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# Determining the origin of the building blocks of the Ice Giants based on analogue measurements from comets

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## ABSTRACT

The abundances of the heavy elements and isotopic ratios in the present atmospheres of the giant planets can be used to trace the composition of volatiles that were present in the icy solid material that contributed to their formation. The first definitive measurements of noble gas abundances and isotope ratios at comet 67P/Churyumov–Gerasimenko (67P/C–G) were recently published by Marty et al. (2017) and Rubin et al. (2018, 2019). The implications of these abundances for the formation conditions of the 67P/C–G building blocks were then evaluated by Mousis et al. (2018a). We add here an analysis of the implications of these results for understanding the formation conditions of the building blocks of the Ice Giants and discuss how future measurements of Ice Giant atmospheric composition can be interpreted. We first evaluate the best approach for comparing comet observations with giant planet composition, and then determine what would be the current composition of the Ice Giant atmospheres based on four potential sources for their building blocks. We provide four scenarios for the origin of the Ice Giants building blocks based on four primary constraints for building block composition: (1) the bulk abundance of carbon relative to nitrogen, (2) noble gas abundances relative to carbon and nitrogen, (3) abundance ratios Kr/Ar and Xe/Ar, and (4) Xe isotopic ratios. *In situ* measurements of these quantities by a Galileo-like entry probe in the atmosphere(s) of Uranus and/or Neptune should place important constraints on the formation conditions of the Ice Giants.

**Key words:** comets: general – planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: individual: Uranus – planets and satellites: individual: Neptune – planet–disc interactions.

## 1 INTRODUCTION AND MOTIVATION

During formation, each of the giant planets accreted a mixture of gas and solid material that contributed to the current composition of their atmospheres. Because of this, the abundances of the heavy elements and isotopic ratios in the present atmospheres of the giant planets can be used to trace the composition of volatiles that were present in the icy solid material that contributed to their formation. In particular, the abundances and isotopic ratios of hydrogen, carbon, nitrogen, and the noble gases are valuable tools for understanding the origin and evolution of heavy elements in the giant planets. However, Jupiter is the only giant planet where the noble gas abundances have been measured (Mahaffy et al. 2000). These observations have been valuable for evaluating how Jupiter formed (Owen et al. 1999; Gautier et al. 2001; Owen & Encrenaz 2006; Mousis et al.

2009, 2012) and are necessary for understanding the formation of Saturn (Mousis et al. 2014a, 2014b), and the Ice Giants, Uranus, and Neptune (Gautier & Hersant 2005; Mousis et al. 2018b). The Ice Giants are of particular interest because they are the least explored class of planet in our Solar system, and many questions remain about they formed.

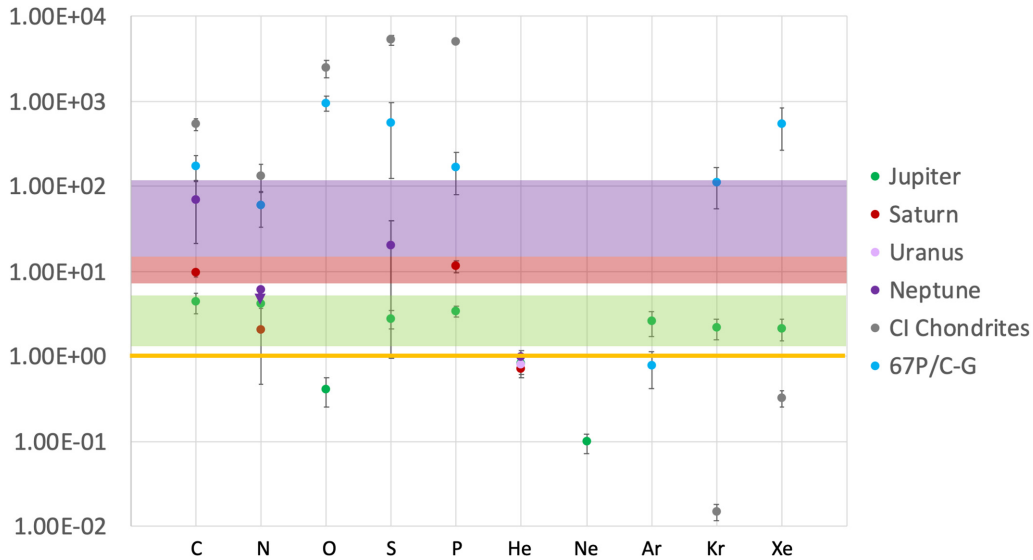
Recent measurements in the coma of comet 67P/Churyumov–Gerasimenko (67P/C–G) provide observations of D/H in water (Altwegg et al. 2015, 2017), noble gas abundances and isotope ratios (Balsiger et al. 2015; Marty et al. 2017; Rubin et al. 2018, 2019) and the abundances of carbon- and nitrogen-bearing molecules relative to water made by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) Double Focusing Mass Spectrometer (Balsiger et al. 2007; Le Roy et al. 2015; Gasc et al. 2017; Rubin et al. 2018, 2019) and the Visual and Infrared Thermal Imaging Spectrometer (Coradini et al. 2007; Bockelee-Morvan et al. 2016). Although not discussed in any of the observation papers listed

