system, respectively). These relative depletions may indicate the extent of hydrogen and helium partitioning from the molecular envelope into Jupiter's metallic layer. A formation scenario for Jupiter is proposed to explain the relative oxygen depletion and, at the same time, the relative carbon enrichment. In essence, the model assumes that at the time of Jupiter's formation, abundant carbonaceous matter was present near 5.2 AU rather than abundant water ice, increasing the surface mass density of solids in the solar nebula accretion disk. Carbonaceous matter, which has high sticking probabilities, was the agent that sped up accumulation of solid matter of proto-Jupiter. This led to runaway accretion of the planet. Major consequences of this scenario are that the water ice condensation front (the snow line) typically placed near 5.2 AU in solar nebula models must be replaced by a carbonaceous condensation/evaporation front (the "tar line") and that the snow line is located farther out in the solar nebula.

Subject headings: planets and satellites: formation — planets and satellites: individual (Jupiter) — solar system: formation

1. INTRODUCTION

The *Galileo* Probe Mass Spectrometer measured the content of noble gases, hydrogen, carbon (as CH₄), nitrogen (as NH₃), oxygen (as H₂O), sulfur (as H₂S), and other minor constituents in Jupiter's atmosphere down to a pressure of ~20 bars (Niemann et al. 1998; Mahaffy et al. 2000; Atreya et al. 1999, 2003). The abundances presented as mixing ratios relative to molecular hydrogen (H₂) show enrichments of C, N, S, Ar, Kr, and Xe relative to solar abundances and depletions of He, Ne, and O.

Here I reexamine the abundance data for two reasons. First, presentation of the abundance data as enrichments or depletions of heavier elements relative to H₂ and solar abundances implicitly assumes that hydrogen is present at solar system abundances in Jupiter's molecular envelope. However, if hydrogen was depleted instead, the implied enrichments and depletions of heavy elements relative to solar are an artifact due to the normalization. With a different element used for normalization, the interpretations of the observed abundances may change. Second, solar elemental abundances have been revised, with substantial changes for C, N, O, and the noble gases, and two abundances scales—one for the solar photosphere and one for the solar system—have been introduced (Lodders 2003). These changes also affect conclusions about the origin of volatiles on Jupiter. The next section (§ 2) compares abundances in Jupiter with solar system abundances. It is followed by a discussion (§ 3) of the origin of volatile elements on Jupiter. Conclusions are given in § 4.

2. JOVIAN ELEMENTAL ABUNDANCES COMPARED TO SOLAR SYSTEM ABUNDANCES

This section compares Jupiter's abundances to solar system elemental abundances, first normalized to hydrogen, and second, normalized to sulfur.

2.1. Jovian Abundances Normalized to Solar System Abundances and Hydrogen

The abundance ratios of volatile compounds to H₂ determined in Jupiter's atmosphere are listed in Table 1, together with the references for and some other information about the individual abundances. The mixing ratios are determined in Jupiter's troposphere down to about the 20 bar pressure level. Methane, NH₃, and H₂O are the major C-, N-, and O-bearing gases in Jupiter's troposphere, and other gases (e.g., CO, N₂) do not significantly contribute to the C, N, and O inventory (e.g., Fegley & Lodders 1994). It is generally assumed that the CH₄, NH₃, and H₂O abundances reflect the total elemental abundances of C, N, and O, respectively, in the observed atmosphere (Niemann et al 1998; Mahaffy et al. 2000; Atreya et al. 1999, 2003), and the same approach is taken here.

The solar system elemental abundances in Table 1, also relative to H₂, are from my recent paper (Lodders 2003). The solar system abundances are different from present-day solar photospheric abundances because elements heavier than He are settling out of the photosphere over time. This leads to a fractionation of heavy elements relative to hydrogen in the

TABLE 1
JUPITER AND SOLAR SYSTEM ABUNDANCES RELATIVE TO H₂

Gas M	Jupiter (M/H ₂)	Reference	Element M	Solar System (M/H ₂)	Jupiter/Solar System
H ₂	≡1.0		H ₂	≡1.0	≡1.0
He.....	0.1574 ± 0.0036	1	He	0.1928	0.816 ± 0.019
Ne.....	(2.48 ± 0.3) × 10 ^{-5a}	2	Ne	1.77 × 10 ⁻⁴	0.14 ± 0.02
Ar.....	(1.82 ± 0.36) × 10 ^{-5b}	2	Ar	8.43 × 10 ⁻⁶	2.16 ± 0.43
Kr.....	(9.3 ± 1.7) × 10 ⁻⁹	2	Kr	4.54 × 10 ⁻⁹	2.05 ± 0.37
Xe.....	(8.9 ± 1.7) × 10 ⁻¹⁰	2	Xe	4.44 × 10 ⁻¹⁰	2.00 ± 0.38
CH ₄	(2.1 ± 0.4) × 10 ⁻³	1	C	5.82 × 10 ⁻⁴	3.6 ± 0.7
NH ₃	(7.1 ± 3.2) × 10 ^{-4c}	3	N	1.60 × 10 ⁻⁴	4.4 ± 2.0
PH ₃	(1.3 ± 0.5) × 10 ⁻⁶	4, 5	P	6.89 × 10 ⁻⁷	1.9 ± 0.7
H ₂ O.....	6.0 ^{+3.9} _{-2.8} × 10 ^{-4d}	3	O	1.16 × 10 ⁻³	0.52 ^{+0.34} _{-0.24}
H ₂ S.....	(7.7 ± 0.5) × 10 ^{-5e}	1	S	3.66 × 10 ⁻⁵	2.10 ± 0.14

^a ²⁰Ne + ²²Ne.

^b ³⁶Ar + ³⁸Ar.

^c At 9–12 bars.

^d At 19 bars.

^e At ≥16 bars.

REFERENCES.—(1) Niemann et al. 1998; (2) Mahaffy et al. 2000; (3) Atreya et al. 2003; (4) Lellouch et al. 1989; (5) Irwin et al. 2004.

solar photosphere when compared to the protosolar abundances. Two solar abundance scales must be distinguished, one for the solar system (=protosolar abundances) and another for the present-day photosphere. Here, Jovian abundances are compared to the solar system (protosolar) abundances.

The last column in Table 1 gives the Jupiter/solar system abundance ratios normalized to molecular hydrogen. These ratios illustrate the enrichments of carbon, sulfur, and the heavy noble gases (Ar, Kr, Xe) in Jupiter relative to solar system values. Relative to molecular hydrogen, heavy noble gases and sulfur are uniformly enriched (~2 times solar system). Within uncertainties, the Jovian P/H₂ ratio from phosphine (PH₃) is also twice the solar system P abundance. Carbon and nitrogen are the most enriched elements with nominal abundance factors of 3.6 and 4.4, respectively (Table 1). The error bars indicate possible carbon enrichments ranging from 2.9 to 4.3, and the larger value coincides with the nominal N enrichment factor. The nitrogen abundance (from NH₃) is the most uncertain abundance and varies from 2.4 to 6.4 times solar system N/H₂. The downward revisions in solar photospheric (and hence solar system) abundances are mainly responsible for the higher C and N enrichment factors than those obtained previously. On the other hand, He, Ne, and oxygen are depleted relative to H₂ and solar system abundances. The decrease in the revised solar system oxygen abundance leads to an increase in the abundance factor to 0.52 from the previous value of 0.35. This factor is still below unity and illustrates the well-known problem that oxygen (in the form of water) is apparently depleted on Jupiter.

Previously, the inferred abundance factors were different because solar abundances from Anders & Grevesse (1989) were used (see, e.g., Owen et al. 1999; Mahaffy et al. 2000; Atreya et al. 2003). For comparison, the abundance factors calculated for the same Jupiter data in Table 1 using solar abundances from Anders & Grevesse (1989) are 2.5 (Ar), 2.9¹ (Kr), 2.6 (Xe), 2.5 (S), 2.9 (C), 3.2 (N), and 0.35 (O).

¹ The enhancement factor of Kr is reported as 2.7 by Mahaffy et al. (2000) but an incorrect Kr/H₂ of 3.4 × 10⁻⁹ rather than the Anders & Grevesse (1989) value (3.2 × 10⁻⁹) was applied. The factor of 2.7 for Kr also appears in Atreya et al. (2003).

Using the revised solar system abundances, the Jovian Ar, Kr, Xe, and sulfur abundances show a remarkably uniform enrichment factor of 2 (Table 1). This strengthens previous conclusions about similar Ar, Kr, Xe, and S enrichments on Jupiter (e.g., Owen et al. 1999; Mahaffy et al. 2000; Atreya et al. 2003). It suggests that Ar, Kr, Xe, and sulfur did not fractionate relative to each other from their initial solar system values. The enrichment of carbon (and possibly N) is clearly larger than that of S and the heavy noble gases. However, there is no uniform enrichment factor that applies to S, Ar, Kr, Xe, and C, as previously asserted (e.g., Owen et al. 1999).

