Influence of the C/O ratio on titanium and vanadium oxides in protoplanetary disks

M. Ali-Dib\textsuperscript{1}, O. Mousis\textsuperscript{1}, G. S. Pekmezc\textsuperscript{2}, J. I. Lunine\textsuperscript{3}, N. Madhusudhan\textsuperscript{4} and J.-M. Petit\textsuperscript{1}

\begin{itemize}
  \item \textsuperscript{1} Institut UTINAM, CNRS-UMR 6213, Observatoire de Besançon, BP 1615, 25010 Besançon Cedex, France e-mail: mdib@obs-besancon.fr
  \item \textsuperscript{2} Dipartimento di Astronomia, Universita’ di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy
  \item \textsuperscript{3} Center for Radiophysics and Space Research, Space Sciences Building, Cornell University, Ithaca, NY 14853, USA
  \item \textsuperscript{4} Department of Physics and Department of Astronomy, Yale University, New Haven, CT 06511, USA
\end{itemize}

Received 26/04/2013; accepted 12/11/2013

ABSTRACT

Context. The observation of carbon-rich disks have motivated several studies questioning the influence of the C/O ratio on their gas phase composition in order to establish the connection between the metallicity of hot-Jupiters and that of their parent stars. 

Aims. We propose a method that allows the characterization of the adopted C/O ratio in protoplanetary disks independently from the determination of the host star composition. Titanium and vanadium chemistries are investigated because they are strong optical absorbers and also because their oxides are known to be sensitive to the C/O ratio in some exoplanet atmospheres.

Methods. We use a commercial package based on the Gibbs energy minimization technique to compute the titanium and vanadium equilibrium chemistries in protoplanetary disks for C/O ratios ranging from 0.05 to 10. Our calculations are performed for pressures in the $10^{-6}$–$10^{-2}$ bar domain, and for temperatures ranging from 50 to 2000 K.

Results. We find that the vanadium nitride/vanadium oxide and titanium hydride/titanium oxide gas phase ratios strongly depend on the C/O ratio in the hot parts of disks ($T \geq 1000$ K). Our calculations suggest that, in these regions, these ratios can be used as tracers of the C/O value in protoplanetary disks.

Key words. protoplanetary disks – stars: abundances – astrochemistry – planets and satellites: formation – planets and satellites: composition – stars: atmospheres

1. Introduction

The recent detection of carbon-rich planets (hereafter CRPs), with C/O ratios $\geq 1$ in their envelopes [Madhusudhan et al. (2011a)], have stimulated research on their physical properties and the scenarios that may lead to their formation (Madhusudhan et al. 2011b; Oberg et al. 2011; Mousis et al. 2012). Carbon-rich disks have also been observed in the last years (Roberge et al. 2011a; ¨Oberg et al. 2011; Mousis et al. 2012). Carbon-rich planets (hereafter CRPs) could have formed in a zone of the disk where carbonaceous matter dominates, rather than water ice. All these models have been investigated by Madhusudhan et al. (2011b). These authors retrieved the composition of the protoplanetary disk from that of planetesimals accreted during WASP 12b’s formation and needed to match the observed volatile abundances in the planet’s atmosphere. They concluded that the C/O ratio of 1 observed in WASP 12b requires a substantial oxygen depletion in the disk (factor of $\sim 0.4$). The same approach was used by Mousis et al. (2012) to propose the formation of Jupiter through the accretion of condensed volatiles in the cold outer part of an oxygen-depleted primordial nebula. This scenario reproduces the measured Jovian elemental abundances at least as well as the hitherto canonical model of Jupiter formed in a disk of solar composition. The resulting O abundance in Jupiter’s envelope is then moderately enriched by a factor of $\sim 2 \times$ solar (instead of $\sim 7 \times$ solar) and is found to be consistent with values predicted by thermochemical models of the atmosphere. This model suggests that water ice might have been distributed inhomogeneously beyond the snowline in the primordial nebula. Alternatively, it has been proposed that the envelopes of CRPs could be formed from an oxygen-depleted gas from the nebula. In this case, the oxygen depletion would result from the water condensation and incorporation at earlier epochs in the building blocks of the planetary cores (Oberg et al. 2011). However, this scenario predicts that the abundances of carbon, nitrogen, and other ultraviolet gases are solar in the envelopes of Hot-Jupiters and is not found consistent with the supersolar abundances measured at Jupiter. Interestingly, another scenario proposed by Lodders (2004) suggests that Jupiter or CRPs could have formed in a zone of the disk where carbonaceous matter dominates, rather than water ice. All these models