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**Table 1.** D/H and the bulk abundance of heavy elements relative to hydrogen for each planet and scaled to the solar abundance of that element relative to solar hydrogen abundance as outlined in Lodders et al. (2009). The CI Chondrite values are also from Lodders et al. (2009), while the 67P/C–G values are from Rubin et al. (2019) and the terrestrial atmosphere values are from de Pater & Lissauer (2010). Uncertainties are based on the propagation of reported uncertainties for each individual measurement.

| Values relative to solar | Jupiter               | Saturn                | Uranus                      | Neptune                     | CI Chondrites                    | 67P/C–G               | Terrestrial Atm.      |
|--------------------------|-----------------------|-----------------------|-----------------------------|-----------------------------|----------------------------------|-----------------------|-----------------------|
| D/H                      | $1.24 \pm 0.45^{(a)}$ | $0.81 \pm 0.39^{(b)}$ | $2.10 \pm 0.53^{(c)}$       | $1.95 \pm 0.50^{(c)}$       | $8.00 \pm 2.00$                  | $25.0 \pm 6.8$        | 7.43                  |
| C/H                      | $4.29 \pm 1.12^{(d)}$ | $9.54 \pm 0.92^{(b)}$ | $\sim 20\text{--}120^{(e)}$ | $\sim 20\text{--}120^{(e)}$ | $533 \pm 91$                     | $171 \pm 58$          | 24.1                  |
| N/H                      | $4.06 \pm 0.02^{(d)}$ | $2.05 \pm 0.66^{(f)}$ | $<6^{(g)}$                  | $<6^{(g)}$                  | $132 \pm 48$                     | $59 \pm 27$           | $3.18 \times 10^5$    |
| O/H                      | $0.40 \pm 0.15^{(d)}$ | —                     | —                           | —                           | $2454 \pm 558$                   | $942 \pm 188$         | $1.24 \times 10^4$    |
| S/H                      | $2.74 \pm 0.66^{(d)}$ | $12.05^{(h)}$         | $10\text{--}30^{(i)}$       | $10\text{--}30^{(i)}$       | $5250 \pm 659$                   | $545 \pm 421$         | $2.05 \times 10^{-3}$ |
| He/H                     | $0.81 \pm 0.04^{(j)}$ | $0.70 \pm 0.13^{(k)}$ | $0.78 \pm 0.17^{(l)}$       | $0.98 \pm 0.17^{(m)}$       | $(1.21 \pm 0.13) \times 10^{-6}$ | —                     | $8.60 \times 10^{-4}$ |
| Ne/H                     | $0.10 \pm 0.03^{(a)}$ | —                     | —                           | —                           | $(3.61 \pm 1.00) \times 10^{-6}$ | $<1.9 \times 10^{-4}$ | 2.36                  |
| Ar/H                     | $2.54 \pm 0.83^{(a)}$ | —                     | —                           | —                           | $(5.24 \pm 1.45) \times 10^{-4}$ | $0.77 \pm 0.36$       | $4.19 \times 10^4$    |
| Kr/H                     | $2.16 \pm 0.59^{(a)}$ | —                     | —                           | —                           | $(1.48 \pm 0.34) \times 10^{-2}$ | $108 \pm 54$          | $7.75 \times 10^3$    |
| Xe/H                     | $2.11 \pm 0.58^{(a)}$ | —                     | —                           | —                           | $0.32 \pm 0.07$                  | $541 \pm 276$         | $7.10 \times 10^3$    |

References: (a) Mahaffy et al. 2000; (b) Lellouch et al. 2001; (c) Feuchgruber et al. 2013; (d) Wong et al. 2004; (e) Mousis et al. 2018b; (f) Fletcher et al. 2011; (g) de Pater et al., 1991, 2018; Irwin et al. 2018, 2019; (h) Briggs & Sackett 1989; (i) de Pater et al., 1991, 2018; Irwin et al. 2018, 2019; (j) von Zahn, Hunten & Lehmacher 1998; (k) Conrath & Gautier 2000; (l) Conrath et al. 1987; (m) Conrath et al. 1991.



**Figure 1.** Illustration of the elemental abundances relative to hydrogen,  $X/H$ , scaled to solar hydrogen  $(X/H)_{\text{Observed}}/(X/H)_{\text{Solar}}$ . The colored bars show the predicted range of enhancement of the heavy elements assuming that the building blocks for the Jupiter (green), the Saturn (red), and the Uranus, and the Neptune (purple) were solar composition. The nitrogen estimate for Uranus and Neptune is an upper limit. All references are given in Table 1.

above, these results combined with our improved understanding of the formation conditions of the 67P/C–G building blocks (BBs; Mousis et al. 2018a) can provide important constraints for the composition of the icy material that contributed to the current composition of the atmospheres of the giant planets. In this study, we apply the results reported above to study the formation of the Ice Giants and the implications of future measurements of the Ice Giant atmospheric composition.