The apparent enrichments of C, N, S, P, and heavy noble gases could suggest that Jupiter somehow accreted larger volatile inventories than the proto-Sun but avoided accretion of oxygen. Furthermore, this must have occurred with different degrees of fractionations among the elements; e.g., C, N, and O were heavily fractionated from each other relative to solar, while Ar, Kr, Xe, P, and S remained unfractionated in relative solar proportions. These similar enrichments, implied by the normalization to hydrogen, prompted several hypotheses about the origin of volatiles on Jupiter (Owen et al. 1999; Gautier et al. 2001), which are discussed in § 3.

2.2. Jovian Abundances Normalized to Solar System Abundances and Sulfur

All previous workers (e.g., Niemann et al. 1998; Owen et al. 1999; Mahaffy et al. 2000; Atreya et al. 1999, 2003) normalized abundances to H₂ = 1, as was also done for Table 1 above. Here I use an abundance scale in which the amount of sulfur is set to S = 100 by number, which gives conveniently manageable values. The rationale for choosing sulfur is explained in § 2.2.1 below.

Jovian abundances from Table 1 normalized to S = 100 atoms are shown in Table 2, together with solar system abundances and data for CI carbonaceous chondrites, also normalized to S = 100 atoms. The last two columns in Table 2 are abundance ratios of Jupiter/solar system and Jupiter/CI chondrites. The CI chondrites are very depleted in volatiles such as the noble gases and nitrogen by comparison to Jovian and solar system abundances, but the CI chondrite data may provide some useful hints about the origin of the carbon and oxygen abundances in Jupiter.

TABLE 2
JUPITER AND SOLAR SYSTEM ABUNDANCES RELATIVE TO SULFUR = 100 ATOMS

Element	Jupiter	Solar System	CI Chondrites	Jupiter/Solar System	Jupiter/CI Chondrites
H.....	2.60×10^6	5.46×10^6	1236	0.476	2104
He.....	$(2.05 \pm 0.05) \times 10^5$	5.27×10^5	1.36×10^{-4}	0.389 ± 0.010	$(1.51 \pm 0.04) \times 10^9$
Ne.....	32 ± 4	483	5.29×10^{-7}	0.066 ± 0.008	$(6.1 \pm 0.8) \times 10^7$
Ar.....	23.6 ± 4.7	23.0	2.16×10^{-6}	1.03 ± 0.20	$(1.1 \pm 0.2) \times 10^7$
Kr.....	0.0121 ± 0.0022	0.0124	3.69×10^{-8}	0.98 ± 0.18	$(3.3 \pm 0.6) \times 10^5$
Xe.....	0.00116 ± 0.00022	0.00121	7.86×10^{-8}	0.96 ± 0.18	$(1.5 \pm 0.3) \times 10^4$
C.....	2727 ± 520	1591	174	1.71 ± 0.33	16 ± 3
N.....	922 ± 416	438	12.4	2.10 ± 0.95	74 ± 34
P.....	1.69 ± 0.65	1.88	1.88	0.90 ± 0.35	0.90 ± 0.35
O _{gas}	779^{+506a}_{-364}	2454 ^b	984 ^b	$0.33^{+0.21}_{-0.15}$	$0.81^{+0.51}_{-0.37}$
O _{rock}	$\equiv 722^c$	722 ^c	722 ^c	$\equiv 1.0$	$\equiv 1.0$
O _{total}	1501^{+506}_{-364}	3176	1706	$0.47^{+0.16}_{-0.12}$	$0.82^{+0.30}_{-0.21}$
S.....	$\equiv 100$	$\equiv 100$	$\equiv 100$	$\equiv 1.0$	$\equiv 1.0$

^a Observed water abundance taken as representative for oxygen in Jupiter’s gas.

^b Oxygen bound to SiO₂, MgO, CaO, Al₂O₃, and TiO₂ assuming solar system abundance ratios of Si, Mg, Al, Ca, and Ti relative to sulfur.

^c Total oxygen (O in rock + O not in rock).

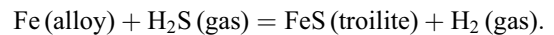
The observed abundances in Jupiter relative to solar system values and normalized to sulfur are shown in Figure 1. The relative depletions of H, He, Ne, and oxygen are prominent, as are the enrichments of carbon and nitrogen. Argon, krypton, xenon, and phosphorous are remarkably uniform at solar abundances, and if any of the three heavy noble gases were used for normalization, sulfur would plot at solar abundances. The question of how these abundances were established in the Jovian atmosphere is discussed in § 3. Before doing so, I discuss the sulfur chemistry in § 2.2.1 and address the oxygen abundance on Jupiter in § 2.2.2.

2.2.1. Why Normalize Abundances to Sulfur?

The rationale for choosing sulfur to normalize the elemental abundances is that sulfur is the most abundant refractory element among those observed in the Jovian atmosphere. The term “refractory” reflects the volatility classification of sulfur during condensation from a solar composition gas. In contrast to any of the more volatile elements considered here (C, N, O, noble gases), sulfur behaves like rock-forming elements such

as Mg, Si, Ca, Al, Na, Fe, and P. These elements completely condense at high temperatures in the solar nebula. However, there is a key difference between sulfur chemistry in Jupiter and in the solar nebula. In Jupiter, sulfur is less refractory than rock-forming elements such as Mg, Si, and Fe because it remains in the atmosphere as H₂S. The same holds for phosphorus, which is mainly found in PH₃ gas in Jupiter’s atmosphere. The difference between sulfur chemistry in the solar nebula and in Jupiter’s atmosphere is responsible for the fact that sulfur accreted to Jupiter ends up as H₂S gas. This provides us with an accessible probe of the amount of rock-forming elements that are deep in the planet, as described below.

In the solar nebula, H₂S gas reacts with previously condensed solid iron (alloy) to form troilite (FeS) and H₂ (gas) at 704 K, described by



This reaction is independent of total pressure assumed for the solar nebula ($P \ll 1$ bar) because there is one molecule of gas on each side of the reaction. Half of all sulfur is condensed in FeS at 664 K, and 99.99% of all sulfur is removed from the gas by 450 K. The ubiquitous presence of troilite in primitive meteorites suggests that planetesimals forming the planets also contained troilite. Therefore Jupiter most likely accreted sulfur in the form of solid troilite when it accreted the other rock-forming elements, and sulfur and the other rock-forming elements are expected to be present in chondritic (=solar) proportions. The rocky planetesimals must have out-gassed or evaporated in the hot proto-Jovian atmosphere during accretion and released sulfur, phosphorus, arsenic, and germanium, which are now observed in the Jovian atmosphere as H₂S, PH₃, AsH₃, and GeH₄. The most refractory rock-forming elements such as Al, Si, Fe, Mg, and Si are sequestered into high-temperature condensate cloud layers deep in the Jovian atmosphere and are not observed. Iron, condensed at high temperatures, is buried in a metallic iron cloud (Lewis 1969), and there is no iron metal present at cooler, shallower altitudes to react with H₂S gas to form FeS. There are some sulfur-bearing condensates at lower temperatures, but for the most part, H₂S remains in the atmosphere.

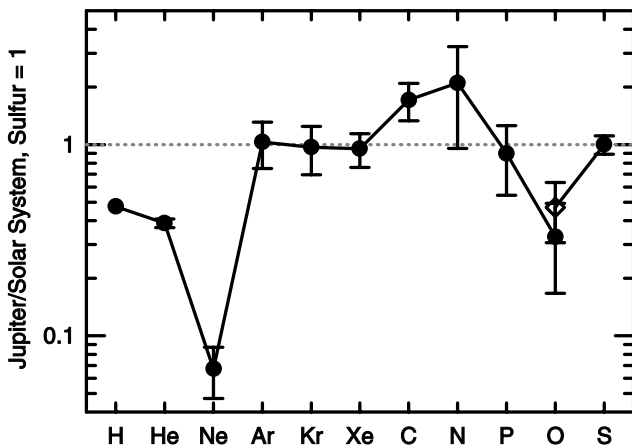


FIG. 1.—Abundances in the Jovian atmosphere relative to solar system and sulfur (Table 2). The error bars include uncertainties in Jovian and solar system abundances. The open symbol for oxygen is for total oxygen in Jupiter including oxygen bound to silicate rock.

The first sulfur-bearing condensate forming in Jupiter's atmosphere is sodium sulfide, Na_2S , which removes a minor fraction of H_2S gas. This is discussed in detail in Lodders (1999). In Jupiter, sodium sulfide condenses around 1250 K because neither Na nor S is condensed into a deep cloud at higher temperatures. The amount of sulfur removed from the atmosphere by Na_2S is limited by the abundance of sodium. If rocky material accreted to Jupiter in protosolar or CI-chondritic meteorite proportions, the maximum amount of sulfur removed from the gas by Na_2S condensation is $\sim 6.5\%$ because the sodium abundance is only $\sim 13\%$ that of sulfur, and two Na atoms are needed to consume one of sulfur.