1 Fractional abundance with respect to H$_2$
and observations outline a non trivial relation between the C/O ratios of the host stars, their protoplanetary disks and eventually their planets. For this reason it is important to establish a reliable probe of this ratio.

Here we suggest that the sampling of the abundances of titanium– and vanadium–bearing minerals could allow to probe the C/O ratio in protoplanetary disks. Titanium oxide (TiO, TiO$_2$, etc) and vanadium oxide (VO, VO$_2$, etc) are strong optical absorbers. They were first observed at optical wavelengths in M-type stars (Merrill et al. 1962). Since then, these molecules have been detected in various astrophysical environments. TiO and TiO$_2$ have been observed at sub-millimeter wavelengths in the circumstellar envelope of YY Canis Majoris (Kaminski et al. 2013). Moreover, TiO and VO have been identified around protostars in optical emission bands (Hillenbrand et al. 2012) and also in the infrared emission spectrum of S-type star atmospheres (Smolders et al. 2012). Recently, TiO and VO have been proposed to be the cause of the thermal inversions observed in several highly irradiated hot-Jupiters (Hubeny et al. 2003; Fortney et al. 2008) in which the determination of the C/O ratio is possible (Madhusudhan 2012). However, it has been found that an implausible eddy coefficient value is needed for the occurrence of the TiO/VO induced thermal inversion (Spiegel et al. 2009; Knutson et al. 2010). The effect of C/O on the abundances of TiO and VO in the atmospheres of hot Jupiters has been investigated by Madhusudhan (2012) who found that C/O = 1 leads to severe depletions in TiO and VO in the atmospheres of CRPs. On the other hand, a recent HST observation of the hot Jupiter WASP 19b shows that this planet has no or low levels of TiO with a moderate C/O ratio, suggesting that this lack of observable TiO is possibly due to rainout or breakdown from stellar activity (Husson et al. 2013). Another recent study also reports that all stars with TiO emission exhibit a low C/O ratio (Smolders et al. 2012). Given the similarities that exist between the atmospheres of giant planets and the gas phase of protoplanetary disks (some common temperature and pressure ranges, H$_2$-dominated compositions, dynamical effects), the influence of the C/O ratio on Ti and V chemistries in disks deserves to be investigated.

In Section 2, we present the chemical model used to relate TiO and VO abundances to C/O for a large range of temperatures and pressures. Section 3 is devoted to the presentation of our major results and to their comparison with observations. Results obtained for some important volatile species are also included. Conclusions are given in Section 4.

2. Computing the chemistries of gas and solid phases in protoplanetary disks

In order to obtain the disk solid and gaseous composition, we use the HSC chemistry commercial package. It is based on the Gibbs energy minimization method, originally developed by White et al. (1958). In this method, the calculation of phase equilibrium is made by minimizing the Gibbs free energy of the system, at constant temperature $T$ and pressure $P$, with respect to the number of moles of each component in each phase $n_i^k$. For a system with $NP$ phases and $NC$ components, we have

$$G = \sum_{k=1}^{NP} \sum_{i=1}^{NC} n_i^k \mu_i^k,$$

where $n_i^k$ and $\mu_i^k$ are the number of moles and the chemical potential of component $i$ in phase $k$, respectively. The chemical potential is a function of the composition of phase $k$ at temperature $T$ and pressure $P$ (Rossi et al. 2009). This method for equilibrium chemistry calculations assumes local thermodynamical equilibrium. Several codes, based on this approach, have been developed in the last decades. The most known are SOLGASMIX (Sharp & Huebner 1990), NASA’s CEA and the HSC Chemistry package developed by Outotec Research. In this work we opted to use the HSC Chemistry package because its built-in database of minerals is the largest existing one. It contains for example ~75 Ti bearing minerals.