## 2 OBSERVATIONS

Observations of the heavy elements in the giant planets are limited, as shown in Table 1 and Fig. 1 where we list and illustrate

the available heavy element abundance measurements relative to hydrogen scaled to the solar values of each element relative to solar hydrogen  $(X/H)_{\text{Observed}}/(X/H)_{\text{Solar}}$ . In some cases, only an upper limit is available. In all other cases, an uncertainty for a ratio is given. We calculate this uncertainty based on the uncertainty in the observation reported for each constituent propagated to the uncertainty in the ratio,  $R$ , using the relationship

$$(\Delta R/R)^2 = (\Delta X_{\text{observed}}/X_{\text{observed}})^2 + (\Delta X_{\text{Sun}}/X_{\text{Sun}})^2.$$

In studying the origin of the giant planets, the bulk abundances of the heavy elements and noble gases have historically been compared relative to hydrogen because hydrogen was the most abundant element of the protosolar nebula (PSN) and is the most abundant

element in the giant planet atmospheres. Scaling to the solar values is used to compare the abundance of the heavy elements in the giant planet's atmosphere to the abundance of that same element in the PSN, which was the source of the gas that contributed to the formation of the giant planets. If the relative abundance of an element is supersolar, or enhanced relative to the solar value, this element was also present in the solid material that contributed to the formation of the giant planet. If the relative abundance is solar, then the primary source of that element is likely to have been the PSN gas. If the relative abundance is subsolar, then there is either some internal loss for the element or the PSN must have been depleted in this element when the giant planet formed. Some evaluations of these observations assume that the BBs also have a relative solar composition for the heavy elements, and suggest that any enhancement relative to solar would be similar for all heavy elements (e.g. Atreya et al. 2019). However, if the BBs have a non-solar composition the enhancement will differ depending on the elemental composition of the BBs.

We illustrate in Fig. 1 the observations given in Table 1 and show using the shaded regions the predicted enhancement of heavy elements assuming solar composition for the solid BB materials. Solar composition of the BBs means that the relative composition of the heavy elements is the same as solar, such as  $(C/N)_{BB} = (C/N)_{Solar}$ . Carbon is supersolar in all four giant planets with an increasing enhancement with increasing distance from the Sun and forms the basis for the predicted enhancements for the other elements relative to solar values.

Jupiter's observations generally support the prediction of enhancements in the heavy elements, or all elements excluding hydrogen and oxygen, of 2–5 times solar composition suggesting that Jupiter's BBs had nearly solar composition of these elements. Exceptions to this include oxygen, helium, and neon, which are all subsolar. The subsolar values of helium and neon have been attributed to helium precipitation as droplets in the deep atmosphere (Stevenson & Salpeter 1977a, 1977b) with neon sequestration within these droplets (Wilson & Militzer 2010). The oxygen depletion is commonly attributed to the Galileo probe descending into a dry portion of Jupiter's atmosphere (Orton et al. 1998), although it cannot be ruled out that the subsolar oxygen observation could reflect the bulk composition of the planet (Mousis et al. 2012). The helium and neon observations are therefore not easily compared to the abundance of these noble gases in the BBs of Jupiter or the other giant planets.

The limited observations for Saturn appear to predict a slightly higher enrichment than Jupiter based on the carbon and phosphorus abundances. The exception is the nitrogen abundance determined using the measured abundance of  $NH_3$  in the 1–3 bar region (Fletcher et al. 2011), which appears to be significantly depleted relative to carbon based on solar composition, suggesting that the BBs may have had supersolar C/N. However, it must be noted that the loss of  $NH_3$  in the formation of  $NH_4SH$  and aqueous-ammonia clouds below the 1–3 bar level could create the appearance of a subsolar C/N at Saturn (Atreya et al. 2018). The nitrogen abundance at Saturn is one of many important outstanding questions that require an atmospheric probe to solve (Mousis et al. 2014a, 2014b).