Hydrogen sulfide is only significantly removed from the atmospheric gas when low-temperature NH_4SH clouds form or by photochemical reactions. These processes occur high in Jupiter's troposphere ($P \leq 2$ bars). Thus, the deeper, hotter atmosphere should contain H_2S , as found by the *Galileo* probe. The H_2S concentration in Jupiter's atmosphere above the 16 bar level of $\text{H}_2\text{S}/\text{H}_2 = (7.7 \pm 0.5) \times 10^{-5}$ reported by Niemann et al. (1998) has an uncertainty of 6.5%, which covers the expected depletion in sulfur if Na_2S removed H_2S from the gas. The H_2S abundance of $\text{H}_2\text{S}/\text{H}_2 = 8.1 \times 10^{-5}$ reported by Folkner et al. (1998) for pressures greater than 15 bars is about 5% higher than the value given by Niemann et al. (1998). Because of the spread and the uncertainties in reported H_2S abundances and the relatively small effect from Na_2S condensation, the observed sulfur abundance is not corrected for Na_2S condensation and the H_2S abundance as reported by Niemann et al. (1998) is used to normalize the Jovian abundances (Table 2).

2.2.2. Oxygen Abundance

The *Galileo* data only measure the amount of oxygen in the form of water in Jupiter's troposphere. This is not the entire oxygen inventory because oxygen is also bound to rock-forming elements that are sequestered deep inside Jupiter. The total oxygen inventory (O_{total}) is the sum of oxygen bound in rock (O_{rock}) and oxygen in water and other O-bearing gases (O_{gas}):

$$O_{\text{total}} = O_{\text{rock}} + O_{\text{gas}}.$$

In Table 2 the oxygen abundances that take this into account are listed. The entry " O_{gas} " is all oxygen that is not bound to SiO_2 , MgO , CaO , Al_2O_3 , and TiO_2 . The next row " O_{rock} " lists the amount of oxygen bound into these oxides. The row " O_{total} " is the overall oxygen abundance. The amount of oxygen tied up in oxides is easily calculated from the known elemental abundances (A_i) for the solar system and for CI chondrites from $O_{\text{rock}} = 2A_{\text{Si}} + A_{\text{Mg}} + A_{\text{Ca}} + 1.5A_{\text{Al}} + 2A_{\text{Ti}} \dots$. The amount of O_{gas} is obtained by subtracting the amount of oxygen in rock from the total oxygen abundance. The CI chondrites, the Sun, and the solar system have the same relative abundances of rocky elements (including sulfur) on the abundance scale chosen here. Thus, once rocky elements are fully condensed, the amount of oxygen tied to the rocky elements is the same for the solar system and CI chondrite composition. However, the total amount of oxygen present in CI chondrites is only about half that in the solar system composition (Table 2). Therefore the fraction of all oxygen that is tied to the rocky elements is $\sim 23\%$ in the solar system composition, whereas 42% of all oxygen in CI chondrites is tied to the rock-forming elements.

Galileo data, Earth-based IR spectroscopy, and chemical models show that water is the predominant oxygen gas in Jupiter's atmosphere; e.g., $\text{H}_2\text{O}/\text{CO} \approx 300,000$ below its condensation level. Thus, for Jupiter O_{gas} is simply the oxygen abundance in water. The amount of Jupiter's oxygen in rock follows by assuming solar rocky element to sulfur ratios. Then the same value for oxygen in rock applies as for the solar system and CI chondrites. The total oxygen on Jupiter is the sum of the atmospheric oxygen (from water) plus oxygen in rock. The sulfur-normalized total oxygen abundance ratio for Jupiter/solar system is 0.47. The oxygen abundance in water on Jupiter relative to the total oxygen in the solar system is $779/3176 = 0.25$. Thus about half of all oxygen in Jupiter is sequestered in silicate rock and about half is in water.

Before moving into § 3 describing how these abundances may have been established, the question of whether the oxygen depletion on Jupiter is real is addressed. Based on models of water ice condensation in the solar nebula (e.g., Lewis 1974; Stevenson & Lunine 1988) and the relative enrichments of carbon and nitrogen, Jovian water abundances of at least solar or higher were expected. Hence the low water abundance detected by *Galileo* was a surprise. Even considering the amount of oxygen in rock does not increase the oxygen abundance to solar system levels.

Explanations of why a larger water abundance was not observed involve the *Galileo* probe entering a "hot spot" and sampling dry Jovian atmosphere, where meteorological phenomena cause local water depletion. These explanations assert that the measured water depletion is not representative for the whole atmosphere (see, e.g., the discussion in Atreya et al. 1999). On the other hand, the low water abundance from *Galileo* is not a complete surprise since prior observations also found low water abundances on Jupiter. West et al. (1986) summarize Jovian water abundance determinations, all of which indicate subsolar water abundances. For example, Bjoraker et al. (1986) found $\text{H}_2\text{O}/\text{H}_2 \leq 4 \times 10^{-6}$ between 2 and 4 bars and $\text{H}_2\text{O}/\text{H}_2 = 3 \times 10^{-5}$ around 6 bars. Lellouch et al. (1989) reported similar results. Bjoraker et al. (1986) derived a *global* water abundance of 50 times less than solar. They conclude that there are "no preferred regions on Jupiter with vastly [within a factor of 3] different H_2O abundances." The only study that derived higher water abundances is Carlson et al. (1992, 1993), who give a preferred mixing ratio of $\text{H}_2\text{O}/\text{H}_2 = 2.76 \times 10^{-3}$ in the well-mixed deep atmosphere around the 5 bar level. However, Roos-Serote et al. (1999) find that subsolar water abundances determined by the *Galileo* entry probe are consistent with *Galileo* NIMS and *ISO* SWS data.

Theoretical modeling also showed that global water and oxygen depletions were possible on Jupiter. Fegley & Prinn (1988) used the observed abundance of CO and the upper limit on the abundance of silane (SiH_4) to constrain the water (O_{gas}) and total oxygen (O_{total}) abundances, respectively, on Jupiter. They found that water depletions of 2.5–6 times and total oxygen depletions of 2–3 times the solar water and oxygen abundances were possible. These values correspond to 17%–40% of the solar O_{gas} and 33%–50% of the solar O_{total} values.

Thus, both observations and theory indicate possible depletions of water and total oxygen on Jupiter. Theoretical models of Jupiter's formation suggested at least solar abundances or enrichments in oxygen (see § 3), but these were model expectations after all. Maybe it is time to accept the

subsolar oxygen abundance at face value and to revise current models.

3. ORIGIN

The abundances discussed in § 2 require that any model of the formation of Jupiter must account for the following observations: (1) solar abundances of Ar, Kr, Xe, P, and S; (2) relative depletions of H, He, Ne, and O; and (3) relative enrichments of C and (possibly) N. In the following, I discuss a formation scenario that may explain these abundance trends.

The formation of Jupiter from a solar nebula disk occurred in at least three stages (e.g., Lissauer 1987; Pollack et al. 1996; Hueso & Guillot 2003). First, a solid rock/ice core (up to $10 M_{\oplus}$) accumulates by fast runaway growth. This requires a surface mass density of solids in the disk 5–10 times higher than can be provided by solids condensing from a solar system composition gas (Lissauer 1987). The next step is further accretion of planetesimals and gas and buildup of a primary atmosphere by degassing. At this stage, incoming planetesimals are likely to be completely vaporized in the proto-atmosphere. This is the stage where I assume that all sulfur is released from the planetesimals into the gas, where it will remain as H_2S in the atmosphere (see § 2.2). The last major step is accretion and capture of nebular gas from Jupiter's feeding zone during hydrodynamic collapse. This step accounts for the accretion of most of Jupiter's mass, which is more than 80% hydrogen and helium.

3.1. *Rock, Ice, and Carbon*

Formation of a protocore and runaway growth requires that the surface density of the solar nebula disk in the giant planet formation region be high enough for accumulating a massive protocore for subsequent gas capture. It seems necessary that heavy elements in excess of solar abundance were incorporated early into the giant planets (e.g., Hueso & Guillot 2003). An increase in the mass density of solids at 5.2 AU in the solar nebula is possible because essentially all nebula models assume water ice condensation (the snow line) near Jupiter's orbit. This assumption is based on the observation of water ice on the Galilean satellites (Lewis 1974). However, note the circular reasoning when some nebula models place the snow line where water ice is required to enable the fast growth of Jupiter.

The amount of rocky condensate from the solar system composition is 0.49% by mass and of water ice is 0.57% by mass (Lodders 2003). For comparison, the solar abundances of Anders & Grevesse (1989) give 0.44% rock and 0.92% water ice. If water condenses in the Jupiter formation region, the mass density of solids doubles because water ice is added to rock. Note that the previous solar abundances would have tripled the amount of solids, which is still below the required 5–10 times higher density required by Lissauer's (1987) model.

Stevenson & Lunine (1988) and Cyr et al. (1998) have proposed that the amount of solids near the Jupiter formation region may have increased by diffusive redistribution of water gas from the inner solar nebula and condensation of water ice. In their models, the cold-trapped water around 5.2 AU and beyond would increase the mass density required for rapid core growth and facilitate the accumulation and growth of rocky grains. However, the depletion of oxygen in Jupiter argues against the presence of large amounts of water ice in Jupiter's formation region. If there was a lot of water ice but

Jupiter shows subsolar oxygen abundances, where did that water go?

