

The deep composition of Uranus and Neptune from in situ exploration and thermochemical modeling

Thibault Cavalié · Olivia Venot · Yamila Miguel ·
Leigh N. Fletcher · Peter Wurz · Olivier Mouis ·
Roda Bounaceur · Vincent Hue · Jérémy Leconte ·
Michel Dobrijevic

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Thibault Cavalié

Laboratoire d'Astrophysique de Bordeaux, Univ. Bordeaux, CNRS
B18N, allée Geoffroy Saint-Hilaire, 33615 Pessac, France
LESIA, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC Univ. Paris
06, Univ. Paris Diderot, Sorbonne Paris Cité
F-92195 Meudon, France
Tel.: +33-540003271
E-mail: thibault.cavalie@u-bordeaux.fr

Olivia Venot

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)
UMR CNRS 7583, Université Paris-Est-Créteil, Université de Paris, Institut Pierre Simon Laplace, Créteil,
France

Yamila Miguel

Leiden Observatory, University of Leiden
Niels Bohrweg 2, 2333CA Leiden, The Netherlands

Leigh Fletcher

School of Physics and Astronomy, University of Leicester
University Road, Leicester, LE1 7RH, UK

Peter Wurz

Universität Bern, Physikalisches Institut, Space Science and Planetology
Bern, Switzerland

Olivier Mouis

Aix Marseille Universit, CNRS, CNES, LAM
Marseille, France

Roda Bounaceur

Laboratoire Réactions et Génie des Procédés, LRGP UMP 7274 CNRS, Université de Lorraine
1 rue Grandville, BP 20401, F-54001 Nancy, France

Vincent Hue

Southwest Research Institute
San Antonio, Texas, USA

Jérémy Leconte

Laboratoire d'astrophysique de Bordeaux, Univ. Bordeaux, CNRS
B18N, allée Geoffroy Saint-Hilaire, 33615 Pessac, France

Michel Dobrijevic

Abstract The distant ice giants of the Solar System, Uranus and Neptune, have only been visited by one space mission, Voyager 2. The current knowledge on their composition remains very limited despite some recent advances. A better characterization of their composition is however essential to constrain their formation and evolution, as a significant fraction of their mass is made of heavy elements, contrary to the gas giants Jupiter and Saturn. An in situ probe like Galileo would provide us with invaluable direct ground-truth composition measurements. However, some of the condensibles will remain out of the grasp of a shallow probe. While additional constraints could be obtained from a complementary orbiter, thermochemistry and diffusion modeling can further help us to increase the science return of an in situ probe.

Keywords Uranus · Neptune · Ice Giants · Thermochemistry · Formation · Evolution

1 Introduction

In the early days of planetary sciences and space exploration, Uranus and Neptune seemed to be very much alike. They share relatively similar masses, radii and color, for example, suggesting these planets could be twins from their formation to their current state. However, even if these distant planets have only been visited once by a spacecraft, data acquired during the Voyager 2 flybys and more recently from ground-based and space-based facilities demonstrate that they are quite different. Their density differ by as much as 30%, Uranus is almost in equilibrium with incoming solar radiation while Neptune emits more than it receives (Pearl et al., 1990; Pearl and Conrath, 1991). Moreover, Uranus has a high obliquity causing an extreme seasonal forcing while Neptune’s obliquity (and thus seasonal cycle) is probably more comparable to Saturn’s one (Moses et al., 2018). Improved gravity field, shape and rotation rate data now seem to point to different internal structures and thermal evolution (Nettelmann et al., 2013, 2016; Helled et al., 2020).

As pointed out in e.g. Guillot (2005), Guillot et al. (2019), Atreya et al. (2020), Mousis et al. (2020), constraining the deep elemental and isotopic composition of the ice giants is one of the keys to better understand their formation and evolution. Unfortunately, and despite some recent progress (Sromovsky and Fry, 2008; Karkoschka and Tomasko, 2011; Irwin et al., 2018, 2019b; Tollefson et al., 2019a), deep abundance measurements in the ice giants remain scarce. The Galileo probe composition measurements in Jupiter’s troposphere (von Zahn et al., 1998; Niemann et al., 1998; Mahaffy et al., 2000; Atreya et al., 1999; Wong et al., 2004) have triggered a tremendous amount of studies on the planet’s formation (e.g. Owen et al., 1999; Gautier et al., 2001; Lodders, 2004; Guillot and Hueso, 2006; Mousis et al., 2012, 2019), now favouring the core accretion scenario for these planets (Pollack et al., 1996; Hubickyj et al., 2005) over the disk instability scenario (Boss, 1997, 2002). The formation and evolution of Uranus and Neptune, on the other hand, remains one of the most outstanding open question. Contemplating these major breakthroughs enabled by the Galileo probe measurements, now complemented by Juno observations (e.g. Bolton et al., 2017; Li et al., 2017, 2020; Kaspi et al., 2018), it seems obvious that the next great leap in understanding the formation and evolution of the Solar System will result from sending orbiters and probes to the ice giants. In addition, the expected advances in this field will undoubtedly have significant repercussions on our understanding of exoplanet formation

and evolution, since a significant fraction of the currently detected exoplanets are in the Neptune size-class¹.

Orbiter and probe missions to the ice giants that are currently under consideration (Mousis et al., 2018; Simon et al., 2018, 2020) will provide us with invaluable measurements in many fields, including bulk composition. In Section 2 of this paper, we will review the current knowledge of ice giants composition, with a comparison to gas giants, and the foreseeable prospects offered by ground-based and space-based observatories in the next decade. We will then show in Section 3 how thermochemical and diffusion modeling can help us further constrain the deep composition of ice giants in the absence of in situ composition measurements, and what the critical parameters of such models are. This will lead us to present in Section 4 the increased science return a descent probe making abundance measurements with a mass spectrometer in Uranus and/or Neptune would have if its results would be coupled to further thermochemical modeling, and to complementary remote sensing observations of the probe entry site for context, as well as the requirements on the instrument that such measurement/model coupling result in. Finally, we will review in Section 5 how deep composition measurements constrain interior and planetary formation models.

2 The composition of ice giants

Thermochemical models attempt to provide fits to the observed composition of a planetary atmosphere, by assuming a temperature profile, a deep mixing profile, and a set of chemical reactions. The bulk composition can only be measured in situ. The abundances measured by probes like Galileo are expected to be representative of the elemental composition at any location on the planet, especially for noble gases. The only known exception for Galileo is H₂O, because the probe descended into a hotspot (Orton et al., 1998). In addition to in situ measurements, remote sensing techniques can provide hints on the deep composition of giant planets, but they generally provide us with lower limits for condensible species and uncertainties are generally too large to be constraining for formation models. In some cases however, remote sensing can probe deeper than a shallow probe and could give better limits on the deep volatile composition. While the ultraviolet and mid-infrared can mostly reveal the stratospheric abundances of hydrocarbons, other wavelength ranges can be used to obtain more useful observations for the deep chemical abundance. For example, methane and hydrogen sulfide (H₂S) can be derived in the troposphere from the near-infrared reflectivity and, potentially, from remote sensing in the (sub)millimeter range, along with CO. Helium can be estimated from the far-infrared collision-induced continuum. These tropospheric species, which are largely pressure broadened, give us the strongest constraints on the deep composition.

In this Section, we will present the current knowledge on the upper tropospheric composition of the ice giants and a comparison with gas giants. We will conclude with the perspectives offered by current and future observatories that could be used prior to an ice giant probe arrival to derive the composition of these planets.

2.1 Observed elemental composition

The elemental abundances reviewed hereafter are summarized in Table 1 and compared to the solar and protosolar values. The present-day solar elemental abundances used in this

¹ <https://exoplanets.nasa.gov/>, <http://exoplanet.eu>

Table 1 Elemental abundances in the protosun and in giant planets.

| Z | Element | Protosun (dex) | Jupiter/ Protosun | Saturn/ Protosun | Uranus/ Protosun | Neptune/ Protosun |
|----|------------------|-------------------|----------------------|---------------------|---------------------|----------------------|
| 2 | He ^a | (10.99±0.01) | 0.80±0.02 | 0.69±0.19 | 0.92±0.20 | 0.90±0.17 |
| 6 | C ^{b,c} | (8.49±0.02) | 3.85±0.95 | 8.58±0.37 | 80±20 | 80±20 |
| 7 | N ^d | (7.88±0.05) | 4.38±1.69 | 3.76±0.44 | see text | see text |
| 8 | O ^e | (8.74±0.03) | >0.45±0.15 | | | |
| 10 | Ne ^f | (7.98±0.10) | 0.13±0.02 | | | |
| 15 | P ^g | (5.46±0.03) | 3.74±0.24 | 12.8±0.9 | | |
| 16 | S ^h | (7.17±0.03) | 3.01±0.72 | ~9 | see text | see text |
| 18 | Ar ⁱ | (6.40±0.13) | 3.23±0.65 | | | |
| 32 | Ge ^j | (3.70±0.07) | 0.058±0.008 | 0.046±0.046 | | |
| 33 | As ^k | (2.37±0.04) | 2.35±0.15 | 7.38±2.49 | | |
| 36 | Kr ^l | (3.30±0.06) | 2.33±0.44 | | | |
| 54 | Xe ^m | (2.29±0.06) | 2.28±0.46 | | | |

^a Grevesse et al. (2010) for the protosun, von Zahn et al. (1998) and Niemann et al. (1998) or Jupiter, Conrath and Gautier (2000) for Saturn, Conrath et al. (1987) for Uranus and Conrath et al. (1993) for Neptune.

^b Amarsi et al. (2019) for the protosun, Wong et al. (2004) for Jupiter, Fletcher et al. (2009a) for Saturn, Stromovsky and Fry (2008) for Uranus and Karkoschka and Tomasko (2011) and Irwin et al. (2019a) for Neptune (at the equator for Uranus and Neptune).

^c As the CH₄ equatorial abundance is non negligible compared to He below its condensation level in both planets, it is accounted for when computing the H₂ mole fraction.

^d Grevesse et al. (2010) for the protosun, Wong et al. (2004) for Jupiter, Fletcher et al. (2011) at the equator for Saturn. The recent Juno microwave measurement of Li et al. (2017) results in N/H=(2.76±0.30) times protosolar. For Uranus and Neptune, N/H is computed from S/H as an upper limit such that S/N>5×solar Irwin et al. (2018, 2019b).

^e Amarsi et al. (2018) for the protosun, lower limit from Wong et al. (2004) for Jupiter.