The carbon enhancement at the Ice Giants predicts an enhancement in all heavy elements relative to solar values of  $\sim 20$ –100 (Feuchtgruber et al. 2013), and the determination that  $H_2S$  is enhanced by a factor of 10–30 appears to support this (de Pater, Romani & Atreya 1991). However, the confirmed detection of  $H_2S$  in the upper atmospheres of Uranus (Irwin et al. 2018) and Neptune (de Pater et al. 2014; Irwin et al. 2019) combined with

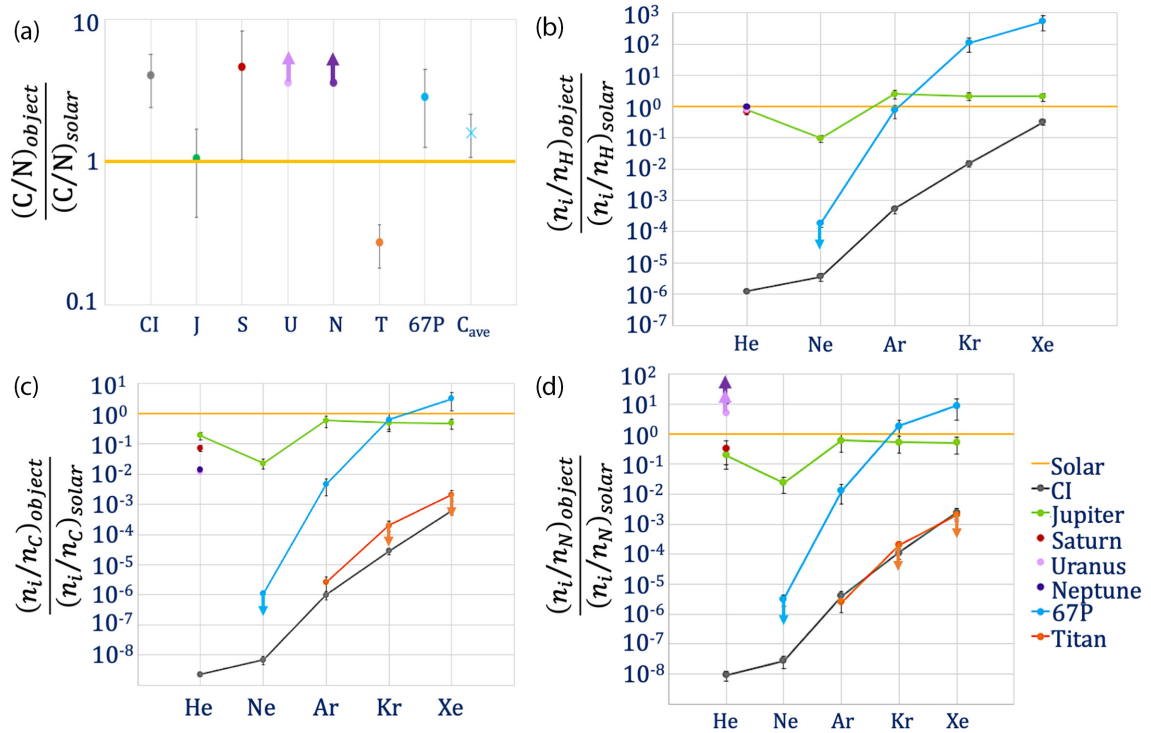
our understanding of cloud formation in the Ice Giant atmospheres requires that the sulfur to nitrogen ratio ( $S/N$ )  $> 1$ . Models of cloud condensation heights assuming a solar composition atmosphere predict that the highest altitude clouds in the Ice Giants atmospheres will be made of methane ice, while water clouds will form at much deeper levels (e.g. Prinn & Lewis 1973; Atreya et al. 2019). These models show that a layer of solid  $NH_4HS$  will form either between the altitudes of the water and methane ice clouds or at the altitude of the water ice clouds (Atreya et al. 2019). Above this altitude either  $NH_3$  ice or  $H_2S$  ice clouds will form depending on whether nitrogen or sulfur is more abundant in the deep atmosphere. This occurs because the formation of the  $NH_4HS$  layer is efficient enough to prevent the less abundant of these two elements (N or S) from reaching altitudes above this layer (Prinn & Lewis 1973). If  $S/N < 1$ ,  $NH_3$  ice clouds will form between the  $CH_4$  and  $NH_4HS$  ice layers. This was predicted to be the case assuming a solar composition for the deep atmosphere because solar  $S/N \sim 0.2$  (Lodders, Palme & Gail 2009). The confirmed lower limit for  $S/N < 1$  at both planets gives an upper limit of N/H of 6 relative to the solar value based on the S/H of 10–30 times solar. This result is not able to distinguish between a subsolar, solar, or supersolar value for N/H. However, the supersolar S/N suggests that the heavy elements in the Ice Giants cannot be enhanced at a similar value relative to solar. That said, it is important to note that both  $NH_3$  and  $H_2S$  could be removed from the atmosphere by an ionic/superionic ocean to differing degrees similar to the depletion of neon in liquid helium in Jupiter's interior (Atreya et al. 2019).