On the other hand, there are large enrichments of carbon in Jupiter's atmosphere and in the other outer planets with increasing heliocentric distance. The CH_4/H_2 ratios are $(2.1 \pm 0.4) \times 10^{-3}$ (Jupiter), $(4.5 \pm 2.4) \times 10^{-3}$ (Saturn), 0.016 ± 0.007 (Uranus), and 0.022 ± 0.006 (Neptune) (Niemann et al. 1998; Courtin et al. 1984; Baines et al. 1995). This indicates that organic carbonaceous matter was abundant in the outer regions of the solar nebula (e.g., Pollack et al. 1986). On Jupiter the C/ H_2 ratio is also larger than the S/ H_2 ratio and the C/S ratio is above the solar ratio (Table 2). This shows that carbon is more enriched than the rock-forming elements and that a source of carbonaceous matter is required.

If so, the question is whether carbonaceous matter, and not water ice, increased the mass density required for rapid core growth and facilitated sticking of rocky particles to form the planetesimals that assembled to proto-Jupiter. This does not contradict the observed water ice on the Galilean satellites that was taken as evidence that water ice was present at 5.2 AU (Lewis 1974). Stevenson & Lunine (1988) note that the Galilean satellites formed later than proto-Jupiter, and protoplanetary accretion disk models predict that the location of the snow line changes during disk cooling (e.g., Ruden & Lin 1986; Stepinski 1998). If the water condensation front was located farther out in the nebula during proto-Jupiter's growth, no water ice could accrete. During cooling of the solar nebula, the snow line moves inward and provides a possibility for late accretion of water to the Galilean satellites.

Carbonaceous material in the formation region of Jupiter (and the other outer planets) could originate from non-vaporized presolar cloud material or from carbonaceous matter formed in the solar nebula under nonequilibrium conditions, e.g., by Fischer-Tropsch, ion-molecule, and photochemical reactions (Prinn & Fegley 1989; Aikawa et al. 1999). Up to 50% of the total carbon in the interstellar medium is estimated to be in organic solids (e.g., Ehrenfreund et al. 1991). The chemical composition of a large fraction of organics in cometary and meteoritic material is consistent with an origin in interstellar space (e.g., Fegley 1997; Sephton & Gilmour 2000). Evaporation experiments show that temperatures above 350 or 450 K are required to completely vaporize two types of interstellar organic analogs under high vacuum (Nakano et al. 2003). Since we do not know the exact kind of organic matter that may have been present in the protosolar molecular cloud, the lower temperature of 350 K for evaporation of interstellar organic analogs is adopted as the upper limit for the temperature during the time when proto-Jupiter accreted. Thus, if temperatures were below 350 K, solid preexisting refractory organic matter may remain.

On the other hand, formation of carbonaceous matter may occur in the solar nebula when the CO to methane (and other hydrocarbons) conversion is kinetically inhibited (Lewis & Prinn 1980; Fegley 1988; Fegley & Prinn 1989; see also discussion in Lodders 2003). At a total pressure of 10^{-6} bars, taken as characteristic for the nebular pressure in the Jupiter region, formation of graphite starts as high as 530 K if hydrocarbon formation is completely inhibited, and below 530 K carbonaceous dust can appear as a nonequilibrium condensation product from the nebula gas. Both possible sources of solid carbonaceous matter require relatively low temperatures: survival of interstellar organics requires $T \leq 350$ K, and production of organics from nebular gas by nonequilibrium

processes requires $T \leq 530$ K. Hence the upper limit of the temperature for the occurrence of refractory organics from either source must be ≤ 350 K.

The temperature at 5.2 AU must also be above the water ice condensation temperature to prevent accretion of water ice to proto-Jupiter. The water ice equilibrium condensation temperature at 10^{-6} bars is 160 K. If chemical equilibrium is attained at low temperatures, CO is converted to CH₄ and H₂O and essentially all oxygen in the gas is present as H₂O. Then the water partial pressure and the water ice condensation temperature is maximized if all CO is converted to CH₄ (see Lodders 2003 for details). If hydrocarbon and graphite formation is kinetically suppressed, the water condensation temperature drops below the equilibrium value because the reaction of $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ lowers the water partial pressure. A conservative approach is to use 160 K for the highest temperature at which water ice condensation proceeds, which gives the lower temperature limit near 5.2 AU. Overall, the temperature limits implied by the stability of water ice and organic solids then constrains the temperature range to $160 \text{ K} < T \leq 350 \text{ K}$ in the 5.2 AU region of the solar nebula at the time when proto-Jupiter formed.

There is observational support for the presence of carbonaceous matter in the solar nebula despite the fact that this material is not stable under thermodynamic equilibrium conditions in a solar system composition gas. In carbonaceous chondrites of type CI, carbonaceous matter coexists with fairly oxidized material and these meteorites contain about 10% of the solar system carbon abundance and about 54% of solar system oxygen abundance (see Table 2). Of this oxygen, $\sim 23\%$ is tied to rock and the rest ($\sim 31\%$) is mainly bound to magnetite and hydrous silicates. Aqueous alteration products in CI chondrites indicate that water was present on the CI chondrite parent body, but any water ice or liquid water is now lost. Still, carbonaceous compounds are present in CI chondrites, as well as in other types of chondrites, which is direct evidence that carbonaceous matter is more refractory than water ice.²

Further support for the presence of carbonaceous material in the outer solar nebula comes from observations of organic compounds in comets (e.g., Mumma et al. 1993; Irvine et al. 2000) and in interplanetary dust particles (IDPs) assumed to be related to comets (Clemett et al. 1993). The presence of tarry organic matter is inferred on the surfaces of C and D asteroids, on some of the outer planet satellites, in the Uranian ring system, and on Kuiper-Edgeworth belt objects (e.g., Prinn & Fegley 1989; Cruikshank 1997). The carbon/hydrogen ratios in the four giant planets are larger than the solar system ratio as noted above, and the relative increase in C/H with heliocentric distance is in line with the hypothesis of abundant carbonaceous matter in the outer solar system.

The referee wondered if the larger abundance of refractory organics at Jupiter's location suggested here is compatible with the composition of objects (Triton, Pluto, Charon) much farther out in the solar system. Prinn (1993) interprets the rock/(total ice + rock) ratios of Triton, Pluto, and Charon as indicating $\sim 10\%$ conversion of CO to organics in the Pluto/Triton region of the solar nebula. However, this modeling assumes that essentially all carbon is initially present as CO (gas) and that organic carbon only originates from catalytic

conversion. The comparison with Jupiter then implicitly assumes that the source of the organics is similar and the same conversion mechanism applies. If so, production of organics at lower temperatures in the outer reaches of the solar nebula would be less efficient and larger amounts of refractory organics could originate by catalytic conversion near Jupiter.

On the other hand, the model by Prinn (1993) does not consider preserved interstellar organics as a source for organics (as mentioned above) in the outer nebula, or other sources of organics such as ion-molecule chemistry (Aikawa et al. 1999). Preserved interstellar organics and ion-molecule chemistry were plausibly much more important in the Triton/Pluto region than at Jupiter's location. Furthermore, the ice/rock ratio does not pose strong constraints for the carbon budget in Pluto and Charon. This is because the densities of Pluto and Charon are still relatively uncertain ($\rho_{\text{Pluto}} = 1.8\text{--}2.1 \text{ g cm}^{-3}$ and $\rho_{\text{Charon}} = 1.6\text{--}1.8 \text{ g cm}^{-3}$; Olkin et al. 2003), and the ice/organic/rock ratios also depend on the assumed composition of the "ice" (e.g., water ice \pm CH₄ ice \pm N₂ ice \pm clathrate hydrates $\pm \dots$) and the type of the rock assumed in the modeling (e.g., dry rock or hydrated rock, iron as metal or oxidized), as well as on the densities adopted for the individual components (see McKinnon et al. 1997).

Refractory organic (tarry) materials may have higher sticking probabilities than water and could provide a much better "glue" than water ice for enabling fast accumulation of solids for proto-Jupiter. Experiments by Kouchi et al. (2002) show that organic materials characteristic of molecular clouds have the highest sticking probability around 250 ± 20 K, where the stickiness of the organic materials is increased by their viscoelastic state. Kouchi et al. (2002) relate the temperature of maximum stickiness to the solar nebula temperature structure from the models by Bell et al. (1997) and find that coagulation of grains aided by interstellar organic matter proceeded rapidly within the current location of the asteroid belt at 2.6–3.8 AU. According to Kouchi et al. (2002), this process would not occur at smaller orbital distances (< 2.2 AU) because organics evaporate, nor at larger distances (e.g., Jupiter's orbit) where sticking probabilities are lower and ice is expected (~ 160 K, > 3 AU). These conclusions about radial distribution of organics are based on temperatures tied to a particular nebular structure at a time when the water ice condensation temperature is near Jupiter's orbit. Considering the following, these and other conclusions based on a solar nebula with the snow line at 5.2 AU may need revision.