^f Scott et al. (2015) for the protosun, Mahaffy et al. (2000) for Jupiter.

^g Scott et al. (2015) for the protosun, Fletcher et al. (2009a) for Jupiter and Saturn.

^h Scott et al. (2015) for the protosun, Wong et al. (2004) for Jupiter, estimate from Briggs and Sackett (1989) for Saturn.

ⁱ Scott et al. (2015) for the protosun, Mahaffy et al. (2000) at the equator for Jupiter.

^j Grevesse et al. (2015) for the protosun, Giles et al. (2017) for Jupiter, Noll and Larson (1991) for Saturn.

^k Lodders (2010) for the protosun, Giles et al. (2017) for Jupiter, Noll and Larson (1991) for Saturn.

^l Grevesse et al. (2015) for the protosun, Mahaffy et al. (2000) for Jupiter.

^m Grevesse et al. (2015) for the protosun, Mahaffy et al. (2000) for Jupiter.

paper are all taken from Grevesse et al. (2010, 2015), Scott et al. (2015), Amarsi and Asplund (2017) and Amarsi et al. (2018, 2019), except for germanium and arsenic (Lodders, 2010). The protosolar elemental abundances are derived from the solar abundances following Grevesse et al. (2010).

The isotopic ratios are also very valuable in that they tell us the main reservoirs for the various elements. Isotopic measurements in hydrogen, noble gases, nitrogen, carbon, oxygen, etc. (e.g. Lellouch et al., 2001; Feuchtgruber et al., 2013; Mahaffy et al., 2000; Fouchet et al., 2000a; Fletcher et al., 2014) are therefore key in constraining protoplanetary disk physico-chemical conditions and planet formation models (e.g. Hersant et al., 2001; Owen and Encrenaz, 2003; Mousis et al., 2014b). However, isotopes have not yet been accounted for in thermochemical models. Recent progress in Titan photochemistry modeling (Dobrijevic et al., 2016) will enable that in the future. They are presented in more details in Atreya et al. (2020) and Mousis et al. (2020) and will not be discussed further in this paper.

2.1.1 Helium and noble gases

Voyager 2 provided the first measurement of the helium abundance of the giant planets from infrared spectroscopy and radio occultation experiments (Gautier et al., 1981; Conrath et al., 1984, 1987, 1991).

In Jupiter, the Galileo probe refined the measurement to an helium-to-hydrogen ratio (He/H) of $(7.85 \pm 0.16) \times 10^{-2}$ (Niemann et al., 1998; von Zahn et al., 1998). In Saturn, the initial He/H of Conrath et al. (1984) was revised to a higher value of $(6.75 \pm 1.25) \times 10^{-2}$ by Conrath and Gautier (2000). The He/H in Saturn remains uncertain and several attempts have been made recently to make new measurements. Using Cassini instrumentation, Koskinen and Guerlet (2018) and Waite et al. (2018) derived an He/H of $(5.5 \pm 1.0) \times 10^{-2}$ and $\sim 8 \times 10^{-2}$, respectively. Helium is therefore subsolar in both gas giant upper tropospheres, and this can be explained by the formation of helium droplets in metallic hydrogen (Wilson and Militzer, 2010).

The initial results at Uranus and Neptune helium indicated mole fractions of 0.152 ± 0.033 (Conrath et al., 1987) and 0.190 ± 0.032 (Conrath et al., 1991), respectively. Accounting for an N_2 mole fraction of 0.003 in Neptune's atmosphere enabled Conrath et al. (1993) to revise their results to 0.15 for Neptune, bringing it in better agreement with the Uranus value. Later Infrared Space Observatory (ISO) observations by Burgdorf et al. (2003) seem to confirm and further refine the Neptune helium abundance to $0.149^{+0.017}_{-0.022}$. The He/H in Uranus and Neptune would thus seem to be slightly subsolar with abundances of $(8.88 \pm 2.00) \times 10^{-2}$ and $(8.96 \pm 1.46) \times 10^{-2}$, respectively. However, the error bars remain too large (from subsolar to marginally supersolar) to constrain interior models accurately (Guillot, 2005; Helled et al., 2011; Helled and Guillot, 2018; Helled et al., 2020; Nettelmann et al., 2013). Remote sensing can only provide tentative results and it is clear that only in situ measurements can provide us with a measurement accurate enough to constrain formation and evolution models. The goal of a probe is to reach an accuracy of 2% (Mousis et al., 2018), similar to Galileo.

Noble gases beyond helium have only been measured in Jupiter by the Galileo probe. Argon, Xenon and Krypton were all found enriched by a factor of 2-4 with respect to the protosolar value. Only neon is found subsolar, because of dissolution in liquid helium deep in the atmosphere of Jupiter (Roulston and Stevenson, 1995; Wilson and Militzer, 2010).

2.1.2 Carbon

Methane is the most abundant species after helium in all giant planets, and it is their main carbon reservoir.

In Jupiter, Galileo measured $C/H = (1.19 \pm 0.29) \times 10^{-3}$ (Wong et al., 2004). At Saturn, Fletcher et al. (2009b) used Cassini to constrain C/H to $(2.65 \pm 0.10) \times 10^{-3}$.

In the ice giants, methane condenses at ~ 1 bar and must be measured below this level. Its mole fraction was initially measured to about 0.02 (Lindal et al., 1987; Lindal, 1992; Baines et al., 1995) in both ice giants, i.e. more than an order of magnitude above its stratospheric abundance (Lellouch et al., 2015). More recent observations have, however, shown that the picture is more complicated than initially thought. Karkoschka and Tomasko (2009, 2011), Sromovsky and Fry (2008), Sromovsky et al. (2011, 2014), and Irwin et al. (2019a) have used near-IR scans that sample both an H_2 -collision induced opacity and a methane opacity to separate the effects of clouds and methane. From these spatially-resolved observations, they have shown that methane is more abundant at low latitudes than at the high latitudes sampled by the earlier observations. The equatorial mole fraction of methane is

0.04 ± 0.01 decreasing towards the poles in the upper troposphere possibly because of tropospheric circulation (Fletcher et al., 2020a). This point will be briefly addressed in Section 3.5.1. In any case, methane is being measured at the CH_4 -ice condensation point, and there is a possibility that there is additional internal stratification, as seen with jovian ammonia that is not well-mixed beneath the expected cloud-condensation level (e.g. Li et al., 2017). The current measurements must therefore be seen as lower limits on the deep C/H in ice giants.

2.1.3 Sulphur and nitrogen

Sulphur and nitrogen should be mainly borne by H_2S and ammonia (NH_3) in the reducing part of the atmospheres of the giant planets, even if the $^{15}\text{N}/^{14}\text{N}$ isotopic ratio in Jupiter and Saturn suggests nitrogen may have originally been delivered from N_2 (Fouchet et al., 2000a; Fletcher et al., 2014; Mousis et al., 2014b). Both nitrogen and sulphur should be enriched over the protosolar value.

Both have been observed in Jupiter by Galileo with $\text{N}/\text{H} = (3.32 \pm 1.27) \times 10^{-4}$ and $\text{S}/\text{H} = (4.45 \pm 1.05) \times 10^{-5}$ (Wong et al., 2004). More recent microwave mapping observations of Juno indicate that NH_3 is not well-mixed in the jovian upper troposphere, at least above the 50-60 bar level (Bolton et al., 2017; Li et al., 2017), raising the question whether the Galileo measurement is representative of the nitrogen deep abundance. They find a deep NH_3 mole fraction of 362 ± 33 ppm, i.e. $\text{N}/\text{H} = (2.09 \pm 0.20) \times 10^{-3}$ only marginally consistent with the Galileo measurement done at 6.5° north. In Saturn, Fletcher et al. (2011) found $\text{N}/\text{H} = 2.85 \times 10^{-4}$ at the equator from Cassini/VIMS, confirmed by Cassini/RADAR observations of Janssen et al. (2013) and Laraia et al. (2013). However, its deep value remains quite uncertain due to meridional variability, similarly to the Jupiter case (Li et al., 2017). The detection of H_2S in Saturn remains uncertain (Briggs and Sackett, 1989).

In the ice giants, H_2S and NH_3 remained undetected for a long time despite repeated efforts. The reason is that both species are thought to form a cloud of ammonium hydrosulfide (NH_4SH) at around 30-50 bars from the $\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{NH}_4\text{SH}(\text{s})$, only leaving traces of the most abundant species among the two up to their own condensation level (DeBoer and Steffes, 1994). The most abundant of the two would then condense in another cloud, at pressures between 5 and 10 bars. de Pater and Richmond (1989) and de Pater et al. (1989) found that NH_3 had to be ~ 0.1 - 0.001 times solar in the probed part of the atmosphere to match their microwave spectra of the two planets. To explain this depletion, de Pater et al. (1991) tentatively proposed an abundance of H_2S 10-30 times solar and an S/N at least 5 times solar in Uranus. Similar conclusion were reached for Neptune by DeBoer and Steffes (1994, 1996). However, these abundances must all be understood as lower limits since none of these observations probed below the NH_4SH cloud base. Using near-infrared observations with the Gemini North telescope, Irwin et al. (2018) detected H_2S above the main cloud deck in Uranus, indicating that sulphur is more abundant than nitrogen and placing a lower limit on their ratio, with $\text{S}/\text{N} > 4.4$ - 5.0 times the solar value (in agreement with de Pater et al. 1991). Using a similar technique, Irwin et al. (2019b) derived a lower limit on H_2S in Neptune. Complementary broadband spectra obtained with the VLA and ALMA enabled Tollefson et al. (2019a,b) to tentatively constrain S in Neptune to be 30 times protosolar and N to be protosolar.

2.1.4 Oxygen

Water, the main oxygen-bearing species in a giant planet interior, played a crucial role when giant planets formed. Water ice at the time of planetesimal formation provided a significant mass reservoir to build the planetary cores beyond the snowline, and the C/O ratio is a good diagnostic of the planet formation location (Ali-Dib et al., 2014; Mousis et al., 2012, 2014b; Öberg et al., 2011; Öberg and Bergin, 2016).

In addition, these ices played a fundamental role in that they trapped the other heavy elements. Depending on the pressure and temperature conditions at which the ices condensed, the heavy elements were either trapped on amorphous ices or in clathrates (Bar-Nun et al., 1988; Owen et al., 1999; Lunine and Stevenson, 1985; Gautier et al., 2001; Gautier and Hersant, 2005; Mousis et al., 2006). If ices condensed in amorphous form, then the oxygen enrichment should be similar to the enrichment of other heavy element (Owen and Encrenaz, 2003, 2006). On the other hand, the clathrate scenario requires a radically different oxygen abundance, i.e., ~ 4 times more, to trap the heavy elements (Mousis et al., 2014b, 2018). This is why constraining the deep oxygen abundance is so important to understand giant planet formation.