In addition to the giant planet observations, we provide measurements for CI Chondrites and 67P/C–G in Table 1 and Fig. 1. In CI Chondrites and 67P/C–G C/H, N/H, O/H, S/H, and P/H are all supersolar. All noble gases are subsolar relative to hydrogen in CI Chondrites. In 67P/C–G, Ar is solar within the uncertainties of the measurements, and Kr and Xe are supersolar. None of the observed enhancements are constant relative to solar values. C/N, S/N, and the noble gas ratios Kr/Ar and Xe/Ar are clearly supersolar in both 67P/C–G and CI Chondrites, ruling out both of these sources as the primary BBs for Jupiter and demonstrating that it cannot be assumed that all BBs had solar composition. The supersolar S/N is of particular interest for the Ice Giants, providing a source material with  $S/N > 1$  that could explain the Uranus and Neptune observations without needing to invoke any loss process for  $NH_3$  in the interior.

### 3 CONNECTING OBSERVATIONS TO BUILDING BLOCKS

The goal in evaluating the observations outlined above is to connect the giant planet composition to the composition of the PSN and of the solid BBs for each planet. Hydrogen is a useful comparison to the gas in the PSN. However, hydrogen in analogues for the solid material, such as CI Chondrites and comets is derived from complex molecules and water. Therefore, hydrogen from these sources is not derived from  $H_2$  in the PSN and cannot provide a direct comparison to the PSN in these objects. For this reason, we consider alternative elements to determine if we can find a more valid comparison between giant planet composition and chondrites and comets. We are particularly interested in comparing giant planet composition with the new ROSINA noble gas abundance measurements for comet 67P/C–G, which were made in the coma and therefore represent noble gases that were trapped in or condensed with ice.

Carbon and nitrogen were important heavy elements in the PSN because they were found in both gas and solid form and can be useful



**Figure 2.** Bulk abundance comparisons for the giant planets, 67P/C–G, Chondrites, and Titan. The error bars represent the uncertainty of the measurements (typically  $1\sigma$ ), while the arrows represent upper or lower limits for elements not detected. All references are given in Table 1. (a) Observed bulk abundance of carbon relative to nitrogen for CI Chondrites (CI), Jupiter (J), Saturn (S), Uranus (U), Neptune (N), Titan (T), the comet 67P/C–G (67P), and the average value for comets ( $C_{ave}$ ; LeRoy et al. 2015). (b) Abundances of the noble gases relative to hydrogen for the giant planets, CI Chondrites, and the comet 67P/C–G scaled to the solar abundances of noble gases relative to solar hydrogen. (c and d) Noble gas abundances relative to bulk carbon (c) and nitrogen (d) abundances scaled to the solar values for the giant planets compared to observations in 67P/C–G and CI chondrites. The Ice Giants’ helium abundance relative to nitrogen is a lower limit because only an upper limit for the bulk nitrogen is available. The neon abundance in 67P/C–G is an upper limit.

for tracing contributions of ices and organics. Although the exact molecular composition of the PSN as a function of distance from the Sun is not fully understood, estimates suggest that approximately  $\sim 50$  per cent of the carbon and  $\sim 10$  per cent of nitrogen in the PSN was in the form of solid organics, while the remainder was in volatile form in gas or ice phases (e.g. Alexander et al. 2007; Willacy & Woods 2009). Rubin et al. (2019) conducted an analysis of the bulk elemental and molecular abundances of 67P/C–G based on the full mission data set from ROSINA. Their results comparing the abundances of carbon and nitrogen to oxygen in both the volatiles and the refractory materials allow us to evaluate their distribution in ices and refractories for this comet. Depending on the dust to ice ratio of the nucleus, between 5 and 15 per cent of the carbon and 14–32 per cent of the nitrogen was observed in the volatiles, while the remaining amount was trapped in refractory. However, the dust to ice ratio is poorly constrained for this comet, and it is not clear how the relative loss of volatiles compared to refractories has impacted this distribution over the history of 67P/C–G’s orbits. Furthermore, the uncertainties in the refractory observations are as large as the measurements in some cases. The noble gas measurements for 67P/C–G are available for the volatiles but not for refractory materials.

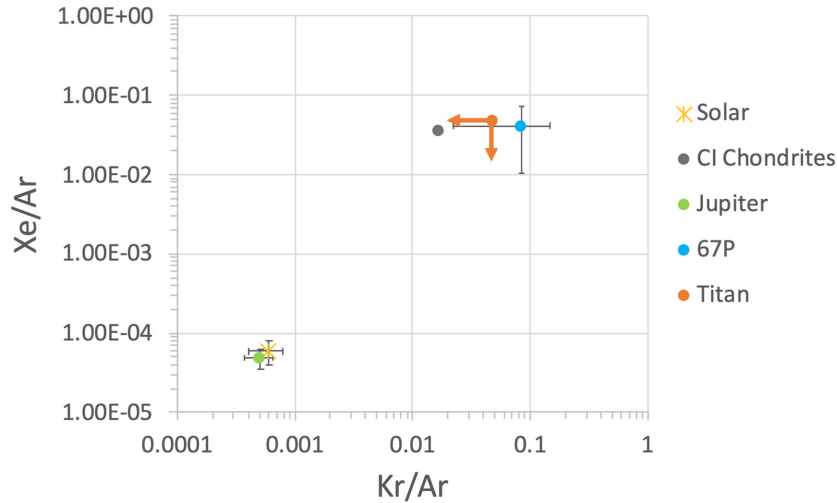
In Fig. 2(a), we show C/N for the volatiles in 67P/C–G, CI chondrites, and the giant planets scaled to the solar C/N in order to compare to the PSN value. C/N from Titan’s atmosphere is also included for comparison. When comparing C/N for the giant planets, Jupiter’s C/N is clearly solar and Titan’s atmosphere is subsolar because methane is a trace constituent of a nitrogen-dominated