The arguments above suggest that solid carbonaceous matter is (1) present and (2) abundant in the outer planet region of the solar nebula. Being more refractory than water ice, any effects that previous models ascribe to water ice during the growth of Jupiter may as well be caused by abundant carbonaceous matter. If carbonaceous matter, and not water ice, is responsible for Jupiter's faster growth, the radial position of the snow line near 5.2 AU should be replaced by a "tar line" at the time of Jupiter's main growth period. Consequently, the snow line of less refractory water ice is located farther out within the nebula. The scenario of a relocated snow line is supported considering that Neptune must contain quite large (~ 440 times solar) enrichments of water to explain the observed CO abundance (see Lodders & Fegley 1994 for additional arguments favoring high water enrichments on Neptune).

It is not expected that the organic matter contributes significantly to the abundances of elements other than carbon.

² Consider a snow-covered asphalt street. The snow eventually melts and evaporates but the tar stays.

For example, nitrogen is among the more common elements encountered in organic compounds. The organic matter in carbonaceous chondrites, micrometeorites, and IDPs has C/N ratios of ~ 20 to ~ 50 (see, e.g., Matrajt et al. 2003 and references therein). These C/N ratios are 10–20 times too large to account for the nominal Jovian nitrogen abundance of 2.1 times solar. This suggests that the known organics are not a likely major source of nitrogen on Jupiter. However, the Jovian nitrogen abundance is too uncertain to make any more detailed modeling attempts.

3.2. Incorporation of Noble Gases

The nebular gas that is captured at stage 2, and mainly during stage 3, of Jupiter's formation should contain H_2 , He, Ne, Ar, Kr, and Xe in solar system proportions, if the inert (hence noble) gases are not removed into any solids by adsorption, trapping, or clathrate formation. The latter processes could occur preferentially for Ar, Kr, and Xe, which would fractionate the noble gas abundances from a solar gas. There are at least two cases to consider, capture of (1) unfractionated and (2) fractionated nebular gas.

If the noble gases remain in the nebular gas in solar proportions, the capture of nebular gas leads to uniform relative solar system abundances of H_2 and all noble gases in Jupiter. This is observed for Ar, Kr, and Xe but not H_2 , He, and Ne. If the observed abundances of H and He are taken to reflect the amount of nebular gas that was captured, the observed abundances of the heavy noble gases are too high, but if Ar, Kr, and Xe reflect the amount of captured nebular gas, H, He, and Ne are too low.

If the heavy noble gases (Ar, Kr, Xe) were fractionated in the nebular gas before gas capture took place, they should be depleted on Jupiter upon gas capture, just the opposite of what is observed. In order to explain the overabundances of the heavy noble gases relative to hydrogen, an extra source in the form of planetesimals could be involved. In the next two sections I discuss why scenarios of volatile delivery to Jupiter by planetesimals are unfavorable, and that the apparent excess may reflect separation of hydrogen and helium from Jupiter's molecular envelope into the metallic H-He layer.

3.2.1. Were Heavy Noble Gases Trapped, Clathrated, or Adsorbed by Carriers in Planetesimals?

Solar nebula gas capture alone cannot explain the observed abundances of the heavy noble gases, carbon, and nitrogen relative to hydrogen because such a captured gas has unfractionated solar system abundances. In order to explain the higher Ar/H, Kr/H, Xe/H, C/H, and N/H ratios in Jupiter than in the solar reference composition, icy planetesimals carrying noble gas bearing phases have been proposed to bring the excess volatiles to Jupiter. Two models (see § 3.2.2) propose that volatiles were either trapped in ice (Owen et al. 1999) or sequestered in the form of clathrate hydrates (Gautier et al. 2001). Here a large enrichment of carbonaceous matter instead of water (ice) is proposed, and various forms of carbon (activated charcoal, graphitized carbon blacks) are known to efficiently adsorb heavy noble gases. Therefore carbonaceous matter instead of clathrate hydrates or water ice could also carry the noble gases in planetesimals.

Irrespective of noble gas carrier phase, the incorporation of heavy noble gases into solids must have been 100% efficient to produce heavy noble gas (and sulfur) abundances in

unfractionated solar proportions on Jupiter by planetesimal delivery. However, the noble gases fractionate during adsorption and clathration (e.g., Barrer & Edge 1967; Sill & Wilkening 1978; Lunine & Stevenson 1985). The reason for this is that the heat of clathration and the heat of adsorption onto potential substrates is different for each noble gas, which is described in § 3.2.3.

3.2.2. Models Involving Volatile Trapping and Clathration

Owen et al. (1999) propose that noble gases are scavenged from the solar nebula by amorphous icy planetesimals that subsequently accreted to Jupiter. This scavenging or trapping is expected to fractionate the heavy noble gases (see below). In order to trap the heavy noble gases in relative solar proportions, very low temperatures (~ 30 K) are needed for icy planetesimal formation. Such low temperatures around 5.2 AU are inconsistent with current solar nebula models, where 30 K is reached only at ~ 30 AU. Owen et al. (1999) discuss that if models for the nebular radial temperature gradients are correct, Jupiter may have formed beyond 30 AU and it subsequently migrated inward to 5.2 AU.

Arguments against these scenarios are given by Gautier et al. (2001), who point out that ice condensing at such very low temperatures is likely crystalline instead of amorphous and that volatile trapping would not work. Instead, Gautier et al. (2001) prefer clathrate-hydrate trapping of volatiles in a cooling solar nebula within the feeding zone of Jupiter. Clathrate hydrates of the generalized form $X \cdot nH_2O$ may trap atoms or molecules X of noble gases, methane, CO, N_2 , H_2S , as well as other gases. Here n is the number of water molecules, with a characteristic value of $n = 6$ (n varies slightly from 5.66 to 5.75 depending on the type of gas clathrate hydrate formed, e.g., Davidson et al. 1984, but the exact value does not matter for the discussion here).

One problem with trapping and clathration scenarios is that large amounts of water ice are required. For example, if carbon (either as CO or CH_4) was delivered to Jupiter as a clathrate, the resulting H_2O/CH_4 ratio would be 6 because six water molecules are required for each C atom. It is easily seen from Table 1 or 2 that the amount of water observed on Jupiter is less than the amount of carbon (the observed H_2O/CH_4 ratio is ~ 0.3), which rules out incorporation of carbon as $CH_4 \cdot 6H_2O$ or $CO \cdot 6H_2O$. Similarly, the amount of water required for formation of ammonia hydrate, $NH_3 \cdot H_2O$, is too small given the nominal NH_3 and H_2O abundances in Table 1. The amount of water present is sufficient for formation of heavy noble gas clathrates, but then even less water is left for any C- or N-bearing clathrate or ammonia hydrate. Gautier et al. (2001) calculate an O/H ratio of about 9.4 times solar (this corresponds to ~ 14 times the solar system oxygen abundance in Lodders 2003), reflecting the large amount of water required for all these clathrates and hydrates. However, their calculated value is much larger than the observed water content on Jupiter.

The model by Gautier et al. (2001) also assumes delivery of sulfur as H_2S clathrate. Although they note that solar nebula sulfur (present as H_2S in the gas) is completely removed into troilite (FeS) at higher temperatures, they assume that H_2S gas was still left at the much lower temperatures where H_2S clathrates form. Gautier et al. (2001) use an initial H_2S/H_2 ratio of 0.65 times solar within the feeding zone of Jupiter in order to match the observed H_2S abundance on Jupiter. This is much too high considering that more than 99.99% of total sulfur is condensed into FeS at 400 K and 10^{-7} bars, which

TABLE 3
PARAMETERS FOR NOBLE GAS ICE CLATHRATION AND REQUIRED PARTIAL PRESSURES

Gas M	$-\Delta S_C/R$	$+\Delta H_C/R$ (K)	ΔH_C (kJ mol ⁻¹)	T Fit Range (K)	P_M Required ^a (bars)	P_M Available ^b (bars)
Ar.....	10.03 ± 0.04	-1497 ± 5	-12.446	90–273	1.96	7.06 × 10 ⁻¹²
Kr.....	9.996 ± 0.04	-1999 ± 8	-16.620	164–273	0.082	3.80 × 10 ⁻¹⁵
Xe.....	11.08 ± 0.04	-2917 ± 9	-24.252	211–273	7.84 × 10 ⁻⁴	3.72 × 10 ⁻¹⁶

NOTE.—Data given by Barrer & Edge (1967) are fitted to $\ln P_M = -\Delta S_C/R + \Delta H_C/RT$, where P_M is the partial pressure of gas M and ΔS_C and ΔH_C are the entropy and the enthalpy of the clathration reaction.

^a Equilibrium partial pressure required to stabilize solid noble gas clathrate hydrate at 160 K.

^b Partial pressure of noble gas at a total pressure of 10⁻⁶ bars in a solar system composition gas.

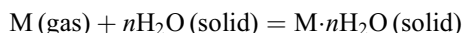
is near the pressure of Jupiter's feeding zone in the model by Gautier et al. (2001).

3.2.3. Noble Gas Fractionation during Clathrate-Hydrate Formation and Adsorption onto Carbon

This section describes noble gas fractionations during clathrate hydrate formation and adsorption onto carbon. The two processes are functions of partial pressure (P_M) for a given gas (M) and temperature. Parameters for noble gas clathration and adsorption are summarized in Tables 3 and 4.