The Galileo probe entered a 5- μm hotspot and failed to reach the levels where water is uniformly mixed in Jupiter (Atreya et al., 2003; Wong et al., 2004). Juno is currently attempting to make this measurement from microwave radiometry during low-altitude perijove passes (Matousek, 2007; Bolton et al., 2017), now that the NH_3 distribution is established (Li et al., 2017). The first result obtained in the equatorial zone, where NH_3 is well-mixed up to its condensation level, indicates an $\text{O}/\text{H}=2.7^{+2.4}_{-1.7}$ times protosolar (Li et al., 2020). This result is key to better understanding the formation of Jupiter (Helled and Lunine, 2014), but will require additional measurements at other latitudes to assess whether this is the bulk abundance.

In the other giants, the tropospheric temperatures are colder than in Jupiter, making water condensation happen deeper. While reaching the well-mixed layers in Saturn will be at the limit of the capabilities of recently proposed probe (Mousis et al., 2014a, 2016; Atkinson et al., 2016, 2018), direct in situ measurement will remain highly improbable in the ice giants because water condenses at a pressure ranging between ~ 200 and ~ 1000 bar, depending on the adopted temperature extrapolation model (Atreya and Wong, 2005; Leconte et al., 2017). Complementary measurements taken by a remote sensing instrumentation suite on future ice giant orbiters (e.g. Arridge et al., 2014) will therefore be needed for additional context and constraints.

In the meantime, indirect measurements are the only possibility to constrain the deep oxygen abundance in these planets. We will detail these techniques and recent progress in Section 3.

2.1.5 Phosphorus and other heavy elements

Phosphorus, mainly carried by phosphine (PH_3), was observed with Cassini by Fletcher et al. (2009a) and the P/H ratio is $(1.08 \pm 0.06) \times 10^{-6}$ in Jupiter and $(3.70 \pm 0.23) \times 10^{-6}$ in Saturn. However, it still remains undetected in the ice giants (Moreno et al., 2009; Teanby et al., 2019). It may result from the destruction of this species by H_2O thermochemistry at depth, provided that the deep oxygen abundance is high enough in both planets (Visscher and Fegley, 2005).

Other heavy-element-bearing species have been observed in Jupiter and Saturn, like GeH_4 and AsH_3 (Giles et al., 2017; Noll and Larson, 1991; Fletcher et al., 2011). As is

supersolar in Jupiter, like most other heavy elements, but Ge is subsolar. This probably results from deep thermochemistry as Ge atoms are partly transferred from GeH_4 to GeS around the GeH_4 quench level (Lodders and Fegley, 1994). A complication arises from the non uniform meridional abundances of these species. While GeH_4 and PH_3 peak at low latitudes and decreases poleward, as expected from models (Wang et al., 2015), AsH_3 is minimal at low latitudes and peaks at the poles (Grassi et al., 2019). Their deep abundance thus remains quite uncertain.

2.1.6 Summary

Most heavy element abundance measurements were made possible by sending an entry probe in Jupiter. This underlines the importance of sending such instrumentation to all giant planets in the Solar System to make comparable ground-truth measurements. If these were coupled to remote sensing from orbiting facilities, the direct measurement would help to break the degenerate effects of gaseous species on the planetary spectrum.

Besides the elements presented previously, Galileo enabled quantifying the abundances of noble gases such as neon, argon, krypton, and xenon (Mahaffy et al., 2000). All elements measured by the probe are 2-4 times solar (except oxygen for the reasons mentioned above). The Juno measurement of oxygen will complete this panorama, but preliminary results that pertain to Jupiter's equatorial zone are compatible with this picture (Li et al., 2020).

In Saturn, helium is subsolar probably because of helium rain, carbon and phosphorus are about 10 times solar, but nitrogen seems to be less enriched. The non uniformity of the meridional distribution of NH_3 (Fletcher et al., 2011), similarly to Jupiter (Bolton et al., 2017; Li et al., 2017), complicates the derivation of the deep nitrogen abundance. The lack of measurements for other heavy elements, especially noble gases which should be uniform with altitude and latitude, makes it difficult to constrain Saturn formation models (e.g. Hersant et al., 2008). Several probe proposals were developed in the recent years (Atkinson et al., 2016, 2018; Mousis et al., 2014a, 2016) but none was selected for flight so far.

In Uranus and Neptune, the scarcity of heavy element abundance measurements is even more dramatic than in Saturn, as only carbon and, to some extent, sulphur have been measured, though the measurements of these condensible species bear large error bars and might be lower limits. The nominal abundance of methane at 1-2 bars and at low latitudes in both planets results in a C/H of 0.04 ± 0.01 , i.e., about 80 times protosolar, as expected from models (Owen and Encrenaz, 2003; Hersant et al., 2004). Sulphur may be 20-30 times protosolar, slightly lower than predictions from those same models.

This summary stresses the need for planetary probes at Saturn, and even more so at the ice giants.

2.2 Perspectives on ice giant elemental composition determination ahead of the 2040s

If a probe-carrying mission is to be selected for Uranus and/or Neptune with a launch window in the 2029-2034 timeframe (Simon et al., 2020), such a mission will arrive in the 2040s. In this Section, we will attempt to list the progress on ice giant composition we can expect from existing and forthcoming ground-based and space-based observatories. In addition, these observations ahead of a mission arrival in the 2040s will enable temporal variation studies which will set the ground for the mission operations and help contextualize them further.

2.2.1 Radio

Radio wave observations probe the giant planet spectra where NH_3 , H_2S and H_2O absorb. Single dish observations in the centimeter to decameter range remain difficult to calibrate accurately enough for the measurements to be constraining (Courtin et al., 2015). Interferometric observations of Saturn with LOFAR (Low Frequency Array, Röttgering 2003) have not yet detected Saturn's emission unambiguously because of the low planetary flux combined with the rapidly varying background sky emission (D. Gautier, private communication, 2015). The implementation of the Square Kilometer Array (SKA) may enable achieving these long wavelength measurements to better constrain the deep NH_3 and H_2O abundances in the giant planets in the 2030s.

In the centimeter wavelengths, the e-VLA (expanded Very Large Array) remains the best radio observatory to date. A project to improve the capabilities in terms of spatial resolution and sensitivity, named the ng-VLA (next generation VLA), may enable to improve on the constraints on deep N, S and O in the ice giants (de Pater et al., 2018). This project is aiming to start early science operations in the late 2020s and full science operations in the mid-2030s.

However, it remains to be seen whether radio measurements can probe deep enough and reach the well-mixed layers with the required accuracy. Juno has shown for NH_3 in Jupiter that reaching the well-mixed region requires probing at tens of bars (Bolton et al., 2017; Li et al., 2017). Interpreting the radio emission uniquely remains a challenge because it is hard to separate the broad spectral effects of temperature and the gaseous opacity.

2.2.2 Millimeter and submillimeter

ALMA (Atacama Large Millimeter/submillimeter Array) and NOEMA (NOthern Extended Millimeter Array) are currently the most sensitive millimeter and submillimeter interferometers. Both will still be operating in the 2020s and 2030s.

Aggregating broadband observations of these arrays with ng-VLA observations will help to improve our understanding of spatial distribution of H_2S and NH_3 (see Tollefson et al. 2019b for results using the current capabilities of these observatories) and of upper tropospheric circulation (Fletcher et al., 2020a) in the ~ 1 -50 bar pressure range. In addition, the determination of the meridional distribution of tropospheric CO in Uranus and Neptune from line spectroscopy will help to constrain further the deep oxygen abundance by coupling the observations to thermochemical modeling (see Section 3).

2.2.3 Near, mid- and far-infrared

In the near-IR, the techniques for separating the reflective aerosols from gaseous composition (specifically CH_4 and H_2S) have been established by ground-based observers using the largest astronomical facilities (e.g., Gemini, Keck, Very Large Telescope, etc.). These have demonstrated latitudinal variations of these volatiles, and provided lower limits on the potential bulk abundances of carbon and sulphur. Future near-infrared ground-based measurements with higher spatial resolutions (e.g., from the next generation of instrumentation on extremely large telescopes, such as the Extremely Large Telescope, Giant Magellan Telescope and Thirty Meter Telescope) might allow for further discrimination between aerosols and gaseous composition, but these may still be hampered by terrestrial atmospheric contamination. In the mid-infrared and far-infrared, measurements from ground- and airborne

facilities (e.g., Stratospheric Observatory for Infrared Astronomy) could continue to determine stratospheric composition and thermal structure, but this may not be of use for the determination of bulk planetary composition (with the exception of deuterium-to-hydrogen ratio measurements, if possible in the far-infrared).

In all of these cases, further progress could be made by being above the complicating effects of the terrestrial atmosphere. The James Webb Space Telescope (JWST, Gardner et al. 2006) carries instruments spanning the 1-30 micron range at exquisite spectral resolution and sensitivity that surpasses anything from the ground (Norwood et al., 2016a,b). In the mid-infrared, the MIRI instrument will place new upper limits on the PH₃ and NH₃ content using bands near 5 and 10 microns that have never been observed before. MIRI will also constrain the collision-induced continuum in the far-infrared, which may enable separation of temperature, para-H₂ and helium, via the same techniques as used on Voyager IRIS. MIRI will also provide our first spatially-resolved glimpses of the stratospheric temperatures and chemistry (Moses et al., 2018).

In the near-infrared, NIRSpec will enable more sensitive measurements of the H₂S and CH₄ abundances using the techniques honed on the ground. Furthermore, they will provide access to fluorescent regions between 3.0-4.5 microns, where CO and CO₂ fluoresce (Encrenaz et al., 2004; Fletcher et al., 2010). Along with sub-millimetre observations of CO, these provide another independent measurement of the CO abundance on the ice giants. In addition, the JWST instruments will further refine the D/H ratio in CH₄ (and potentially other species), as a further constraint on planetary formation.

At longer wavelengths in the far-infrared and sub-millimetre, the proposed Origins Space Telescope (OST, Leisawitz et al. 2018) and the SPace Infrared telescope for Cosmology and Astrophysics (SPICA, Roelfsema et al. 2018) will both offer sensitive observations of the spectrum, potentially allowing new constraints on the shape of the hydrogen-helium continuum, and on the isotopic ratios within hydrogen (from far-IR HD features). Depending on the final architecture of these missions, they may also provide new measurements of rotational lines of CO and CH₄. Even with these new and sensitive instruments, the ice giants will likely be unresolved, such that no spatial variability in these gases will be measured. For this, we have to be reliant on future orbital missions to the ice giants. These future observations concern several species that can be further used to constrain the deep abundance of some key elements by combining these observations with thermochemical modeling. This is the subject of the next Section.

