Astrochemistry VII – Through the Cosmos from Galaxies to Planets
Proceedings IAU Symposium No. 332, 2017
M. Cunningham, T. Millar & Y. Aikawa, eds.

doi:10.1017/S1743921317009802

Chemical evolution in planet-forming regions. Impact on volatile abundances and C/O ratios of planet-building material

Christian Eistrup[1], **Catherine Walsh**[1,2] **and Ewine F. van Dishoeck**[1,3]

[1]Leiden Observatory, Niels Bohrweg 2, 2333RA Leiden, Netherlands
email: eistrup@strw.leidenuniv.nl

[2]School of Physics and Astronomy, E C Stoner Building, University of Leeds, Leeds, UK
[3]Max-Planck-Institut für extraterrestrische Physik, P.O. Box 1312, D-85741, Garching, Germany

Abstract. Connecting the observed composition of exoplanets to their formation sites often involves comparing the atmospheric C/O ratio to a disk midplane model with a fixed chemical composition. In this scenario chemistry during the planet formation era is not considered. However, kinetic chemical evolution during the lifetime of the gaseous disk can change the relative abundances of volatile species, thus altering the C/O ratios of planetary building blocks. In our chemical evolition models we utilize a large network of gas-phase, grain-surface and gas-grain interaction reactions, thus providing a comprehensive treatment of chemistry. The results show that, if sufficient ionisation is present, then chemistry does alter the C/O ratios of gas and ice during the epoch of planet(esimal) formation. This modifies the picture of C/O ratios in disk midplanes defined simply by volatile ice lines in a midplane of fixed chemical composition. Chemical evolution thus needs to be addressed when predicting the makeup of planets and their atmospheres.

Keywords. Protoplanetary disks, Planet formation, Kinetic chemistry, Chemical composition

1. Introduction

Since the first detection of an exoplanet 22 years ago, the field of exoplanetary science has moved from detection to also characterisation. Several studies show detections of molecular absorption in the transmission spectra of exoplanet atmostpheres (Seager & Deming 2010;Snellen *et al.* 2010;Birkby *et al.* 2013;Fraine *et al.* 2014;Crossfield 2015;Sing *et al.* 2016). Atmospheric abundances of molecules such as CO and H_2O are used to infer the elemental C/O ratio of the atmospheres, which in turn points to the elemental composition of the material that went into forming the planets, in the protoplanetary disk midplanes. Thereby, a connection between observed planets and the disk midplanes where they formed can be established, shining light on planet formation.

Such a connection is, however, not straightforward to make. Several different processes take place during the evolution of the planet-forming midplanes of disks, which could all affect how, when, and from what material planets form. Such processes include dynamical effects such as grain settling from upper layers to midplane, grain growth, grain radial drift and accumulation of grains into larger bodies, and eventually into planets. These effects have been studied extensively (see e.g. Lambrechts & Johansen 2012;Alibert *et al.* 2013;Ali-Dib *et al.* 2014;Madhusudhan *et al.* 2014;Bitsch & Johansen,and references therein) and the chemical composition of the material have been considered in order to track which chemical abundances the planets are made up of.

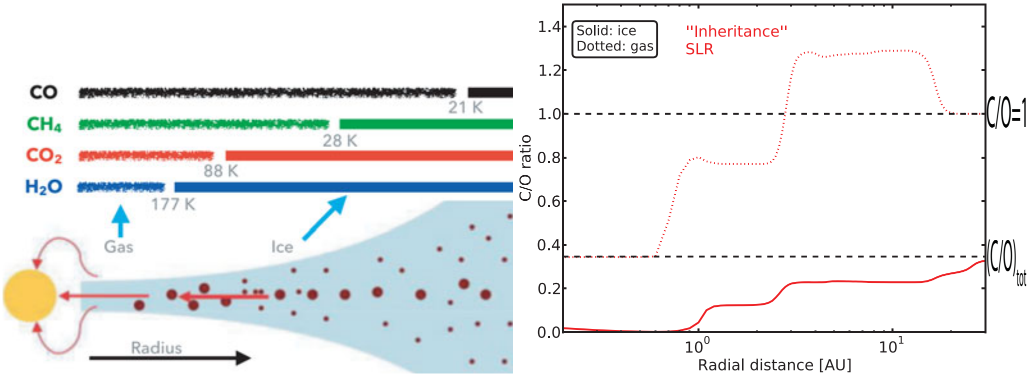

Figure 1. Left panel: modified disk illustration from Williams & Cieza (2011), showing the regions of the disk midplane (indicated by the radius) where four selected volatile species are gas or ice, with freeze-out temperatures depending on the species' binding energies. Right panel: the C/O elemental ratios of gas and ice as function of radius from Eistrup *et al.* (2016), as only defined by icelines. Dashed lines indicate C/O=1 as well as the total assumed C/O ratio of 0.34. Comparable to Fig. 1 in Öberg *et al.* (2011).

The volatile composition of the planet-forming material is usually taken to be fixed. That is, certain abundances of volatiles species such as H_2O, CO, CO_2 and CH_4 have been assumed, and depending on their binding energies (freeze-out temperatures), these species are assumed to be either in the gas-phase, or ices on grain surfaces, depending on the radial temperature profile in the disk midplane. The iceline of a species is the radius marking the transition from gas to ice for that species (see Fig. 1, left panel), and based on icelines an impression of the C/O elemental ratios in gas and ice of the midplane material can be obtained, as shown in Fig. 1, right panel.