In our equilibrium calculations, usually one favors a long list of elements to get the most precise results possible, and to avoid any possible hidden non linear effect from an ignored molecule. For this reason, we chose to use the entire HSC Chemistry database of elements relevant to solar elemental abundances totaling 1224 gases and solids (excluding C$_6$H$_6$ for n≥3). Once the initial list of elements and their respective abundances have been defined (see Table 1), we have selected the set of molecular species that form from these elements (with null initial abundances). We made the reasonable assumption that the gas phase composition of the disk under study has the same elemental composition as that of the host star. Here, all our calculations are based on the solar photosphere abundances taken from Asplund et al. (2009).

| Element | Solar abundance in Kmol | X/H$_2$ |
|---------|-------------------------|---------|
| H       | 1.00 × 10$^{-4}$        |         |
| He      | 9.55 × 10$^{-5}$        | 1.90 × 10$^{-1}$ |
| N       | 7.41 × 10$^{-8}$        | 1.48 × 10$^{-4}$ |
| O       | 5.37 × 10$^{-10}$       | 1.07 × 10$^{-3}$ |
| C       | 2.95 × 10$^{-9}$        | 5.90 × 10$^{-4}$ |
| Na      | 1.91 × 10$^{-8}$        | 3.80 × 10$^{-7}$ |
| Mg      | 4.37 × 10$^{-10}$       | 4.60 × 10$^{-8}$ |
| Al      | 3.09 × 10$^{-10}$       | 6.00 × 10$^{-6}$ |
| Ni      | 1.88 × 10$^{-8}$        | 3.60 × 10$^{-7}$ |
| Si      | 3.55 × 10$^{-10}$       | 7.00 × 10$^{-5}$ |
| P       | 2.82 × 10$^{-10}$       | 5.60 × 10$^{-6}$ |
| S       | 1.45 × 10$^{-10}$       | 2.90 × 10$^{-5}$ |
| Ca      | 2.40 × 10$^{-10}$       | 4.80 × 10$^{-6}$ |
| Ti      | 9.77 × 10$^{-10}$       | 1.94 × 10$^{-7}$ |
| Cr      | 4.79 × 10$^{-10}$       | 9.40 × 10$^{-7}$ |
| Fe      | 3.47 × 10$^{-10}$       | 6.80 × 10$^{-5}$ |
| V       | 9.33 × 10$^{-10}$       | 1.86 × 10$^{-8}$ |

3. Results

3.1. Influence of C/O on Ti and V chemistries

Figure 1 displays the abundances of solid and gaseous Ti and V bearing species, for C/O = 0.55 and 1. In order to get C/O = 1 in the disk’s gas phase, we opted to decrease the initial abundance of oxygen (Madhusudhan et al. 2011B; Mousis et al. 2012). For the sake of clarity, we just represented the abundances of species that are at most 10 times lower than the most abundant one, as more than 1,000 abundances of species are simultaneously computed. All our calculations are made for a total gas pressure of 10$^{-4}$ bar, which corresponds to the average pressure in the inner disk.

2 http://www.grc.nasa.gov/WWW/CEAWeb/ceaHistory.htm
3 http://www.outotec.com/en/Products–services/HSC-Chemistry
4 † For C/O = 1, we used O/H$_2$ = C/H$_2$ = 5.90 × 10$^{-4}$.
As a function of the temperature for C/O bar as a function of the temperature for C/O.

Fig. 1: (a) Abundances of titanium-bearing solid and gaseous compounds computed at equilibrium at a disk’s pressure of $10^{-4}$ bar as a function of the temperature for C/O = 0.55. Solid lines are for solid species and dashed lines for gases. (b) Same as (a) but for C/O = 1. (c) Abundances of vanadium-bearing solid and gaseous compounds computed at equilibrium at a disk’s pressure of $10^{-4}$ bar as a function of the temperature for C/O = 0.55. (d) Same as (c) but for C/O = 1.