3 Thermochemical modeling of giant planet atmospheres

In this Section, we will first present the principle of inferring deep planet composition from thermochemical modeling. We will then review the models that dealt with giant planet thermochemistry through the quench level approximation and show the recent progress enabled by the development of more comprehensive thermochemical and diffusion models. Finally, we will detail the parameters these models rely on and what the prospects on improving their predictability is.

The deep hot troposphere of the giant planets is in thermochemical equilibrium. If applied to the upper troposphere and to the stratosphere, this equilibrium predicts extremely small abundances for many species that have nonetheless been detected (Prinn and Barshay, 1977; Fegley and Prinn, 1985, 1986; Fegley and Lodders, 1994), among which the methyl radical (CH₃; Bézard et al. 1998, 1999, Fouchet et al. 2018a), stable hydrocarbons (Gladstone and Yung, 1983; Fouchet et al., 2000b; Courtin et al., 1984; Orton et al.,

2014; Burgdorf et al., 2006; Meadows et al., 2008), phosphine (PH_3 ; Knacke et al., 1982; Bregman et al., 1975; Fletcher et al., 2009a), carbon monoxide (CO ; Beer, 1975; Bézard et al., 2002; Noll et al., 1986; Noll and Larson, 1991; Encrenaz et al., 2004; Marten et al., 1993, 2005), carbon dioxide (CO_2 ; Feuchtgruber et al. 1997, Burgdorf et al. 2006), hydrogen cyanide (HCN ; Lellouch et al. 1995, Bézard et al. 1997, Fouchet et al. 2018b, Marten et al. 1993), carbon sulfide (CS ; Lellouch et al. 1995; Moreno et al. 2017). These species are generally observed in the stratosphere. They are produced from CH_4 photochemistry (Moses et al., 2000a, 2005, 2018; Dobrijevic et al., 2010, 2011, 2020; Hue et al., 2015, 2016, 2018) or injected in the atmosphere from external sources (Feuchtgruber et al., 1997; Moses et al., 2000b; Ollivier et al., 2000), like interplanetary dust particles (Landgraf et al., 2002; Moses and Poppe, 2017), large comet impacts (Lellouch et al., 1995, 2005, 2006; Cavalié et al., 2008, 2010, 2012, 2013; Moreno et al., 2017), and icy rings and satellites (Connerney and Waite, 1984; Connerney, 1986; Prangé et al., 2006; Hartogh et al., 2011; Waite et al., 2018; Perry et al., 2018; Cavalié et al., 2019). However, others like CO and PH_3 are observed in the upper troposphere² with abundances that are tens of orders of magnitude above thermochemical equilibrium predictions. Their presence at these levels is caused by convective vertical mixing that quenches thermochemical equilibrium where the vertical transport timescale becomes shorter than the chemical timescale.

Thermochemical and diffusion modeling can then be a powerful tool to infer the deep elemental composition of the giant planets from disequilibrium species, especially when the main carrier of an element does not reach the observable levels. The disequilibrium species abundances is used to track back their abundance at their respective quench level to then tie them back to the main element-carrier abundance.

In this Section, we will present the modeling principle of thermochemistry to constrain deep composition and show how it has been applied in the past decades, first using the quench level approximation, and then using more comprehensive chemical models. We will detail the parameters that are fundamental in getting accurate simulations and the prospects regarding future improvements.

3.1 Principle

Oxygen is mainly carried by water, but water condenses in the troposphere of the giant planets. While its condensation level occurs at ~ 10 bar in Jupiter, it occurs at pressure ranging from ~ 200 to ~ 1000 bars in both Uranus and Neptune, according to temperature extrapolation models (Leconte et al., 2017). Only microwaves can probe that deep (Janssen et al., 2005; de Pater et al., 2016), but limited calibration accuracy often prevents any direct constraint on the water abundance (de Pater and Richmond, 1989; de Pater et al., 1989; Courtin et al., 2015). The idea then lies in measuring the upper tropospheric abundance of CO , which does not condense in giant planet atmospheres and is in disequilibrium because of efficient vertical mixing, and to tie it back to the deep water abundance with a chemistry and diffusion model. As CO is chemically linked to water, thermochemical and diffusion models have been used with this species to constrain the deep oxygen abundance ever since it was first detected in Jupiter by Beer (1975).

Other carbon bearing species can, in principle, be used similarly to constrain the deep water, like ethane (C_2H_6) (Fegley and Lodders, 1994). Another example is phosphorus, which has been detected in PH_3 in Jupiter and Saturn, but neither in Uranus nor in Neptune

² CO can actually have an internal and an external component (Bézard et al., 2002; Lellouch et al., 2005).

(Moreno et al., 2009). This species can be destroyed by water if water is abundant enough. Its detection then results either from the relatively low water abundance or from its quenching at levels that are deeper than where it gets destroyed by water (Fegley and Lodders, 1994). On the other hand, its absence can help to put additional constraints on the deep water abundance (Visscher and Fegley, 2005).

We come back to the example of carbon monoxide and water, as it is the most studied case to date. In the deep hot tropospheres of giant planets, CO and H₂O are in thermochemical equilibrium through the reaction



Rearranging the equilibrium constant of the above equation enables to express the CO mole fraction as follows:

$$y_{\text{CO}} = \frac{y_{\text{CH}_4} y_{\text{H}_2\text{O}}}{y_{\text{H}_2}^3 p^2} K_{\text{eq}} \quad (2)$$

where p is the total pressure and K_{eq} is the equilibrium constant of reaction (1). At higher and colder levels, the H₂O-CO equilibrium moves towards the reduced H₂O-CH₄ mixture and the conversion kinetics slows down. There is a level in the troposphere at which the temperature is low enough for the kinetics to become slower than the vertical mixing caused by convection. This is the level where the chemical lifetime of CO destruction τ_{chem} equals the vertical mixing timescale τ_{mix} . Thermochemistry is quenched and the CO mole fraction fixed for all levels above this quench level.

There are two techniques that have been used to find the abundances of CO and water at the quench level: the quench level approximation and comprehensive thermochemical and diffusion modeling. In both cases, presented below, the determination of convective mixing is crucial.

3.2 Estimating convective mixing strength

The magnitude of vertical mixing caused by convection is key in fixing the level at which thermochemistry is quenched, and in turn in fixing upper tropospheric abundances of disequilibrium species: the stronger the mixing, the deeper the quench level.

The vertical mixing timescale τ_{mix} is given by

$$\tau_{\text{mix}} = \frac{L^2}{K}, \quad (3)$$

where K the vertical mixing coefficient and L the length over which mixing occurs. The latter was taken as the atmospheric scale height H in early studies. Convective mixing can be estimated from free-convection and mixing-length theories (Stone, 1976; Gierasch and Conrath, 1985) and modeled in 1D models by means of an eddy mixing coefficient. The scaling relationship

$$K \simeq \left(\frac{F k_{\text{B}}}{\rho m c_p} \right)^{\frac{1}{3}} H, \quad (4)$$

where F is the internal heat flux of the planet, k_{B} is the Boltzmann constant, ρ is the atmospheric mass density, m is the atmospheric mean molecular mass, and c_p is the atmospheric specific heat at constant pressure, applies in the absence of rapid rotation and a strong magnetic field. It is therefore only an approximation for giant planets. These estimates show that tropospheric K is of the order of $10^8 \text{ cm}^2 \cdot \text{s}^{-1}$, with a factor of 10 uncertainty, in the giant

planets. Visscher et al. (2010) derived an altitude-latitude dependent expression for K for fast rotating planets. They showed that K decreased both with latitude and depth. The decrease with depth can however be neglected in thermochemical simulations because the variation is less than an order of magnitude between the top of the troposphere and the quench level. More recently, Wang et al. (2015) used rotating tank experiments to refine the scalings in the expression of K , and thus decrease the uncertainty on their estimation down to about 25%. They also predicted that K would be maximum at low latitudes and then decrease towards the high latitudes. They found that the decrease caused by depth and latitude was steeper for Saturn than for Jupiter. We illustrate the application of their prescription to Uranus and Neptune in Fig. 1. It essentially shows that disequilibrium species like CO, GeH₄ and PH₃ that are quenched where their abundance decreases with height should be more abundant in the upper troposphere at low latitudes. On the contrary, disequilibrium species like AsH₃ that are quenched where their abundance increases with height (Fegley and Lodders, 1994) should be more abundant at high latitude in the upper troposphere. This seems to be qualitatively in line with Juno/JIRAM observations of Jupiter (Grassi et al., 2019).

3.3 Quench level approximation

By decomposing the thermochemical equilibrium reaction (Equation 1) into the series of reactions that lead H₂O to be converted into CO (and vice versa), one can then try and identify the reaction which has the slowest kinetics, i.e. the rate-limiting reaction. The estimation of the rate-limiting reaction kinetics constrains the kinetics of the whole conversion scheme. By equating τ_{chem} and τ_{mix} , it is then possible to derive the temperature at the quench level. Assuming a pressure-temperature relationship (e.g., dry or wet adiabat), it is then possible to compute p in Equation 2. The measured upper tropospheric mole fractions of CO and CH₄, which are the same as the one at the quench level, can eventually be used to solve the system and derive the deep value of $y_{\text{H}_2\text{O}}$.

(Prinn and Barshay, 1977) first identified this rate-limiting reaction to be $\text{H}_2 + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3 + \text{OH}$. By assuming a solar composition, they constrained vertical mixing to reproduce the CO detection of Beer (1975), thus using thermochemistry the other way around. Later work by Fegley and Prinn (1985, 1988) and Fegley and Lodders (1994) further explored the deep composition of Jupiter and Saturn. Bézard et al. (2002) performed high spectral resolution observations in the 5 μm window in the North Equatorial Belt of Jupiter to refine the planet's CO upper tropospheric abundance to 1.0 ± 0.2 ppb. They applied the less ambitious kinetic scheme of Yung et al. (1988) for the CO-CH₄ conversion, in which the rate-limiting reaction is $\text{H} + \text{H}_2\text{CO} + \text{M} \rightleftharpoons \text{CH}_3\text{O} + \text{M}$. They also used the new method of Smith (1998) to estimate the vertical scale for diffusion (in replacement of H in Equation 3). They derived a jovian deep oxygen abundance of 0.2 to 9 times the solar value.