atmosphere. All other C/N are supersolar, but the uncertainty of the Saturn measurements does not rule out a solar ratio. Assuming that there is not a significantly larger loss of  $\text{NH}_3$  relative to  $\text{H}_2\text{S}$  in an ionic/superionic ocean, both Ice Giants have supersolar C/N. This means that the abundance of carbon relative to nitrogen in the BBs of Jupiter had the same composition as the PSN, and that Saturn’s either had the same composition as the PSN or were slightly supersolar. For the Ice Giants, it is likely that the BBs for Uranus and Neptune had enhanced C/N similar to the enhancements shown for CI Chondrites and 67P/C–G.

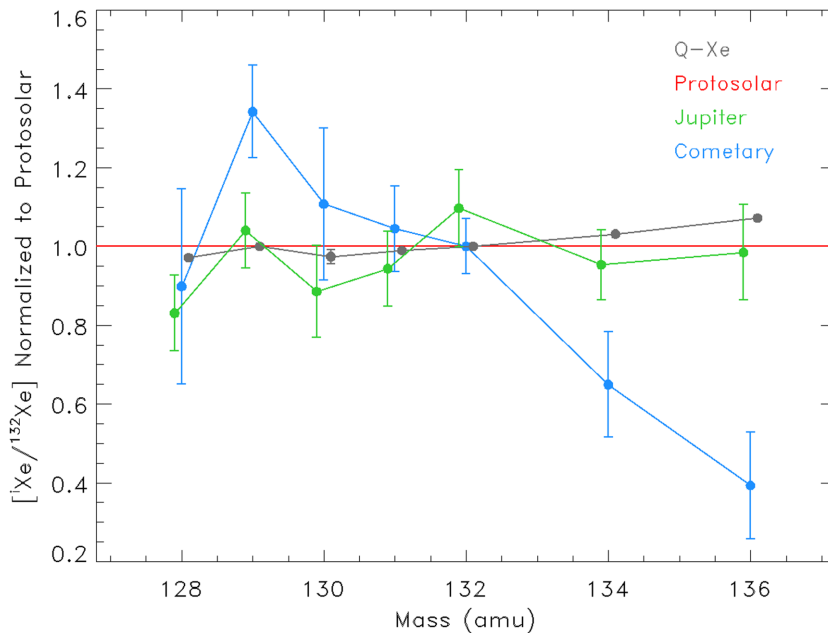
We illustrate the noble gas abundances relative to hydrogen and scaled to solar in Fig. 2(b), where the significant depletion in helium, neon, and argon in CI Chondrites and the upper limit for neon in 67P/C–G are now visible. We also provide comparisons with carbon and nitrogen in Figs 2(c) and (d), where all noble gas abundances are subsolar with the exception of xenon in 67P/C–G, which is supersolar relative to both carbon and nitrogen, and krypton in 67P/C–G that is solar relative to nitrogen within the uncertainty of the measurements. An observation of noble gas abundances relative to either C or N in the Ice Giants would need to determine the degree of depletion of Ar/C and Kr/C relative to the solar value and if Xe/C is supersolar to discriminate between BBs with solar, chondritic, or 67P/C–G-like composition. Either comparison (C or N) has value, but carbon may provide the most feasible comparison since it has already been observed in the Ice Giants.

The slope in each of the lines connecting the heavy noble gas abundances relative to other elements in Fig. 2 is very different from Jupiter when compared to CI chondrites and 67P/C–G. This





**Figure 3.** Krypton relative to argon compared to xenon relative to argon in the Sun and CI chondrites (Lodders et al. 2009), Jupiter’s atmosphere (Mahaffy et al. 2000), Titan (Niemann et al. 2010), and 67P/C–G (Rubin et al. 2018).