Figures 2 to 4 show the evolution of the gas phase abundances of TiO, TiH, VO and VN as a function of temperature for C/O values of 0.55 and 1 in the disk. The abundances of these species increase with the growth of temperature at both C/O values. One can note that TiO and VO are significantly higher at lower C/O values and at high temperatures. On the other hand, TiH is more abundant at high C/O irrespective of temperature and the abundance of VN only weakly depends on the C/O value.

Figure 5 represents the VN/VO and TiH/TiO gas phase ratios computed as a function of C/O ranging between 0.1 and 10 in protoplanetary disks. As mentioned above, the C/O ratio is set to the desired value by varying the oxygen abundance. Computations have been conducted at 1700 K and at disk pressures of $10^{-6}$, $10^{-4}$ and $10^{-2}$ bar. These molecules have been selected because their abundance ratios heavily depend on the regions ( ~ 1-2 AU) of protoplanetary disks [Hueso & Guillot 2005]. For C/O = 0.55 and in the case of Ti chemistry, we note the dominance of the solid (s) mineral $K_2TiO_3(s)$ at all temperatures except in the range 100-200 K where $4CaO_3TiO_2(s)$ is the most abundant. At temperatures higher than 1600 K, we note the existence of substantial amounts of the gaseous (g) compounds TiO, TiH, VO and VN. In the case of V chemistry, $Na_2V_2O_7(s)$ and VO(s) are the most abundant minerals at temperatures lower than ~1500 K and the gaseous compounds VO(g), VO(g), and V(g) become dominant at higher temperatures. For C/O = 1, and in the case of Ti-bearing solids, $K_2TiO_3(s)$ now dominates in the 1500–1600 K interval and also at temperatures lower than ~1200 K, except in the 100–200 K interval where $4CaO_3TiO_2(s)$ is the most abundant species. TiC(s) and TiH(g) become the most abundant solid species in the 1200–1500 K and 1650–2000 K temperature ranges, respectively. In the case of V-bearing solids, $Na_2V_2O_7(s)$ becomes dominant only for temperatures lower than ~800 K. Solid VO(s) now exists at temperatures centered around ~800 K and its maximum abundance is 4 times less than in the first case. At this value of C/O, we note that the abundances of gaseous VO(g), VO(g) and TiO(g) are ~ one thousand times lower than in the former case, making them not visible in the panels of Fig. 1. Our calculations then suggest that Ti and V oxides present in the gas phase are orders of magnitudes more abundant in the solar C/O case than in the C/O = 1 case. It should be noted that Ti and V bearing minerals were studied in a large number of meteorites (Nittler et al. 2008, Rubin 1997, Lodders 2006, Simon et al. 2007).

The details of the used disk model are presented in section 3.3.
value of the adopted C/O ratio. Gaseous VN also exists in the same temperature range as VO but its abundance is too low (by ~4.5 orders of magnitudes in both C/O cases) to make it visible in Fig. 1. At the considered pressures, there is a strong dependence of VN/VO and TiH/TiO gas phase ratios with the adopted value of C/O ratio. For example, an increase of the C/O ratio from 0.3 to 2 induces a steep increase of the TiH/TiO and VN/VO ratios by ~10 orders of magnitudes at $P = 10^{-4}$ bar, respectively. Between C/O = 0.1 and 0.3 and beyond C/O = 2, the two molecular ratios increase slightly linearly.

Our calculations suggest that these ratios can be used as tracers of the C/O ratio in protoplanetary disks. It is worth mentioning that calculations similar to those presented above have been done by varying the C abundance and fixing the O abundance, i.e. the opposite approach, in order to investigate the existence of any hidden non linear effect. The results obtained were found almost identical to those presented above, with a slight increase in the abundances of C bearing species for C/O>0.5. One should note that among the four species, VN has the lowest abundance for solar C/O, making its detection more critical than the other molecules.