The quench level approximation was later used in several studies (Visscher and Fegley, 2005; Cavalié et al., 2009; Luszcz-Cook and de Pater, 2013) following the detections of CO in Saturn and Neptune by Noll et al. (1986) and Marten et al. (1993) to try and constrain the deep oxygen abundance in these planets.

3.4 1D kinetic and diffusion models

Another approach used to constrain the deep water abundance consists in using detailed kinetic and diffusion models that are able to reproduce accurately the chemical composition

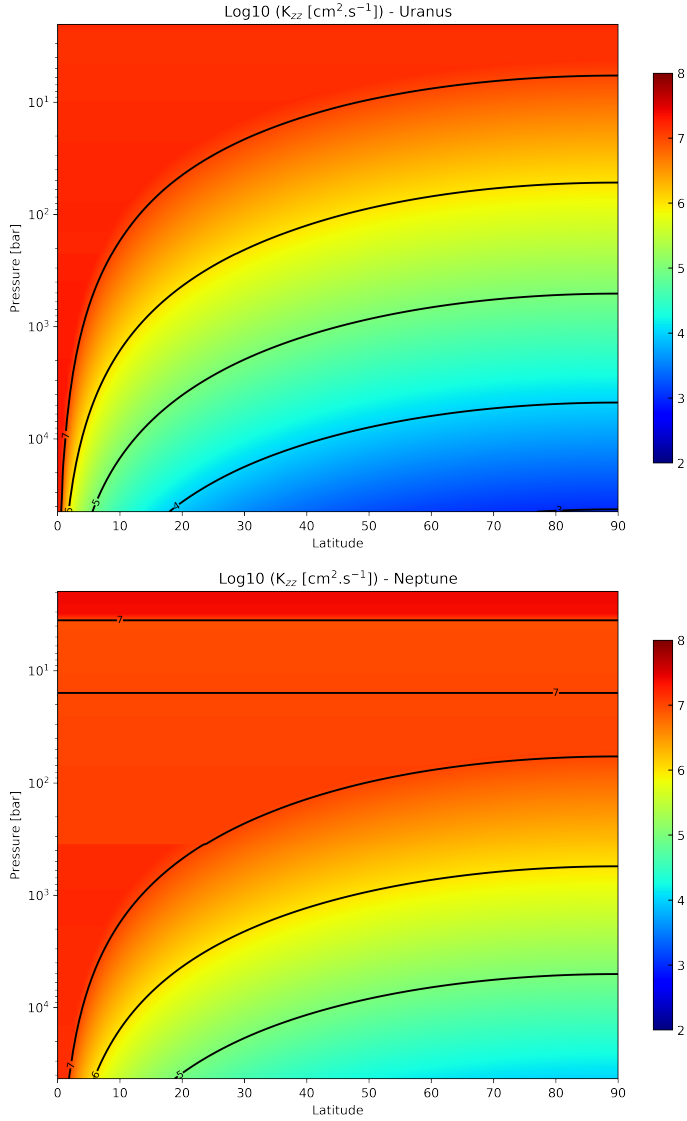


Fig. 1 Vertical mixing in the tropospheres of Uranus (top) and Neptune (bottom) as a function of pressure and latitude, using the prescription of Wang et al. (2015) and the temperature and abundance profiles of Venot et al. (2020).

of hot atmospheric regions. The development of such models has been motivated by the discovery of hot giant exoplanets and the interpretation of their infrared spectra. Despite the high temperatures prevailing in their atmospheres, the regions probed by spectroscopic observations are not at thermochemical equilibrium. Disequilibrium processes are important and disturb the atmospheric composition. Thus, thermo-photochemical models have been developed specifically for the study of these peculiar atmospheres in which thermochemical

Table 2 Deep oxygen abundance in giant planet deep atmospheres.

| | CO mole fraction (upper troposphere) | Deep O/H (\times protosun) | Reference |
|---------|---|----------------------------------|---|
| Jupiter | (1.0 ± 0.2) ppb | 0.26-6.3 | Bézard et al. (2002), Visscher et al. (2010) |
| Saturn | ~ 1 ppb | 10-70 | Fouchet et al. (2017), Wang et al. (2016) |
| Uranus | < 2.1 ppb | < 45 | Teanby and Irwin (2013), Venot et al. (2020) |
| Neptune | (0.20 ± 0.05) ppm | 250 | Luszcz-Cook and de Pater (2013), Moreno et al. (2011), Venot et al. (2020) |

^a Oxygen abundances have been rescaled using the protosolar abundances of Table 1.

equilibrium, mixing and photochemistry are at play (e.g. Moses et al., 2011; Visscher and Moses, 2011; Venot et al., 2012; Drummond et al., 2016; Tsai et al., 2017).

These models enable an accurate computation of the vertical profiles in the key pressure range where quenching occurs. They have been used for each solar system giant planet (Visscher et al., 2010; Wang et al., 2016; Cavalié et al., 2014, 2017) to further constrain their deep oxygen abundances. Table 2 summarizes the current status of model results regarding deep oxygen abundance in all giant planets.

3.5 Perspectives prior to an ice giant probe mission

Thermochemical and diffusion models, like quench level models, still have to rely on several parameters that have to be assumed, i.e. the vertical mixing and the pressure-temperature profile. The main differences between their results then boil down to the differences in their chemical schemes. In this Section, we will review the progress we anticipate prior to the arrival of an ice giant probe in the 2040s regarding the determination of these input parameters.

3.5.1 Vertical mixing

Visscher et al. (2010) showed that vertical mixing caused by convection in giant planet tropospheres depends on latitude and altitude, because of the planet rotation. Wang et al. (2015) further refined these calculations and concluded that the magnitude of this vertical mixing would decrease with latitude and depth. Its maximum is anticipated at the low latitudes. This means that the deepest quench levels, and therefore the highest abundances for species like CO and GeH₄, are expected to be observable at these same low latitudes. This is confirmed by recent Juno observations at Jupiter for GeH₄ (Grassi et al., 2019).

However, the picture in giant planet upper tropospheres seems to be more complex than initially thought. In Jupiter, the abundance of NH₃ is far from the idealized well-mixed picture in the 1-50 bar range, with only a narrow band slightly north of the equator being uniformly mixed up to the NH₃ cloud (Bolton et al., 2017; Li et al., 2017; de Pater et al., 2019). Guillot et al. (2019) proposed that this distribution is likely caused by the formation of NH₃-H₂O mesh balls in convective storms. Such an equatorial plume had already been identified by Fletcher et al. (2009a) in Jupiter's and Saturn's PH₃ distributions. In Neptune, Tollefson et al. (2019a,b) showed that condensibles like H₂S and NH₃ were subject to tropospheric circulation and/or meteorology and that the circulation pattern extends down to the ~ 30 bar level.

Disk-resolved tropospheric observations with facilities like e.g., ALMA, e-VLA and JWST, and 3D general circulation model (GCM) are therefore required to better understand upper tropospheric circulation and chemistry (Fletcher et al., 2020b,a). Venot et al. (2019, 2020) have proposed a reduced chemical scheme from their more complete 1D thermochemical model in view of their implementation in more complex 3D GCMs. Nailing down the latitude range where vertical mixing is most efficient in transporting disequilibrium species up to observable levels will be key in setting the entry latitude to target in priority with a shallow probe to increase its chances to access the well-mixed region of the explored atmosphere.

3.5.2 Temperature profile

One of the main unknown in giant planet tropospheres is the temperature-pressure field. It bears implication on circulation, kinetics, condensation layers, vertical mixing, etc. Except the Galileo probe measurements, which probed Jupiter down to the 22 bar level (Seiff et al., 1998), there is no such deep temperature measurement in any other giant planet. The fact that Galileo entered a $5\mu\text{m}$ hot spot further questions the representativeness of the measurements. In the other giants, there is a large uncertainty beneath the 2 bar level, which is the deepest level probed by occultation with Voyager 2 (Lindal et al., 1985, 1987, 1990; Lindal, 1992). Moreover, latitudinal variability remains unconstrained, even if the observed tropospheric distributions of several condensibles are hints of such variability (Sromovsky and Fry, 2008; Karkoschka and Tomasko, 2011; Irwin et al., 2019a; Tollefson et al., 2019a; Molter et al., 2019).

Extrapolation to higher pressures are required for thermochemical computations and a dry or a wet adiabat has often been used (Luszcz-Cook and de Pater, 2013). However, Guillot (1995) first showed that Uranus and Neptune are in a situation where mean molecular weight gradients could inhibit convection at the condensation level of CH_4 and produce in a steep increase of the temperature. Later, Leconte et al. (2017) demonstrated that the effect of convection inhibition would be even more dramatic deeper, at the H_2O condensation level. The resulting profile would then be a “3-layer profile”, starting from a wet adiabat in the uppermost levels, a radiative layer where the water vapor mixing ratio is between a fixed critical value and its maximum internal value, and a dry adiabat deeper down. The range of possible temperature profiles in Uranus and Neptune, between the wet adiabat (the coldest) and the convection inhibited one (the warmest), are shown in Fig. 2. Cavalié et al. (2017) showed that the implications on the deep composition as derived from thermochemical modeling are significant. Therefore, any improvement in our knowledge of the tropospheric temperature is regarded as highly valuable.

3.5.3 Chemical scheme

The chemical scheme adopted in thermochemical calculation is obviously key on determining the quench level of the species of interest. Wang et al. (2016) compared the chemical schemes of Moses et al. (2011) and Venot et al. (2012) in applications to Jupiter and Saturn. They found that these two schemes resulted in differences of about an order of magnitude on the abundance of CO, all other parameters and deep composition being kept similar. Moses (2014) already pointed out a significant difference in their carbon-oxygen chemistry, identifying a methanol (CH_3OH) conversion reaction as the main responsible. Venot et al. (2020) fully revised their CH_3OH chemistry, adopting recent experimental results of Burke et al. (2016). The new scheme was validated over a wide range of temperature and pressure.