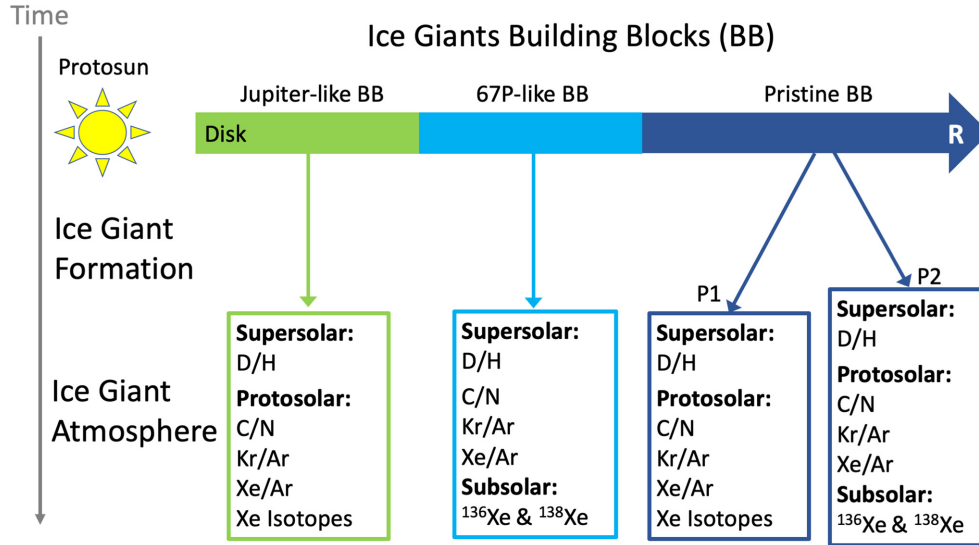


**Figure 4.** The abundance of each xenon isotope relative to  $^{132}\text{Xe}$  and scaled to the solar abundance (Lodders et al. 2009) of each isotope,  $(^{i}\text{Xe}/^{132}\text{Xe})_{\text{Observed}}/(^{i}\text{Xe}/^{132}\text{Xe})_{\text{Solar}}$  for Jupiter (Mahaffy et al. 2000), 67P/C–G (Marty et al. 2017), and the value representing chondritic xenon, designated as Q–Xe, based on the work of Busemann, Baur & Wieler (2000).

provides another useful comparison for evaluating the composition of the BBs of the giant planets. This slope is best illustrated by the ratio of krypton to argon ( $\text{Kr}/\text{Ar}$ ) compared to xenon to argon ( $\text{Xe}/\text{Ar}$ ), as shown in Fig. 3. These ratios in Jupiter’s atmosphere are solar, while CI chondrites and 67P/C–G have strongly supersolar ratios that can be best differentiated using the  $\text{Kr}/\text{Ar}$  ratios. The upper limits for krypton and xenon due to the non-detection of these species in Titan’s atmosphere do not allow a clear determination of whether Titan’s noble gases are solar or supersolar. Because the Titan upper limit overlaps the error bars for 67P/C–G, a 67P-like composition also cannot be ruled out.

The final observation relevant to evaluating the composition of the BBs of the giant planets is the xenon isotopes, which is illustrated

in Fig. 4. The Jupiter observations show that, excluding  $^{128}\text{Xe}$ , Jupiter abundances appear to be solar within the uncertainties of the measurement. The Q–Xe abundances are solar for all but  $^{128}\text{Xe}$  and  $^{130}\text{Xe}$ , which are slightly subsolar, and  $^{136}\text{Xe}$  and  $^{138}\text{Xe}$ , which are supersolar. The cometary observation is most notable, in particular the clear depletion in the two heaviest isotopes of xenon, which is distinctly lower than Jupiter and Q–Xe. Marty et al. (2017) ruled out any mass-dependent fractionation processes to account for this depletion, and compared the cometary values to two or three distinct nucleosynthetic processes observed in pre-solar grains (Gilmour & Turner 2007) to conclude that the xenon observed in 67P/C–G is the result of a mix of nucleosynthetic sources that is different from the processes that produced solar xenon. Following the conclusions



**Figure 5.** Illustration of four scenarios for the origin of the Ice Giants building blocks based on the composition of their current atmospheres. All of the building blocks would have a supersolar D/H from water ice enriched in D/H. Jupiter-like and the first category of pristine building blocks, P1, would have protosolar values for all other constraints and represent the end members of reprocessing in the PSN. The 67P-like building blocks would be similar in all constraints to the observations made for 67P/C–G and represent the partially reprocessed pristine building blocks, P2, which would be protosolar in all constraints except for the xenon isotopes, which would be like those observed in 67P/C–G.

of Marty et al. (2017), there would be at least two distinct reservoirs of Xe that were incorporated in the ices entering the PSN – see discussion in Section 4. The final important measurement to make in an observation of the xenon isotopes in the Ice Giants would be to determine if the ratios of  $^{136}\text{Xe}$  and  $^{138}\text{Xe}$  to  $^{132}\text{Xe}$  are subsolar-like 67P/C–G, solar-like Jupiter, or supersolar-like Q–Xe.