### 3.2. Influence of the disk’s pressure

To quantify the effect of pressure on the Ti and V chemistries, we performed the same calculations as above but for total disk pressures in the $10^{-6}$–$10^{-2}$ range, and for C/O = 0.55 and 1. Results for TiO, TiH, VO and VN are presented in Figure 3. The main conclusion is that a variation of pressure over several orders of magnitude induces some non linear effects on the abundances of the considered species. Despite the fact that it is difficult to describe clear trends for these variations, we note that at $P = 10^{-2}$ bar and for C/O = 0.55, the abundances of all four gaseous species are depleted by several orders of magnitude with respect to $10^{-3}$ bar, except for the very high temperatures (~1900–2000 K). This depletion is balanced by an important increase in the abundance of solid TiO$_2$. At the same pressure, we also note that the abundance of TiO is more important for C/O = 1 than for C/O = 0.55 at disk temperatures $\leq$ 1800 K. This last effect is also present at $P \sim 10^{-5}$–$10^{-3}$ bar and temperatures $\leq$ 1500 K, but is absent at $10^{-6}$ bar. At this latter pressure, we also note a decrease in the abundances of most of species over two orders of magnitude at C/O = 0.55, balanced by an increase in the abundances of solid minerals (mostly FeTiO$_3$). This decrease is restricted to the abundances of TiH and VN at C/O = 1. Figure 4 shows that the pressure variation can affect the abun-

![Fig. 2: Gas phase equilibrium abundances of TiO, TiH, VO and VN computed at a disk pressure of $10^{-4}$ bar for C/O = 0.55 (dashed lines) and C/O = 1 (solid lines).](image1)

![Fig. 3: VN/VO$_2$ and TiH/TiO gas phase ratios as a function of C/O in protoplanetary disks for pressures ranging from $10^{-6}$ to $10^{-2}$ bar and for $T = 1700$ K.](image2)
dances of TiO, TiH, VO and VN but it is not certain that a significant pressure drop can alter their detection. As mentioned below, TiO is detectable in some circumstellar environments with pressures of $\sim 10^{-4}$ bar and the abundance of this species computed at $10^{-6}$ bar is quite close.

We also computed the TiH/TiO and VN/VO ratios as a function of pressure. The results are presented in Figure 3. The same general trend as in Figure 1 is found for the other investigated pressures, but with some slight differences. In particular, with increasing disk pressure, the TiH/TiO and VN/VO ratios increase by 2 orders of magnitude for C/O ratios $\ll 1$. On the other hand, the ratios will decrease by 2 orders of magnitude with increasing disk pressure for C/O ratios $\gg 1$.

3.3. Comparison with observations

In this section, we are going to investigate the observability of TiO, and compare our model to observations.

Using Spitzer infrared data, Smolders et al. (2012) derived a TiO column density of $\sim 10^{17}$ cm$^{-2}$ in the circumstellar environment of the star NP Aurigae at temperatures higher than 1900 K [Kaminski et al. (2013)] also reported the observation of TiO and TiO$_2$ at sub-millimetric wavelengths in the stellar environment of VY Canis Majoris, with column densities of $\sim 10^{14}$ cm$^{-2}$ for both species, but for $T = 1000 \pm 870$ K. On the other hand, our calculations predict TiO abundances of $\sim 1.0 \times 10^{-8}$ and $\sim 1.0 \times 10^{-11}$ for respectively $T$ = 1800 K and $T$ = 1600 K, at $P = 10^{-4}$ bar (typical gas pressure in circumstellar environments) in the C/O = 0.5 case (see Figure 2). For a typical scale height $H \sim 5.0 \times 10^{-3}$ AU, we find column densities $N_{\text{TiO, 1600K}} = \frac{x_{\text{TiO}} \rho_{\text{disk}}}{M_{\odot}} \sim 2.9 \times 10^{-7}$ cm$^{-2}$ and $N_{\text{TiO, 1800K}} \sim 2.9 \times 10^{-14}$ cm$^{-2}$ for the computed TiO abundance. $N_{\text{TiO, 1600K}}$ is almost equal to the column density observed by Smolders et al. (2012) and $N_{\text{TiO, 1800K}}$ is very close to the value derived by Kaminski et al. (2013). Hence, it should be possible in principle to observe TiO in the hot inner disk. The TiO$_2$ abundance in our calculations is $\sim$ twice lower than that of TiO for $T \geq 1600$ K, a result also compatible with Kaminski et al. (2013).