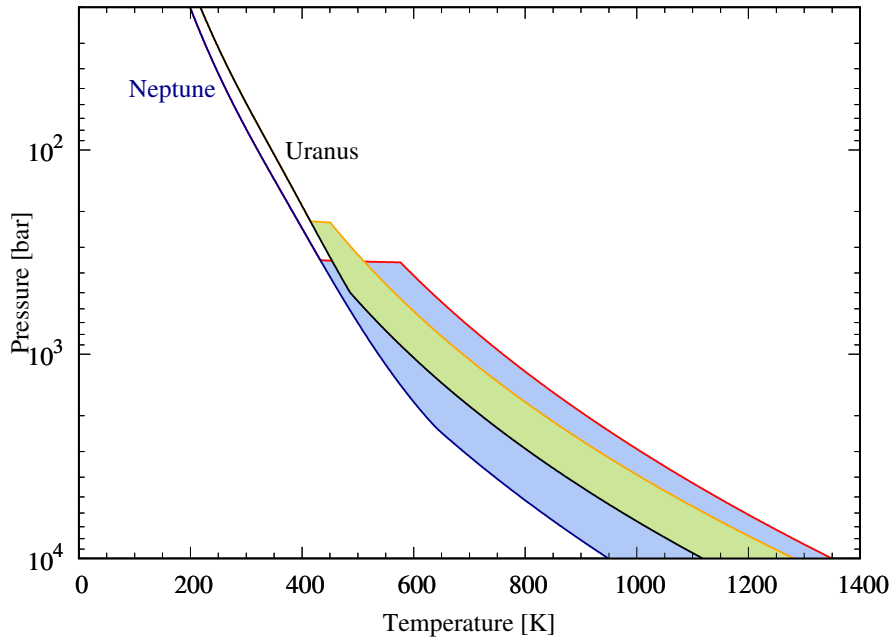


Fig. 2 Range of possible temperature profiles in the tropospheres of Uranus and Neptune, following Leconte et al. (2017) and Cavalié et al. (2017). The coldest profiles, corresponding to the wet adiabat, are shown in black (Uranus) and dark blue (Neptune). The warmest profiles, corresponding to the “3-layer profile”, are shown in orange (Uranus) and red (Neptune). The filled areas (green for Uranus and blue for Neptune) indicate the range of possible temperatures.

The main changes concern the replacement of the reaction outlined by Moses (2014) by a more detailed mechanism, in which pressure dependent reaction rates are adopted. Planets in which CO quenching occurs at high pressures are affected by the modifications. For Uranus and Neptune, the effect of this update is to lower the CO quenching level towards higher pressures, compared to the results obtained with the chemical scheme of Venot et al. (2012). Consequently, to reproduce observational constraints of CH_4 and CO in the upper troposphere, a lower amount of H_2O is required in the deep tropospheric region where thermochemical equilibrium prevails. The O/H values found by Cavalié et al. (2017) using Venot et al. (2012)’s chemical scheme have been revised downwards. The O/H ratios necessary to reproduce current observations are <45 and 250 times protosolar value, for Uranus and Neptune respectively (Table 2).

Chemical schemes currently used to model tropospheres of the ice giants contains only species made of C, H, O, and N. However, the recent detection of H_2S in Uranus and Neptune (Irwin et al., 2018, 2019b) make really necessary the addition of sulphur species. Such models would then require to account for cloud formation (Atreya and Wong, 2005) as H_2S is involved in the formation of an NH_4SH cloud which consumes all NH_3 at these levels, and of an H_2S cloud above. Although not detected in ice giants, PH_3 might be present in these atmospheres also, as it is in Jupiter and Saturn. Alternately, its absence may serve as additional constraints for the deep oxygen abundance (Visscher and Fegley, 2005). The addition

of phosphorous species in chemical schemes is one of the next necessary step concerning the improvement of chemical schemes used to study ice giant atmospheres.

As we said in Sect. 3.5.1, the heterogeneity of the troposphere, as seen in disk-resolved tropospheric observations, makes necessary the development of GCMs including a detailed chemistry. Full chemical schemes are too heavy (~ 100 species and ~ 2000 reactions) to be incorporated in 3D models, as it would result to unreasonable computational time. The solution is to include a reduced chemical scheme, valid for a limited number of species of interest. In this purpose, reduced schemes have already been proposed by Venot et al. (2019, 2020) for H, C, N and O species. Such reduced schemes must be regularly updated, e.g. to account for sulphur and phosphorus species.

3.5.4 Summary

Cavalié et al. (2017) have shown the range of O/H values one can derive for Uranus and Neptune given the current limited knowledge of several key parameters in thermochemical modeling. Future progress in deep composition derivation from thermochemical modeling of the tropospheres of the ice giants require improvements to be made on the knowledge of the parameters this kind of models rely on. A better understanding of the 3D dynamics and chemistry to better constrain the disk variability of vertical mixing and temperature, both crucial in fixing quench levels, will involve a combination of disk-resolved observations, chemical and general circulation modeling work. Chemical networks will need to be extended to other key element bearing species and will have to include phase change processes for condensable species. Reaction rates for which either the temperature validity range or the accuracy are insufficient will need to be identified and improved (see e.g. Dobrijevic et al., 2010).

4 Thermochemical modeling in support of an ice giant atmospheric probe mass spectrometer

In this Section, we will briefly remind the baseline objectives of an ice giant mass spectrometer. We will then present the synergistic coupling of mass spectrometry with thermochemical modeling, and the requirements on the instrument such coupling drives. We will finally show how increasing the probe penetration depth could improve the science return of the probe mission. More details on the possible mass spectrometer can be found in Vorburger et al. (2020).

4.1 Baseline ice giant probe mass spectrometer

In the current baseline scenario proposed for ice giant atmospheric probes (e.g. Mousis et al. 2018 and Vorburger et al. 2020, and references therein), inherited from recent Saturn probe proposals (Mousis et al., 2014a, 2016; Atkinson et al., 2016, 2018), the nominally targeted depth is the 10-bar level. The mass spectrometer proposed for the Hera mission to Saturn and that is now considered for an ice giant probe mission consisted of several units, among which a time-of-flight mass spectrometer (TOF-MS) which has a nominal mass resolution of ~ 1000 used for neutral gas composition, and a tunable laser spectrometer used for selected isotopic ratio measurements (Mousis et al., 2016; Wurz et al., 2012). The TOF-MS will

be 1000 times more sensitive than the Ion and Neutral Mass Spectrometer of the Cassini mission.

Reaching the 10-bar level with such an instrument will ensure accurate measurements of helium (within 2%) and the other noble gases (within 10%) that are expected to be well-mixed in both altitude and latitude. If the entry latitude is close to the equator, where methane is most abundant (see Section 2.1.2), the probe may also measure a carbon abundance representative of the deep C/H value. However Juno has shown with NH₃ that the well-mixed region for condensible species can occur much below than the cloud base of that species (Bolton et al., 2017; Li et al., 2017).

It will also measure the abundance of sulphur above the NH₄SH cloud, and thus the minimum S/N. However, N/H and S/H will remain out of reach, as the NH₄SH cloud deck is expected at 40 bars or so. Oxygen will also remain out of reach for a direct measurement, as water condenses as deep as a few hundred bars already in the ice giants (Atreya and Wong, 2005; Cavalié et al., 2017).

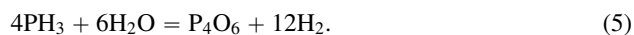
4.2 Synergistic coupling of in situ mass spectrometry and thermochemical modeling in ice giants

During its descent in the upper troposphere of an ice giant, the probe mass spectrometer will be sensitive to several gases (beyond helium, nobles gases, and methane) of key importance to constrain the deep composition of the ice giant from thermochemical modeling, provided that more ambitious mass resolution requirements are fulfilled.

The first species of interest is CO especially in Uranus, where its tropospheric component has not yet been unambiguously identified (Encrenaz et al., 2004; Cavalié et al., 2014). Combining mass spectrometry determination of the CO abundance within 10%, accurate temperature-pressure measurements of the Atmospheric Structure Instrument (Ferri and colleagues, 2019), and thermochemical modeling as detailed in Section 3, it will be possible to constrain the deep O/H of the ice giants more accurately than possible before. One limitation though regarding the deep O/H derivation is the single entry point of the probe which will result in a single temperature-pressure profile. Any variability over the planet, that is likely to occur, will remain out of reach to the probe. One key will then consist in picking the probe entry point such that we get a profile which is as much as possible representative for the whole planet by trajectory design and by knowing what places to avoid (e.g., avoid Great Dark Spots).

But directly measuring the abundance of CO bears several implications for the mass spectrometer. First, carbon dioxide (CO₂) needs also to be measured accurately as well as its fragmentation into CO inside the instrument. As CO₂ has the same mass as propane (C₃H₈), a mass resolution $m/\Delta m > 600$ is already required. Moreover, the instrument must be able to mass-separate CO from dinitrogen (N₂) and ethylene (C₂H₄). These species all reside at mass 28 on a mass spectrum. To separate them, a mass resolution $m/\Delta m > 3000$ is required at comparable abundance of CO and N₂.

As already stated in 2.1.5, additional constraints on the deep O/H can be obtained from measuring the abundance of PH₃ by solving the following thermochemical equation:



This would, in turn, require a mass resolution $m/\Delta m > 4000$, or a suitable chemical pre-separation (Vorburger et al., 2020), to separate PH₃ from H₂S, another mass-34 species detected in both ice giants. In the same spirit, ethane (C₂H₆) and acetylene (C₂H₂) can also

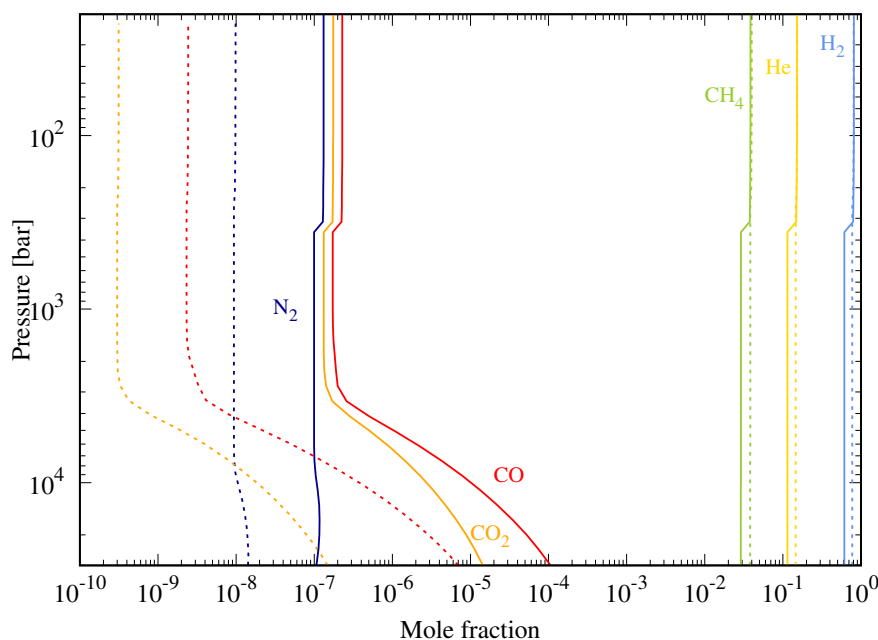


Fig. 3 Vertical profiles of CO (red), CO₂ (orange) and N₂ (dark blue) for Uranus (dashed lines) and Neptune (solid lines). Other main species like H₂, He and CH₄ are also shown with the corresponding layout.

be used as an additional constraint in the carbon-oxygen thermochemistry (Fegley and Prinn, 1985; Fegley and Lodders, 1994).