#### 4 THE ICE GIANTS BUILDING BLOCKS

The formation process of each giant planet results in a planet consisting of partial masses of solar composition PSN gas and of icy planetesimal BBs (Owen & Encrenaz 2006). The composition of the current atmosphere therefore can be used to constrain the composition of the icy BBs. This is important because the BBs provide important constraints on the conditions of the PSN during the formation of the giant planets and the locations where each of the giant planets initially formed. We summarize in Fig. 5 four scenarios for connecting the Ice Giants BBs with the current atmospheric composition. The composition of the BBs varies with distance from the young Sun. The D/H in the Ice Giants is predicted, and measured, to be supersolar in all cases resulting from the enhanced D/H in the water ice of the BBs. The other predicted observations are either protosolar, supersolar, or subsolar.

The understanding of the composition of icy BBs in the PSN has evolved over time. Gautier et al. (2001) and Mousis et al. (2009) proposed two potential reservoirs of icy BBs, an inner and an outer reservoir. The inner reservoir is thought to consist of pristine water ice that was volatilized in the PSN and then recondensed as crystalline ice on refractory grains at 150 K (Kouchi et al. 1994). The elemental abundances would have remained protosolar if sufficient water was present to trap all of the material. If insufficient water was available, everything condensed as crystalline ices at much lower temperatures retaining solar composition for everything except oxygen (Mousis et al. 2009, 2012). The second reservoir is pristine ices in the outer nebula that have not been reprocessed. As shown in Figs 2(a), 3, and 4, Jupiter’s C/N, Kr/Ar, Xe/Ar, and xenon isotopes

are all protosolar when compared to the solar values published by Lodders et al. (2009). These represent the inner reservoir described above and are the reprocessed material that originated as the first category of pristine BBs, P1, which are considered to be the same ices that contributed to the volatile composition of the PSN with a bulk elemental composition that is protosolar.

More recently, to explain 67P/C–G’s current composition Mousis et al. (2018b) proposed a third ice reservoir based on the noble gas abundances in the comet’s coma (Rubin et al. 2018) that is intermediate between these two reservoirs. The intermediate reservoir was heated to the point of transition from amorphous to crystalline, inducing the release of the volatiles previously adsorbed in the ice matrix. During the cooling of the PSN, clathration happened in the 25–80 K range, and possibly the condensation of the remaining species. In this scenario, the primordial solids coming from the ISM are represented by the pristine BBs P2, which had a bulk elemental composition that was protosolar prior to being reshaped by the devolatilization of amorphous ice and the subsequent entrapping of the volatiles in clathrate. This process does not significantly affect the isotopic composition so the subsolar  $^{136}\text{Xe}$  and  $^{138}\text{Xe}$  tracer would have originated with the pristine BBs and have been retained in the reprocessed, 67P-like BBs.

#### 4 CONCLUSIONS

The observations by ROSINA at 67P/C–G provide the first definitive measurements of noble gas abundances and noble gas isotope ratios at a comet. Typical studies using noble gas abundances in giant planet atmospheres to understand conditions in the PSN and the composition of their BBs use the abundance of noble gases relative to hydrogen. This approach is not ideal for comparing with comet abundances because the bulk abundance of hydrogen in a coma is derived from water and not from  $\text{H}_2$ . We have provided comparisons of the bulk abundance of the noble gases to carbon and nitrogen as well as C/N and S/N for several targets and find the apparent supersolar S/N in the Ice Giants rules out BBs with a solar

composition for the heavy elements. We provide four scenarios for compositional constraints based on potential measurements of C/N, Kr/Ar, Xe/Ar, and the xenon isotopes in the Ice Giants atmospheres. Measurements of the nitrogen, carbon, and noble gas abundances, as well as the Xenon isotope ratios will allow us to connect the composition of the Ice Giants with the origin of their BBs.

If the relative abundances of C/N, S/N, and the noble gases Kr/Ar and Xe/Ar are protosolar, the BBs for the Ice Giants are likely to have either been pristine solar-composition ices from the pre-stellar cloud or fully reprocessed ices similar to those that formed Jupiter. On the other hand, if these tracers are found to be supersolar, like has been observed for 67P/C–G, the BBs for the Ice Giants could have had a composition similar to the BBs for 67P/C–G. This would mean that the Ice Giants and 67P/C–G formed in similar regions of the PSN. Ground-based observations suggest that S/N and C/N are supersolar in both Ice Giants atmospheres providing potential evidence in support of 67P-like BBs. However, the question of whether these signatures are created by removal of NH<sub>3</sub> into the interior must be resolved before this conclusion can be made.

An important additional constraint is the relative abundances of the xenon isotopes. If <sup>136</sup>Xe and <sup>138</sup>Xe in the atmospheres of the Ice Giants are subsolar as measured at 67P/C–G, the BBs of the Ice Giants were either similar to those of 67P/C–G or the pristine version of the 67P/C–G BBs prior to reprocessing in the PSN.

*In situ* measurements of these quantities by a Galileo-like entry probe in the atmosphere of Uranus or Neptune, such as the one currently under investigation in the context of a NASA–ESA mission towards these planets, should place important constraints on the formation conditions of the Ice Giants.

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