Following the referee’s request, we also compared our equilibrium calculations to observations of volatile species in protoplanetary disks. To calculate the column densities, we used the one-dimensional $\alpha$-disk model of Hueso & Guillot (2005) to derive the thermodynamic parameters (temperature and scale height) needed. The model follows the evolution of a cloud-disk-star system with the following initial conditions (see Hueso & Guillot (2005) for details): $\alpha = 0.01$, $M_{\text{cloud}} = 1 M_{\odot}$, $\Omega_{\text{cloud}} = 3.0 \times 10^{-6}$ rad s$^{-1}$, $T_{\text{cloud}} = 10$ K, $M_{\text{disk, 1600K}} = 0.1 M_{\oplus}$ and $T_{\text{disk, 1600K}} = 4000$ K. We chose the model at $10^5$ years.

Carr & Najita (2011) determined an average column density for HCN of $\sim 6 \times 10^{10}$ cm$^{-2}$ at $T \sim 700$ K from Spitzer observations of inner regions of six different T-Tauri disks. However, this value is model dependent since it is defined by Carr & Najita (2011) as the average averaged from two different (optically thin and optically thick) disk models. In the case of the optically thin disk model, these authors found $N \sim 4 \times 10^{11}$ cm$^{-2}$, which is one order of magnitude lower than the average column density. Since HCN is observed at $\sim 700$ K, we used the disk pressure of $\sim 10^{-3}$ bar and $H = 6 \times 10^{-2}$ AU as calculated using the employed disk model. The calculated HCN abundance for C/O = 0.55 is found to be $\sim 6 \times 10^{-11}$, corresponding to a column density of $\sim 4.2 \times 10^{14}$ cm$^{-2}$, a value within an order of magnitude from observations for thin disks. Furthermore, we computed the abundance ratio C$_2$H$_2$/HCN, which is found to be $\sim 5 \times 10^{-5}$ at these disk conditions. This ratio is lower by several orders of magnitude compared to the value found by Carr & Najita (2011) ($\sim 10^{-7}$ to $10^{-10}$). However, this important difference might be due to non-equilibrium effects (chemical kinetics, photochemistry) not taken into account in our model. For the sake of completeness, we also presented in Fig. 3 the fractional abundances with respect to H$_2$ of some major volatiles ($H_2O$, CO, CO$_2$, CH$_4$ and OH) that have been observed in disks and that are believed to be important in the planetary formation process. Another interesting observable for disk evolution and planetary formation is the HCN/H$_2$O ratio, since Carr & Najita (2011) proposed that it is correlated to the value of C/O ratio in T-Tauri disks. In order to illustrate this correlation, we computed the HCN/H$_2$O ratio as a function of C/O in disks. The results, displayed in Fig. 3, show that the HCN/H$_2$O ratio increases as a function of the C/O ratio, with a particularly sharp slope for C/O$\geq 2$. Finally, it is worth mentioning that our calculations performed in the C/O = 1 case are consistent with the conclusions of Lodders (2006) who finds that TiC (observed in meteorites) is formed naturally at equilibrium under these conditions.

4. Conclusions and prospects

We have performed calculations of equilibrium chemistry describing the fate of Ti- and V-bearing species in protoplanetary disks as a function of the C/O ratios, and using the Gibbs energy minimization method. This allowed us to find that the VN/VO and TiH/TiO gas phase ratios strongly depend on the degree of the C/O ratio in the hot parts of disks. Gaseous TiO and VO have been detected at optical wavelengths in the 1000–2000 K range in stellar envelopes and photospheres [Hillenbrand et al. (2012)] Smolders et al. (2012)] at pressure regimes very close to those encountered in the inner part of protoplanetary disks [Asplund et al. (2004)].