The direct benefit of such a high mass resolution would be a measurement of the N₂ abundance. In the same way CO is used to constrain the deep H₂O, N₂ can be used in thermochemical modeling to reproduce its upper tropospheric abundance and constrain the deep NH₃ abundance and thus the deep N/H, without the need for the probe to go beneath the NH₄SH cloud deck. Fig. 3 shows the vertical profiles of CO and N₂ for Uranus and Neptune using the model described in Venot et al. (2020) and assuming the deep N/H of Table 1. It shows that N₂ could be present in both planets with abundances comparable or even higher than CO. Having the deep N/H established this way, it would then be possible to derive the deep S/H from the combined reconstruction of the deep NH₃ and H₂S abundance profiles below the NH₄SH cloud deck and current H₂S observations above its own cloud (Irwin et al., 2018, 2019b). The current limitation of a descent probe in ice giants to measure directly N/H and S/H because of end-of-operations at 10 bars, i.e. before reaching the NH₄SH cloud deck at 40 bars or so, would thus be waived.

4.3 The question of depth

It is obvious that even more robust N/H and S/H values could be directly measured by an ice giant probe mass spectrometer, provided that it would reach below the NH₄SH cloud. However, such a depth goal bears implications on several technical aspects.

The descent would take longer to reach this level rather than the 10-bar level. The relay spacecraft would thus have to fly slower above the entry point to keep the radio link with the probe. For an orbiter, this would imply a higher orbit. However, placing the relay spacecraft further away from the probe would degrade the data rate. The situation on the data rate side is even more challenging as the atmospheric opacity increases exponentially with depth, especially beyond 15 bars, even though the situation is less critical now that it has been established that the main absorber in the altitude range will be H_2S rather than NH_3 . To overcome this problem, two possibilities are being discussed: a second relay spacecraft could be sent or the communication system could use optical laser instead of radio frequencies.

4.4 The question of the probe entry latitude

To measure abundances of major species that are representative of their deep values, a probe should target an entry site where the material is uniformly mixed. There is already observational evidence that the high latitude may be depleted, at least in the upper troposphere, in CH_4 and H_2S (Sromovsky et al., 2014; Irwin et al., 2019a; Tollefson et al., 2019a). This, in turn, implies targeting latitudes where tropospheric mixing is maximum, i.e. the low latitudes in the ice giants according to Fig. 1. For disequilibrium species, which are quenched in layers where their abundance increase with depth (e.g., CO and PH_3), to be more likely detected by a mass spectrometer, low latitudes should also be favored. It should be noted however that there are some disequilibrium species (e.g., AsH_3) for which high latitudes should be more favorable.

Now that we have reviewed how the bulk composition of the ice giants can be constrained from the combination of in situ measurements and thermochemical modeling (possibly supplemented by remote sensing observations), we will review how it can help us better understand the interior of these planets and the processes that led to their formation.

5 Link between deep composition, interior models, and planet formation

Because the atmospheres and interiors of the giant planets are intimately linked and there is no probe that can go very deep into either planet, a proper understanding of Uranus and Neptune's atmospheres is crucial to characterise their interiors. The atmospheric thermal profiles and deep compositions put constraints and impact directly on the interior model calculations (Guillot, 2005; Guillot and Gautier, 2015; Helled and Guillot, 2018).

The internal structure of Uranus and Neptune is estimated using interior models that fit the observational data for mass, radius, luminosity, atmospheric temperature, atmospheric abundances and gravity data. With only one mission (Voyager 2) visiting these planets so far, the gravity data that was obtained by remote sensing is much more limited than what we have for Jupiter (Bolton et al., 2017; Iess et al., 2018) and Saturn (Iess et al., 2019). In Table 5, we show the parameters used for interior model calculations for Uranus and Neptune with the exception of the atmospheric abundances, already shown in Table 1. The data for Jupiter and Saturn are shown for comparison.

The information in Table 5 is combined with interior models to calculate the mass of heavy elements and their distribution in the interior, investigating all possible interior structures for Uranus and Neptune (see Section 5.2). Given that one of the most accepted theories for the formation of these planets requires that a core forms first and the gas is accreted later

| Parameter | Jupiter | Saturn | Uranus | Neptune |
|--------------------------------------|--------------------------|--------------------------|---------------------------|-------------------------|
| Mass/ 10^{24} (kg) | 1898.187 ± 0.088^a | 568.336 ± 0.026^b | 86.8127 ± 0.0040^c | 102.4126 ± 0.0048^d |
| Equatorial radius (km) | 71492 ± 4^e | 60268 ± 4^e | 25559 ± 4^e | 24764 ± 15^e |
| Temperature _{1bar} (K) | 165 ± 4^f | 135 ± 5^f | 76 ± 2^f | 72 ± 2^f |
| Intrinsic flux ($J s^{-1} m^{-2}$) | 5.44 ± 0.43^g | 2.01 ± 0.14^g | $0.042^{+0.047}_-0.042^g$ | 0.433 ± 0.046^g |
| J ₂ /10 ⁶ | 14696.572 ± 0.0046^h | 16290.573 ± 0.0093^i | 3516 ± 3.2^j | 3408.4 ± 3404.5^d |
| J ₃ /10 ⁶ | -0.042 ± 0.0033^h | 0.059 ± 0.0076^i | — | — |
| J ₄ /10 ⁶ | -586.609 ± 0.0013^h | -935.314 ± 0.0123^i | -35.4 ± 34.1^j | -33.4 ± 32.9^d |
| J ₅ /10 ⁶ | -0.069 ± 0.0026^h | -0.224 ± 0.018^i | — | — |
| J ₆ /10 ⁶ | 34.198 ± 0.003^h | 86.340 ± 0.029^i | — | — |
| J ₇ /10 ⁶ | 0.124 ± 0.0056^h | — | — | — |
| J ₈ /10 ⁶ | -2.426 ± 0.0083^h | -14.624 ± 0.0683^i | — | — |
| J ₉ /10 ⁶ | -0.106 ± 0.0146^h | — | — | — |
| J ₁₀ /10 ⁶ | 0.172 ± 0.023^h | 4.672 ± 0.14^i | — | — |
| J ₁₂ /10 ⁶ | — | -0.997 ± 0.224^i | — | — |

^a Jacobson 2003 - published in the JPL website: https://ssd.jpl.nasa.gov/?planet_phys_par

^b Jacobson et al. (2006)

^c Jacobson (2014)

^d Jacobson (2009)

^e Archinal et al. (2018)

^f Lindal (1992), note that Seiff et al. (1998) derived 166.1 K for Jupiter

^g Pearl and Conrath (1991)

^h Jess et al. (2018)

ⁱ Jess et al. (2019)

^j Lindal et al. (1981), Helled and Guillot (2013) derive slightly different values

on (see Section 5.1), the constraints obtained from the interior models are crucial to understand the history of these planets.

Uranus and Neptune are usually referred to as twin planets, but in reality they have many differences. When looking at their masses and radii we notice that Neptune is denser than Uranus, by approximately 30%. The reason for this difference is not clear, but it was suggested that giant impacts during their formation and evolution might have affected their structure (Podolak and Helled, 2012). Uranus has a much higher obliquity when compared with Neptune and all the other giants, that is also explained with a giant impact during its formation, and that may cause differences in the atmospheres between the two ice giants (Safronov, 1966). In addition, Table 5 shows that the intrinsic flux of these two planets is quite different. While Neptune emits more energy than it receives from the Sun, Uranus has an emitted flux an order of magnitude lower than its neighbour. This implies that while Neptune is still cooling, Uranus is almost in equilibrium with the solar irradiation, which implies differences in the energy transport in their interiors and points towards different evolution for these two planets.

Regarding the link between the atmosphere and interior, one of the most important constraints needed for interior models are the atmospheric abundances, which have been extensively discussed in the previous Sections. Uranus and Neptune are different from Jupiter and Saturn because they are not merely dominated by hydrogen and helium, and may be highly enriched in heavy elements. While H and He are consistent with the protosolar abundances, C has an enrichment of 80 ± 20 compared to the protosun (Atreya et al., 2018), but this may as well be a lower limit only.

Another relevant parameter used in interior models is the temperature at 1 bar, that sets the upper boundary for these calculations. This parameter is obtained from stellar and ring occultations, that also provides determination of the shape of the planets. However, we have

to note that this data are limited to low-pressure values, approximately 0.1 bar and even lower pressures (French et al., 1998), and this can bring uncertainties in the radius used to model these planets (Helled et al., 2010). In addition to this, the thermal profile inferred to reach the 1 bar level is highly degenerate (it depends on many unknown parameters such as the refractivity which depends on the mean molecular weight and the temperature at each pressure level). Therefore, the temperature inferred corresponds to one possible solution, but there might be other possibilities (Guillot, 1995; Sromovsky et al., 2011).

The magnetic field is another observable quantity that provides constraints to understand the boundary between the deep atmosphere and the interior. Observations suggest that there is a convective and electrically conductive region that extends down to 20% of the radius (Stanley and Bloxham, 2004, 2006; Redmer et al., 2011). This is directly linked with the dynamics of Uranus and Neptune’s atmospheres, with zonal winds that extend down to approximately 1000 km below the clouds (Kaspi et al., 2013) and putting constraints on the interior models and linking it with the deep atmosphere.