3.2.3.1. Noble Gas Clathration

The equilibrium vapor pressures determined by Barrer & Edge (1967) for the clathration reaction



are fitted to

$$\ln P_M = -\Delta S_C/R + \Delta H_C/RT,$$

where ΔS_C and ΔH_C , given in Table 3, are the reaction entropy and reaction enthalpy for clathrate hydrate formation, P_M is the partial pressure of the noble gas, R is the gas constant, and T is the temperature in kelvins. The lower enthalpy of clathration for Xe indicates that Xe clathrate is more stable than either the Kr or Ar clathrate (assuming the same P_M for each gas). Also listed in Table 3 are the necessary partial pressures required to stabilize the clathrates at 160 K, which is the ice formation temperature in a solar system composition gas at a total pressure of 10⁻⁶ bars. These partial pressures are contrasted with the noble gas partial pressures in the nebular gas, which are many orders of magnitude lower, so noble gas clathrates are unstable at this temperature. The temperatures at which the noble gas clathrates start to form in a solar system composition gas (at $P_{\text{tot}} = 10^{-6}$ bars) are 42 K (Ar), 46 K

(Kr), and 63 K (Xe), assuming that extrapolation of the available experimental data is valid. It is important to realize that even at these temperatures, most of the noble gases are still in the gas. In order to reduce the gas concentration by a factor of 100 for approximately quantitative retention, the temperatures must be 37, 42, and 57 K, respectively.

The nebular temperature in the Jupiter region is typically placed at the water ice condensation temperature (e.g., Lewis 1974) of around 160–180 K, which is much higher than required for clathrate formation. Clathrates could have formed at larger distances and subsequently been delivered to Jupiter. If so, these clathrates had to be preserved until they arrived at and accreted to Jupiter rather than releasing the noble gases by out-gassing when entering warmer regions of the nebula. One could argue that temperatures may have been much lower at 5.2 AU and clathrates could have formed closer to Jupiter. This is at odds with the low Jovian water abundance, which should be solar or above, if nebular temperatures were near or below the water ice condensation temperature. As discussed in § 3.1, nebular temperatures of 160–180 K are already too low because of the observed water depletion in the Jovian atmosphere. At the higher temperatures (~350 K) favored here, preservation of clathrate hydrates during delivery to Jupiter is even less likely.

Quantitative, unfractionated retention of all three noble gases (Ar, Kr, and Xe) from a solar composition gas at nebular total pressures and temperatures generally assumed for the Jupiter region is unlikely to happen by clathrate formation. It also has yet to be shown experimentally that there is no fractionation between Ar, Kr, and Xe during exposure of a solar composition gas to amorphous ice (trapping) or crystalline ice (clathrate formation) at low total pressures. The often-quoted trapping experiments (e.g., Bar-Nun et al. 1985, 1988; Bar-Nun & Kleinfeld 1989) do not include Kr and Xe, but only Ar, Ne, H₂, CO, CO₂, CH₄, and N₂. It is also

TABLE 4
PARAMETERS FOR NOBLE GAS ADSORPTION ON CARBON AND REQUIRED PARTIAL PRESSURES

Gas	$\ln k_H^0$ (ccmSTP atm ⁻¹ cm ⁻²)	$\ln k_H^0$ (mol bar ⁻¹ gC ⁻¹)	E_{ads}/R (K)	E_{ads} (J mol ⁻¹)	T Fit Range (K)	P_M Required ^a (bars)	P_M Available ^b (bars)
Ne.....	-19.88 ± 0.14	+3.94 ± 0.14	539 ± 13	4480 ± 111	60–378	8.42 × 10 ⁻⁶	1.48 × 10 ⁻¹⁰
Ar.....	-19.02 ± 0.02	+4.78 ± 0.02	1176 ± 3	9777 ± 27	140–393	3.91 × 10 ⁻⁹	7.06 × 10 ⁻¹²
Kr.....	-19.05 ± 0.05	+4.77 ± 0.05	1490 ± 16	12388 ± 136	245–393	2.84 × 10 ⁻¹³	3.80 × 10 ⁻¹⁵
Xe.....	-18.77 ± 0.19	+5.05 ± 0.19	1844 ± 60	15331 ± 500	279–393	2.23 × 10 ⁻¹⁵	3.72 × 10 ⁻¹⁶

NOTES.—Data from Sams et al. (1960) and Ash et al. (1973) are fitted to amount sorbed $N_s = P_M k_H = P_M k_H^0 \exp(E_{\text{ads}}/RT)$, where P_M is the partial pressure of gas M. The conversion of k_H^0 in ccmSTP atm⁻¹ cm⁻² to mol bar⁻¹ gC⁻¹ assumes a surface area of 100 m² per gram of carbon.

^a Equilibrium partial pressure required to adsorb amount of noble gas at 160 K to match observed Jovian noble gas/carbon ratio.

^b Partial pressure of noble gas at a total pressure of 10⁻⁶ bars in a solar system composition gas.

inconsistent that the same noble gas trapping experiments by Bar-Nun and colleagues are used to explain the origin of the fractionated noble gas abundances in the terrestrial planet atmospheres by accretion of cold planetesimals (comets; see, e.g., Owen & Bar-Nun 1995), but that essentially the same scenario is used to explain the unfractionated noble gas inventory on Jupiter (e.g., Owen et al. 1999). Similarly, ice clathrates are suggested as a possible source for the fractionated noble gas abundances on the terrestrial planets (e.g., Sill & Wilkening 1978), but quantitative, unfractionated noble gas removal from a solar system composition gas by clathrate formation is required in the model by Gautier et al. (2001).

3.2.3.2. Noble Gas Adsorption onto Carbon

Adsorption of noble gases onto carbon provides another trapping mechanism for noble gases in planetesimals and could be of interest because of Jupiter's large carbon enrichment. In addition to temperature and partial pressure, adsorption depends on the specific surface area of the adsorbent. The amount of noble gas sorbed is conveniently expressed in units of volume (ccmSTP)³ of noble gas adsorbed per gram adsorbent (ccmSTP g⁻¹), which requires knowledge of the specific surface area to convert measurements to units of ccmSTP cm⁻² or mol cm⁻². In Table 4 I combine low-temperature data from Sams et al. (1960) and the high-temperature data from Ash et al. (1973) for Ar, Kr, and Xe adsorption on graphitized carbon (graphon). Ash et al. (1973) do not report data for Ne on graphon, and their carbolac data are used instead. Adsorption at very low partial pressures follows Henry's law, and the literature data for the amount sorbed (N_M) are fitted to the equation

$$N_M = P_M k_H = P_M k_H^0 \exp(E_{\text{ads}}/RT),$$

where k_H is the temperature-dependent Henry's law constant and E_{ads} is the adsorption energy. These two studies use carbon blacks with different surface areas, and all fits here were done after converting the experimental data given (per gram adsorbent) to the respective surface areas. The resulting fit parameters $\ln k_H^0$ (with k_H^0 in ccmSTP atm⁻¹ cm⁻²) and adsorption energies are listed in Table 4.

The adsorption energies show that Xe adsorption is preferred over light noble gas adsorption and that fractionations will occur. In order to apply the fits to Jupiter, a more practical unit of k_H^0 is mol bar⁻¹ gC⁻¹, which makes it easier to compare the amount of noble gas adsorbed at a given temperature and given noble gas/carbon ratio. I assume a specific surface area of 100 m² per gram of carbon, which is a characteristic value for graphitized carbon blacks (e.g., Ash et al. 1973; Sams et al. 1960). Changing the specific surface area by an order of magnitude will not change the conclusions below. The values of $\ln k_H^0$ converted from ccmSTP atm⁻¹ cm⁻² to mol bar⁻¹ gC⁻¹ are also given in Table 4.

If the noble gases were brought to Jupiter adsorbed onto a carbon carrier, the observed noble gas/carbon ratio (in moles per gram C) can be taken as proxy for the amount sorbed N_M . This is a best-case scenario where the maximum amount of carbon available for adsorption is used. The required partial pressures to match noble gas/carbon ratios are easily obtained from the fit parameters and the Henry's law constants in Table 4. For comparison with the data in Table 3, I use the

same temperature of 160 K. The required partial pressures for adsorption on carbon are compared to the available nebular partial pressures in Table 4. Xenon is the best case, but the required Xe partial pressure is still about 6 times higher than the Xe nebular partial pressure. The situation is even worse for Kr, Ar, and Ne, where the required partial pressures are about 75, 550, and 57,000 times larger, respectively, than the available pressures. This problem is not solved by arbitrarily increasing the nebular pressure to a higher value because the noble gases still will be fractionated during adsorption.