The results presented in this study are based on equilibrium calculations. We opted to neglect the influence of photochemistry and of turbulent diffusion for the following reasons: the proposed observations will be mainly in millimeter-wavelength, probing deep in the midplane of the disk, away from the surface photochemically active zone. The effects of turbulent diffusion are however less straightforward. Since we did not find any kinetic data concerning the gas phase chemistries of Ti- and V-bearing species, we have not been able to quantify the quenching effects caused by the different chemical and dynamical timescales if any. Experimental studies of the kinetic properties of the Ti- and V-bearing species will be needed to investigate further these effects.

Finally, observations of gaseous TiO and VO in disks must be spatially resolved in order to eliminate any confusion from stellar emissions. Such a high resolution should be attained with the new generation sub-millimetric instruments such as ALMA, from which several spatially resolved observations of different types of disks have been recently reported with angular resolutions sufficient to resolve the inner disks, where the molecules considered in the present work are observable [van Dishoeck & Jørgensen (2008)] [Krumholz et al. (2007)]. However, the midplane of the inner disk might be inaccessible to these instruments if dust extinction is significant at sub-mm/mm wavelengths. Observations of TiO emission in the 10 micron spectral region from circumstellar environments around AGB stars will be more sensitive (by an order of magnitude[6]), and with higher sensitivities.

---

[6] The reason why it is not visible in Fig. 1.

[7] http://www.stsci.edu/jwst/science/sensitivity
Fig. 4: Abundances of gaseous TiO, TiH, VO and VN for total disk pressures of $10^{-2}$ bar (a), $10^{-3}$ bar (b), $10^{-4}$ bar (c), $10^{-6}$ bar (d). Solid and dashed lines represent the C/O = 1 and 0.55 cases, respectively.

spatial resolution than, those of Spitzer. Detection or a better upper limit by JWST of TiO$_2$ and other titanium oxides not seen by Spitzer (Smolders et al. 2012) will allow testing of the chemical calculations presented here. The detection of TiO and TiO$_2$ in the cooler region of late-type stars, implies that other small transition metal–bearing molecules such as VO, might be found with sensitive interferometers in the submillimeter wave band (Kaminski et al. 2013). It is interesting to note that one might prefer the VN/VO$_2$ ratio over the one we chose above, since the VO$_2$ molecule exists in gaseous form at relatively lower temperatures than VO (VO$_2$ peaks at 1600 K, VO at 1850 K; see panel (c) of Fig. 1), and thus farther in the disk from the host star, a feature that might allow the region to be better resolved, decreasing the chance of stellar contamination.

Acknowledgements. We thank an anonymous Referee for his useful comments that helped us in improving our manuscript. O. Mousis acknowledges support from CNES. JIL acknowledges support from the JWST program through a grant from NASA Goddard. We thank T. Guillot and R. Hueso for having provided us with their accretion disk model. We thank A. Rajpurohit for his useful comments on stellar temperatures.