5.1 Formation theories

The most accepted scenario to explain the formation of the giant planets is the core accretion model, where the planets grow first their cores and then, once they reach a critical core mass, start accreting gas and forming their gaseous envelopes (Pollack et al., 1996). There are different theories to explain how the core was first formed, that can be either by accreting planetesimals, bodies of some km in size (e.g. Alibert et al., 2005), or by pebbles of some mm to cm in size (e.g. Lambrechts and Johansen, 2014). Regarding their gaseous envelope, once the critical core mass is reached, the giant planets start accreting gas in a runaway fashion, and one of the long standing questions in the case of Uranus and Neptune is how to stop such gas accretion to prevent them of accreting a massive gaseous envelope and becoming gas giants. One of the ideas to solve this problem suggests that, in a planetesimal-driven scenario, the planets formed in a region with a smaller density of solids when compared to where Jupiter and Saturn were formed. Their cores therefore grew slowly enough for the protoplanetary disk to be almost dissipated by the time the protoplanets started the gas accretion phase. This is why they are sometimes referred as “failed giants” (Pollack et al., 1996; Helled et al., 2014). Other ideas require fine tuning of the models to prevent the planets of entering the gas accretion mode (Freikh and Murray-Clay, 2017).

The other theory to explain the formation of these planets is the disk instability. According to this scenario, clumps formed in the protosolar disk due to gravitational instabilities that gave rise to the giant planets. Uranus and Neptune could have been formed in this scenario if there was substantial gaseous mass loss in the disk caused by tidal stripping or photo-evaporation (see Helled and Bodenheimer 2014 and references therein).

Given the different possible scenarios and competing theories, interior model calculations are crucial to disentangle these competing scenarios, and thus better understand the formation and evolution of these planets.

5.2 Internal Structure of Uranus and Neptune

Interior models are constructed assuming hydrostatic, thermodynamic, mass and energy conservation, solving the following set of differential equations:

$$\frac{\partial P}{\partial r} = -\rho g \quad (6)$$

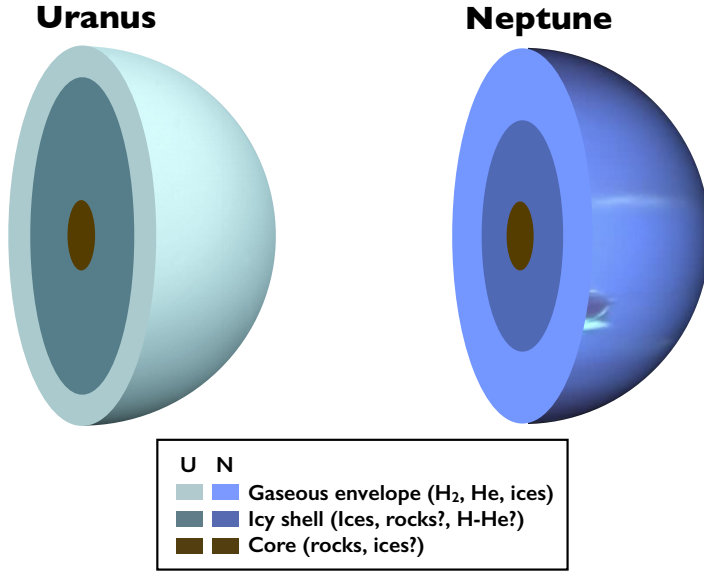


Fig. 4 Schematic view of Uranus and Neptune's interior structures.

$$\frac{\partial T}{\partial r} = \frac{\partial P}{\partial r} \frac{T}{P} \nabla_T \quad (7)$$

$$\frac{\partial m}{\partial r} = 4\pi r^2 \rho \quad (8)$$

$$\frac{\partial L}{\partial r} = 4\pi r^2 \rho \left(\dot{\epsilon} - T \frac{\partial S}{\partial t} \right) \quad (9)$$

with P the pressure, r the radius, ρ the density, g the gravitational acceleration, T the temperature, m the mass, L the planet luminosity and S its entropy.

Given the poor gravity constraints for these planets (see Table 5), one of the major obstacles found when modeling their interiors and constraining the ice-to-rock ratio is the significant degeneracies in their potential composition (Podolak et al., 1991; Hubbard et al., 1995; Baraffe et al., 2014). Some of the structure models for Uranus and Neptune use three fully adiabatic layers (a rocky core, an icy shell and a gaseous envelope) and *ab initio* equations of state (EOS) (Nettelmann et al., 2013). Nevertheless, other methods using no pre-established assumption regarding the structure or equations of state (e.g. Marley et al., 1995; Helled et al., 2011) also proved to be useful. All these approaches find that the heavy element concentration increases towards the planetary centre, as shown by Fig. 4. Note that Fig. 4 is a schematic representation where there are sharp boundaries between the different layers, but a more realistic idea is to consider a gradient of heavy elements and change in composition towards the interior (Helled and Guillot, 2018) (see also Section 5.3). More specific values for the metallicities in the gaseous envelope and the icy shell can be found in Fig. 5, which

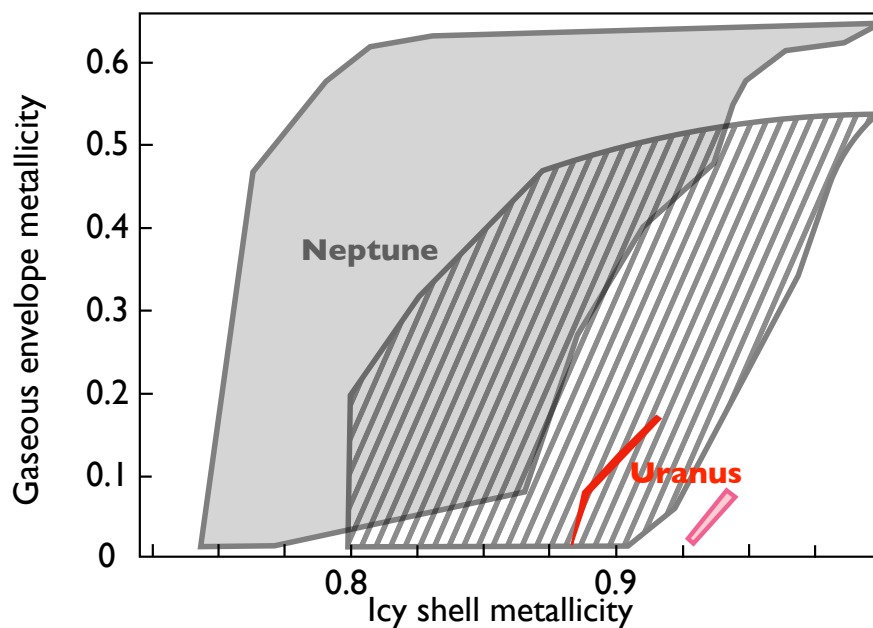


Fig. 5 Heavy elements mass fraction in the icy shell vs. the gaseous envelope. Structure models solutions for Uranus models are shown in red and for Neptune in grey (dashed). Models with a modified shape and rotation data for Uranus (pink) and Neptune (solid grey) are also shown. Adapted from Nettelmann et al. (2013).

shows results found by Nettelmann et al. (2013). As seen in Fig. 5, there are still big uncertainties in the internal structure of these planets. Some of the uncertainties are related to the fact that the core mass, the ice-to-rock ratio, the equations of state of mixtures of materials, the pressure of separation between the different layers, the depth of the winds and extent of differential rotation and the extent of compositional gradients, are highly unknown for these planets. Because the observational data are crucial to tackle these degeneracies, a more accurate determination of the gravity field and a proper characterization of the atmospheres of Uranus and Neptune are needed to get a better knowledge of their interior structures.

5.3 Remaining questions and challenges for the future

Despite the substantial progress in the modeling of planetary interiors in the last decades, there are still several unsolved questions regarding the nature of Uranus and Neptune. One of the most important parameters when modeling the interior of these planets is EOS. In the last decade, there has been great progress in this area, with new EOS published for hydrogen and helium (Militzer and Hubbard, 2013; Becker et al., 2014; Chabrier et al., 2019) and also in heavier material such as water (Nettelmann et al., 2008; Mazevet et al., 2019). Nevertheless, disagreement between the different EOS still cause differences in the internal structure of these planets (e.g. Miguel et al. 2016 for Jupiter), and better constraints on EOS not only of individual elements but also in mixtures, together with higher pressure experiments could deeply improve interior structure models. Another important aspect of the interior modeling

is the energy transport mechanism. The source of the different cooling rates of the planets is still unsolved. Better modeling, especially with potentially non-adiabatic models and a more realistic distribution of heavy elements in the interior, could help unveiling this story (Helled and Guillot, 2018; Vazan and Helled, 2020). Last but not least, we need to understand the bulk composition of these planets: are they really formed by ices or do they have a substantial amount of rocks in their interiors? And how are these heavy elements distributed? These are questions that are far from being solved.

When thinking of formation mechanisms, there are still several key questions that remain open: Where in the primitive nebula were Uranus and Neptune formed? Was pebble accretion or planetesimal accretion the primary mechanism that formed their cores? What are the mechanisms at play regarding gas accretion? What is the enrichment of the gaseous envelope and the radial distribution of heavy elements during the planet formation and subsequent evolution? Understanding the connection between the atmosphere, interior and link with formation of these planets is still incomplete and one of the big challenges in planetary science for the future. New studies on the deposition of heavy elements in the forming giant planet (Valletta and Helled, 2019) and recent results in exoplanet studies indicate that measurements of the envelope metallicities are relevant diagnostics of the bulk metallicity (Thorngren and Fortney, 2019). Measurements from the Earth, but more importantly, at least for the gravity data and bulk composition, future space missions to Uranus and Neptune carrying in situ probes will provide constraints to reduce the degeneracies in calculations towards a better understanding on the atmosphere-interior connection, on the internal structure and ultimately the history of these worlds.

6 Conclusion

An entry probe is the only means to measure the deep abundance of a number of species of key importance, notably the noble gases. These can put significant constraints on formation of Uranus and Neptune (Mousis et al., 2018). The difficulty with those cold distant worlds lies in the condensation of some key species, like CH_4 , and to a more critical extent, H_2S , NH_3 , and H_2O , which render their direct in situ measurement complicated, or even impossible.

Designing a probe that would reach the 40-50 bar level and return data to measure not only He/H (and other noble gases) and C/H, but also N/H and S/H, will be very challenging in the current timeframe (possible launch dates range from 2029 to 2034, Simon et al. 2020). The coupling of high resolution mass spectrometry ($m/\Delta m > 4000$) with accurate temperature-pressure measurements with thermochemical modeling at 10 bar is thus an interesting combination to infer the deep elemental abundances of condensable species not reachable by a shallow probe, like H_2O , NH_3 and H_2S , in the ice giants.

The results of such an entry probe, combined with a better knowledge of gravity moments and magnetic field obtained from an orbiter, will undoubtedly result in major breakthroughs in our understanding of the formation and evolution of the ice giants of our Solar System, Uranus and Neptune.

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