As shown by the carbon data in Table 4, adsorption of noble gases onto carbon leads to fractionated abundances of Ar, Kr, and Xe, with the largest effect for Xe. Such fractionations are observed in experimental studies simulating noble gas adsorption during carbon condensation (e.g., Frick et al. 1979; Niemeyer & Marti 1981). Indeed, many studies invoke adsorption processes to explain the incorporation of noble gases into phase "Q" (most likely a carbonaceous phase) in meteorites and the associated fractionated "planetary" noble gas pattern (e.g., Göbel et al. 1978; Swindle 1988). Adsorption onto substrates other than carbon also yields fractionations and shows preferred adsorption of heavy noble gases over light ones (e.g., Fanale & Cannon 1972). In conclusion, delivery to Jupiter of noble gases incorporated (trapped, clathrated, or adsorbed) in any kind of substrate is unfavorable as their sole source because Ar, Kr, and Xe would be fractionated from solar system values.

3.3. Capture of Solar Nebula Gas and Subsequent H and He Segregation into Jupiter's Metallic Layer

While any volatile trapping scenario may have some attractive points, it seems too much a coincidence that sulfur, included in rocky planetesimals and therefore unlikely to be a trapped or clathrated component in an icy planetesimal, has the same relative abundance as the heavy noble gases on Jupiter. There is also another conceptual problem with delivery of noble gases to Jupiter by planetesimals that incorporated noble gases at low temperatures. If these planetesimals formed in a cooler, distant part of the solar nebula, they can only incorporate the noble gases from that distant region. Then Jupiter should contain the noble gases from the planetesimals *plus* the ambient amount of noble gases present in the nebula gas that was captured together with H₂ and He. If indeed H₂ and He indicate the fraction of captured solar gas, about half of the observed Ar, Kr, and Xe stems from gas capture and the other half from cold planetesimals. Considering that the noble gas abundances in the planetesimal source would be fractionated from solar, the question is why the sum of the planetesimal and captured gas sources adds up to solar abundances for Ar, Kr, and Xe without any fractionation.

The most plausible explanation of the observed unfractionated abundances of Ar, Kr, and Xe is their delivery to Jupiter by gravitational capture of nebular gas. By definition, this produces unfractionated heavy noble gas abundances of unity relative to solar system values, as is observed (Table 2). Nebular gas capture would also bring solar abundances of H₂, He, and Ne to Jupiter, but they are depleted in Jupiter's envelope. A large fraction of Jupiter consists of a metallic H₂ and He layer. This layer has to form at some point in time, and the H and He have to come from somewhere. What if Jupiter initially had H and all noble gases in protosolar proportions, and the relative depletions in H₂ and He (and Ne) observed in Jupiter's envelope were caused by their subsequent removal, which produced the metallic layer?

³ Cubic centimeters at standard temperature (0°C) and total pressure (1 atm).

TABLE 5
MASS FRACTIONS

Mass Fraction	Protosolar	Proto-Jupiter	Jupiter Envelope	Jupiter Metallic Layer
X	0.711	0.712	0.739	0.689
Y	0.274	0.274	0.233	0.309
Z	0.015	0.014	0.028	0.002

NOTES.—Protosolar values are from Lodders (2003). See text for proto-Jupiter values. Jupiter envelope values are from Table 2 and chondritic element/sulfur ratios for heavy elements. See text for Jupiter metallic layer values.

Assume that initially, proto-Jupiter did not yet have a metallic H+He layer and that the proto-Jovian composition was more or less homogeneous. Upon cooling, the H+He layer begins to form. If the layer mainly consists of H, He, and some Ne, the elemental abundance ratios in the envelope relative to hydrogen (e.g., C/H₂, Xe/H₂) must increase, as observed. This scenario is similar to freezing pure water ice out of a salty solution. The water ice is essentially pure because salt does not form a solid solution with ice. The residual solution becomes more saline as a consequence of mass balance. In this analogy, freezing out a H+He layer on Jupiter corresponds to the freezing out of pure water ice, where the assumption made is that the H+He layer cannot accommodate much of the heavier elements, except for neon. This scenario requires that the heavy elements be soluble in molecular H₂+He fluid but not soluble (or much less soluble) in the metallic H+He fluid. This suggests that the molecular-to-metallic transition is a first-order phase transition. However, it is not clear whether such a phase transition exists, and the details of the hydrogen phase diagram are still very much under debate. As noted by Hubbard et al. (2002) in their review, “The treatment of the transition from molecular to metallic hydrogen (pressure ionization of hydrogen) is handled differently by various models and is still not well understood either experimentally or theoretically.”

The following results depend on the assumption that heavy elements are more soluble in the molecular than in the metallic regions of Jupiter (i.e., the molecular H₂+He to metallic H+He transition is of first order). Then the scenario proposed here may be used to derive the mass distribution between Jupiter’s molecular envelope and metallic layer. The composition of Jupiter’s envelope, expressed as mass fractions of hydrogen (X), helium (Y), and heavy elements (Z), is easily derived from the elemental abundances listed in Table 2 and from assuming that the heavy elements are present in chondritic element/sulfur abundance ratios. This way, X , Y , and Z are calculated for Jupiter’s envelope considering *all* abundant elements (e.g., including Mg, Si, Fe, etc.). The mass fractions X , Y , and Z for the envelope are listed in Table 5, together with the respective protosolar mass fractions. Note that the mass fraction of helium from the *Galileo* data (Niemann et al. 1998) is calculated as $Y_{\text{env}} = 0.238$ from $Y_{\text{env}} = M(\text{He})/[M(\text{He}) + M(\text{H})]$, where M is the relative mass of He and H, respectively, and the mass contribution of heavy elements in the denominator is neglected. Taking the latter into account gives a slightly lower value of $Y_{\text{env}} = 0.233$.

In order to model proto-Jupiter, the protosolar abundances are altered so that the relative C/S, N/S, and O/S ratios are the same as in Jupiter’s envelope. This would result from positioning the tar line near Jupiter’s orbit and moving the snow line beyond it to larger radial distance within the early solar nebula. The mass fractions of proto-Jupiter calculated from

the proto-solar values modified for C, N, and O are given in the second column of Table 5. This gives essentially the same mass fractions as for the protosolar values, but note that only the masses of C, N, and O incorporated into Z are different. The next step is to find the amount of H, He, and Ne that must be removed from the proto-Jovian composition to obtain the element-to-hydrogen ratios in the envelope, where the assumption is made that no heavy elements other than neon enter the metallic H+He layer. Knowing the contributions of sulfur and other heavy elements to Z for the proto-Jovian composition and Jupiter’s envelope (third column of Table 5), the composition of Jupiter’s metallic layer can be obtained using the mass-balance relationship for hydrogen (X),

$$X_{\text{proto-Jupiter}} = F_{\text{env}}X_{\text{env}} + F_{\text{met}}X_{\text{met}},$$

and similar equations written for the mass fractions of helium (Y) and heavy elements (Z). In these equations, two other unknowns, F_{env} and F_{met} , are the total mass fractions of Jupiter’s molecular envelope and the metallic layer, defined so that $F_{\text{env}} + F_{\text{met}} = 1$. Solving these equations gives the mass fractions of the metallic layer listed in the fourth column of Table 5. The metallic layer consists of about 69% (by mass) of hydrogen, 31% helium (atomic H:He \approx 9:1), and only a small amount ($Z = 0.2\%$) of heavy elements. In this calculation, Z for the metallic layer equals the mass fraction of neon because other heavy elements are assumed to be absent, which is treating the compositions for the envelope and the metallic layer as possible end-member compositions derived from protosolar abundances. However, the constancy of the heavy noble gas to sulfur ratios in the solar system and envelope compositions indicates that there are no fractionations among the heavy elements. If the metallic layer contains heavier elements than neon, they must be there in relative solar proportions, as seen in the envelope. However, there is no chemical constraint for what the heavy-element contribution to the metallic layer could be.

The simple mass-balance calculation gives the overall mass distribution between the envelope and the metallic layer as $F_{\text{env}} = 45.8\%$ and $F_{\text{met}} = 54.2\%$. No information about a possible core size on Jupiter can easily be obtained this way, but the presence of a solid core may not be required for Jupiter (see Hueso & Guillot 2003). It would be interesting to see if evolutionary and interior models of Jupiter based on the model composition and size of the metallic layer derived here are able to provide consistent results with observational tests (radius, luminosity, age). However, this is beyond the scope of this paper.

4. CONCLUSIONS

Jupiter’s abundances have been compared to recently revised solar system abundances. When abundances are normalized

to sulfur, the most refractory element observed in Jupiter's atmosphere, the relative abundances of Ar, Kr, Xe, and P are solar, C and possibly N are enriched, and H, He, Ne, and O are subsolar. The remarkably uniform solar abundances of Ar, Kr, and Xe are most easily explained by direct gravitational capture of solar nebula gas, but these uniform abundances would not have been preserved if the noble gases were delivered to Jupiter as trapped or adsorbed components in planetesimals.

The oxygen abundance from observed water is only about one-quarter times solar, and accounting for oxygen bound in silicate rock gives the total oxygen abundance about one-half times solar for Jupiter. The absence of abundant water on Jupiter is at odds with accretion models that invoke an increased surface density in the solar nebula disk by water ice

(i.e., placing the snow line) near Jupiter's orbit. If water ice was an abundant constituent, Jupiter should be enriched in oxygen relative to solar. Here it has been proposed to replace the water ice snow line by a tar line as a consequence of the relative enrichment of carbon observed in Jupiter's atmosphere. Taking the absence of abundant water on Jupiter at face value, the snow line in the solar nebula should be positioned at larger radial distances during Jupiter's main growth episode.