References

Asplund, M., Grevesse, N., Sauval, A. J., Allende Prieto, C., & Kiselman, D. 2004, A&A, 417, 751
Asplund, M., Grevesse, N., Sauval, A. J., & Scott, P. 2009, ARA&A, 47, 481
Cyr, K. E., Sears, W. D., & Lunine, J. I. 1998, Icarus, 135, 537
Carr, J. S., & Najita, J. R. 2011, ApJ, 733, 102
Croat, T. K., Bernatowicz, T., Amari, S., Messenger, S., & Stadmann, F. J. 2003, Geochim. Cosmochim. Acta, 67, 4705
Cyr, K. E., Sears, W. D., & Lunine, J. I. 1998, Icarus, 135, 537
De Marco, O., Crowther, P. A., Barlow, M. J., Clayton, G. C., & de Koter, A. 2001, MNRAS, 328, 527
Fortney, J. J., Lodders, K., Marley, M. S., & Freedman, R. S. 2008, ApJ, 678, 1419
Johnson, T. V., Mousis, O., Lunine, J. I., & Madhusudhan, N. 2012, ApJ, 757, 192
Harrington, J., & Weisshaar, J. C. 1992, J. Chem. Phys., 97, 2809
Hillenbrand, L. A., Knapp, G. R., Pudgett, D. L., Rebull, L. M., & McGeehee, P. M. 2012, AJ, 143, 37
Hrivnak, B. J., Lu, W., Maupin, R. E., & Spitzbart, B. D. 2010, ApJ, 709, 1042
Hubeny, I., Burrows, A., & Sudarsky, D. 2003, ApJ, 594, 1011
Hueso, R., & Guillot, T. 2005, A&A, 442, 703
Huitson, C. M., Sing, D. K., Pont, F., et al. 2013, MNRAS, 434, 3252
Guillot, T., & Hueso, R. 2006, MNRAS, 367, L47
Kaminski, T., Gottlieb, C. A., Menten, K. M., et al. 2013, A&A, 551, A113
Knutson, H. A., Howard, A. W., & Isaacson, H. 2010, ApJ, 720, 1569
Krumholz, M. R., Klein, R. I., & McKee, C. F. 2007, ApJ, 665, 478
Fig. 5: (a) Fractional abundances of selected volatile species for C/O = 0.55 as a function of temperature (b) HCN/H$_2$O ratio as a function of the C/O ratio. All calculations were done at P = 10$^{-4}$ bar for T = 700 K.

Lodders, K. 2004, ApJ, 611, 587
Lodders, K. 2006, ApJ, 647, L37
Madhusudhan, N., Harrington, J., Stevenson, K. B., et al. 2011a, Nature, 469, 64
Madhusudhan, N., Mousis, O., Johnson, T. V., & Lunine, J. I. 2011b, ApJ, 743, 191
Madhusudhan, N. 2012, ApJ, 758, 36
Marboeuf, U., Mousis, O., Ehrenreich, D., et al. 2008, ApJ, 681, 1624
Merrill, P. W., Deutsch, A. J., & Keenan, P. C. 1962, ApJ, 136, 21
Mousis, O., Lunine, J. I., Madhusudhan, N., & Johnson, T. V. 2012, ApJ, 751, L7
Nittler, L. R., Alexander, C. M. O., Gallino, R., et al. 2008, ApJ, 682, 1450
Øberg, K. I., Murray-Clay, R., & Bergin, E. A. 2011, ApJ, 743, L16
Ramirez, R. 2011, IAU Symposium, 280, 188P
Roberge, A., Feldman, P. D., Weinberger, A. J., Deleuil, M., & Bouret, J.-C. 2006, Nature, 441, 724
Rossi, L. Cardozo-Filho, & R. Guirardello 2009, Fluid Phase Equilibria, Volume 278, Issues 1–2, Pages 117-128
Rubin, A. E. 1997, Meteoritics and Planetary Science, 32, 231
Sapryk, A. D., Eiden, G., Harrington, J. E., & Weisshaar, J. C. 1989, J. Chem. Phys., 90, 1415
Semeno, D., & Wiebe, D. 2011, ApJS, 196, 25
Sharp, C. M., & Huebner, W. F. 1990, ApJS, 72, 417
Simon, S. B., Sutton, S. R., & Grossman, L., 2007, Geochim. Cosmochim. Acta, 71, 3098
Smolders, K., Verhoeft, T., Neyes, P., et al. 2012, A&A, 543, L2
Spiegel, D. S., Silverio, K., & Burrows, A. 2009, ApJ, 699, 1487
van Dishoeck, E. F., & Jørgensen, J. K. 2008, Ap&SS, 313, 15
White, W. B., Johnson, S. M., & Dantzig, G. B. 1958, J. Chem. Phys., 28, 751