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REFERENCES

- Aikawa, Y., Umebayashi, T., Nakano, T., & Miyama, S. M. 1999, *ApJ*, 519, 705
- Anders, E., & Grevesse, N. 1989, *Geochim. Cosmochim. Acta*, 53, 197
- Ash, R., Barrer, R. M., Clint, J. H., Dolphin, R. J., & Murray, C. L. 1973, *Philos. Trans. R. Soc. London A*, 275, 255
- Atreya, S. K., Mahaffy, P. R., Niemann, H. B., Wong, M. H., & Owen, T. C. 2003, *Planet. Space Sci.*, 51, 105
- Atreya, S. K., Wong, M. H., Owen, T. C., Mahaffy, P. R., Niemann, H. B., de Pater, I., Drossart, P., & Encrenaz, T. 1999, *Planet. Space Sci.*, 47, 1243
- Baines, K., Mickelson, M. E., Larson, L. E., & Feguson, D. W. 1995, *Icarus*, 114, 328
- Bar-Nun, A., Herman, G., Laufer, D., & Rappaport, M. L. 1985, *Icarus*, 63, 317
- Bar-Nun, A., & Kleinfeld, I. 1989, *Icarus*, 80, 243
- Bar-Nun, A., Kleinfeld, I., & Kochavi, E. 1988, *Phys. Rev. B*, 38, 7749
- Barrer, R. M., & Edge, A. V. J. 1967, *Proc. R. Soc. London A*, 300, 1
- Bell, K. B., Cassen, P. M., Klahr, H. H., & Henning, T. 1997, *ApJ*, 486, 372
- Bjoraker, G. L., Larson, H. P., & Kunde, V. G. 1986, *ApJ*, 311, 1058
- Carlson, B. E., Lacy, A. A., & Rossow, W. B. 1992, *ApJ*, 388, 648
- . 1993, *J. Geophys. Res.*, 98, 5251
- Clemett, S. J., Maeching, C. R., Zare, R. N., Swan, P. S., & Walker, R. M. 1993, *Science*, 262, 721
- Courtin, R., Gautier, D., Marten, A., Bezaud, B., & Hanel, R. 1984, *ApJ*, 287, 899
- Cruikshank, D. P. 1997, in *ASP Conf. Ser. 122, From Stardust to Planetesimals*, ed. Y. P. Pendleton & A. G. G. M. Tielens (San Francisco: ASP), 135
- Cyr, K. E., Sears, W. D., & Lunine, J. I. 1998, *Icarus*, 135, 537
- Davidson, D. W., Handa, Y. P., Ratcliffe, C. I., Tse, J. S., & Powell, B. M. 1984, *Nature*, 311, 142
- Ehrenfreund, P., Robert, F., d'Hendecourt, L., & Behar, F. 1991, *A&A*, 252, 712
- Fanale, F. P., & Cannon, W. A. 1972, *Geochim. Cosmochim. Acta*, 36, 319
- Fegley, B. 1988, in *Workshop on the Origins of Solar Systems*, ed. J. A. Nuth & P. Sylvester (Tech. Rep. 88-04; Houston: Lunar and Planetary Inst.), 51
- . 1997, in *Analysis of Returned Comet Nucleus Samples*, ed. S. Chang (NASA CP-10152; Washington, DC: NASA), 75
- Fegley, B., & Lodders, K. 1994, *Icarus*, 110, 117
- Fegley, B., & Prinn, R. G. 1988, *ApJ*, 324, 621
- . 1989, in *The Formation and Evolution of Planetary Systems*, ed. H. Weaver & L. Danly (Cambridge: Cambridge Univ. Press), 171
- Folkner, W. M., Woo, R., & Nandi, S. 1998, *J. Geophys. Res.*, 103, 22847
- Frick, U., Mack, R., & Chang, S. 1979, *Lunar Planet. Sci. Conf.*, 10, 1961
- Gautier, D., Hersant, F., Mousis, O., & Lunine, J. I. 2001, *ApJ*, 550, L227 (erratum 559, L183)
- Göbel, R., Ott, U., & Begemann, F. 1978, *J. Geophys. Res.*, 83, 855
- Hubbard, W. B., Burrows, A., & Lunine, J. I. 2002, *ARA&A*, 40, 103
- Hueso, R., & Guillot, T. 2003, *Space Sci. Rev.*, 106, 105
- Irvine, W. M., Schloerb, F. P., Crovisier, J., Fegley, B., & Mumma, M. J. 2000, in *Protostars and Planets IV*, ed. V. Mannings, A. P. Boss, & S. S. Russell (Tucson: Univ. Arizona Press), 1159
- Irwin, P. G. J., Parrish, P., Fouchet, T., Calcutt, S. B., Taylor, F. W., Simon-Miller, A. A., & Nixon, C. A. 2004, *Icarus*, in press
- Kouchi, A., Kudo, T., Nakano, H., Arakawa, M., Watanabe, N., Sirono, S. I., Higa, M., & Maeno, N. 2002, *ApJ*, 566, L121
- Lellouch, E., Drossart, P., & Encrenaz, T. 1989, *Icarus*, 77, 457
- Lewis, J. S. 1969, *Icarus*, 10, 393
- . 1974, *Science*, 186, 440
- Lewis, J. S., & Prinn, R. G. 1980, *ApJ*, 238, 357
- Lissauer, J. J. 1987, *Icarus*, 69, 249
- Lodders, K. 1999, *ApJ*, 519, 793
- . 2003, *ApJ*, 591, 1220
- Lodders, K., & Fegley, B. 1994, *Icarus*, 112, 368
- Lunine, J. I., & Stevenson, D. J. 1985, *ApJS*, 58, 493
- Mahaffy, P. R., Niemann, H. B., Alpert, A., Atreya, S. K., Demick, J., Donahue, T. M., Harpold, D. N., & Owen, T. C. 2000, *J. Geophys. Res.*, 105, 15061
- Matrajt, G., Taylor, S., Flynn, G., Brownlee, D., & Joswiak, D. 2003, *Meteoritics Planet. Sci.*, 38, 1585
- McKinnon, W. B., Simonelli, D. P., & Schubert, G. 1997, in *Pluto and Charon*, ed. S. A. Stern & D. J. Tholen (Tucson: Univ. Arizona Press), 295
- Mumma, M. J., Weissman, P. R., & Stern, S. A. 1993, in *Protostars and Planets III*, ed. E. H. Levy & J. I. Lunine (Tucson: Univ. Arizona Press), 1177
- Nakano, H., Kouchi, A., Tachibana, S., & Tsuchiyama, A. 2003, *ApJ*, 592, 1252
- Niemann, H. B., et al. 1998, *J. Geophys. Res.*, 103, 22831
- Niemeyer, S., & Marti, K. 1981, *Lunar Planet. Sci. Conf.*, 12B, 1177
- Olkin, C. B., Wasserman, L. H., & Franz, O. G. 2003, *Icarus*, 164, 254
- Owen, T., & Bar-Nun, A. 1995, *Icarus*, 116, 215
- Owen, T., Mahaffy, P., Niemann, H. B., Atreya, S., Donahue, T., Bar-Nun, A., & de Pater, I. 1999, *Nature*, 402, 269
- Pollack, J. B., Hubickyj, O., Bodenheimer, P., Lissauer, J. J., Podolak, J. I., & Greenzweig, Y. 1996, *Icarus*, 124, 62
- Pollack, J. B., Podolak, M., Bodenheimer, P., & Christofferson, H. 1986, *Icarus*, 67, 409
- Prinn, R. G. 1993, in *Protostars and Planets III*, ed. E. H. Levy & J. I. Lunine (Tucson: Univ. Arizona Press), 1005
- Prinn, R. G., & Fegley, B. 1989, in *Origin and Evolution of Planetary and Satellite Atmospheres*, ed. S. Atreya, J. Pollack, & M. S. Matthews (Tucson: Univ. Arizona Press), 78
- Roos-Serote, M., Drossart, P., Encrenaz, T., Carlson, R. W., & Leader, F. 1999, *Icarus*, 137, 315
- Ruden, S. P., & Lin, D. N. C. 1986, *ApJ*, 308, 883
- Sams, J. R., Constabaris, G., & Halsey, G. D. 1960, *J. Phys. Chem.*, 64, 1689
- Sephton, M. A., & Gilmour, I. 2000, *ApJ*, 540, 588
- Sill, G. T., & Wilkening, L. L. 1978, *Icarus*, 33, 13
- Stepinski, T. F. 1998, *ApJ*, 507, 361
- Stevenson, D. J., & Lunine, J. I. 1988, *Icarus*, 75, 146
- Swindle, T. D. 1988, in *Meteorites and the Early Solar System*, ed. J. F. Kerridge & M. S. Matthews (Tucson: Univ. Arizona Press), 535
- West, R. A., Strobel, D. F., & Tomasko, M. G. 1986, *Icarus*, 65, 161