However, most models of planet formation do not allow chemical evolution of the material. That is, chemical reactions that can alter relative abundances of the chemical species, or even produce new species, are not included in the models. This work focuses on chemical evolution in the disk midplane, and how this evolution might modify the view of a chemically static midplane with C/O ratios in gas and ice defined by icelines only.

2. Allowing chemical evolution in the disk midplane

We have used the physical structure for a disk midplane (temperature, density and ionisation level, as functions of radius) that is evolving in time from Alibert *et al.* 2013, i.e. the disk is cooling and losing mass over time. Temperature and ionisation levels at different timesteps are featured in Fig. 2. The initial disk mass is 0.1 Minimum Mass Solar Nebula (see Eistrup *et al.* 2016), and we considered radii out to 30 AU. We utilised an extensive gas-phase, gas-grain and grain-surface chemical network. The gas-phase chemistry is from the latest release of the UMIST Database for Astrochemistry (McElroy *et al.* 2013) termed RATE12. The rates for gas-grain interactions and grain-surface chemistry are calculated as described in Walsh *et al.* (2015), and references therein.

We assumed a constant gas-to-dust ratio of 100, as well as spherical grains of constant size 0.1 μm. The initial chemical abundances are assumed those from the "inheritance" scenario in Table 1 in Eistrup *et al.* (2016). A high level of ionisation (including the contribution from short-lived radionuclides and cosmic rays) is adopted. We evolve the midplane chemistry for up to 7 Myr.

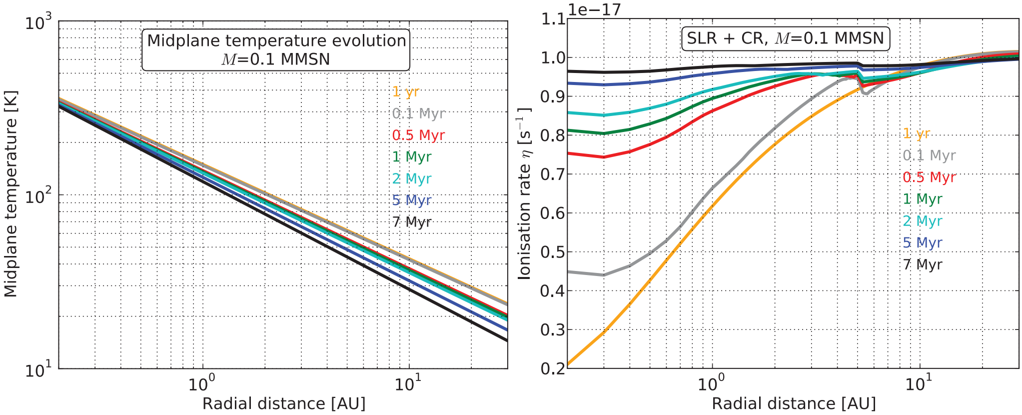

Figure 2. Midplane temperature (left) and ionisation rate (right) as functions of disk radius for different evolutionary times.

3. Effects of chemical evolution

For the conditions assumed here, in particular the high level of ionisation, large changes to the initial chemical composition are seen at all radii. Chemical evolution becomes important after a few times 10^5 yrs (which is evident at 5 AU radius as seen in Fig. 3, left panel), and continues until at least 7 Myr. By 7 Myr, chemical steady state is reached in the outer icy parts of the disk midplane (outside the O_2 iceline). This means that the fingerprint of the initial chemical abundances has been erased.

Chemical evolution changes the relative abundances of the initial species, but it also causes production of new species. Most prominently, O_2 gas is abundantly produced between the H_2O and the O_2 icelines, and HCN and C_2H_6 ices becomes important carriers of elemental carbon in the cold outer disk midplane. The changes to the chemical composition also affect the elemental carbon and oxygen ratios in gas and ice. This evolution is featured in Fig. 3, left panel. Here, the orange profile by 0.1 Myr is identical to the plot in Fig. 1 right panel, as the C/O ratio without chemical evolution, defined by icelines alone.

Fig. 3 right panel shows that chemical evolution acts to significantly lower the gas C/O ratio, so it drops from $\sim$1.2 initially to 0.3 by 7 Myr at 5 AU. Alongside that, the C/O ratio in the ice at 5 AU increases to 0.5 by 7 Myr, making the ice between 3 and 10 AU more carbon rich than the gas (opposite of the initially condition, where the gas was more carbon rich than the ice). Overall, by 7 Myr the C/O ratios in both gas and ice are below 0.5 (given that the total assumed C/O ratio is 0.34), showing that with chemical evolution included, C/O ratios may change significantly over the disk lifetime.

The results presented here suggest that coupling the chemical makeup of a disk midplane to the chemical makeup of the planets that form out of it may not be straightforward. Indeed, if planet formation lasts for longer than a few times 10^5 yrs in the disk midplane and a high level of ionisation is present, then the chemical abundances and elemental ratios in gas and ice will change alongside with planet formation. Henceforth, chemical evolution needs to be addressed when predicting the chemical makeup of planets and their atmospheres, as well as when inferring formation locations of exoplanets based on their observed atmospheric elemental ratios.

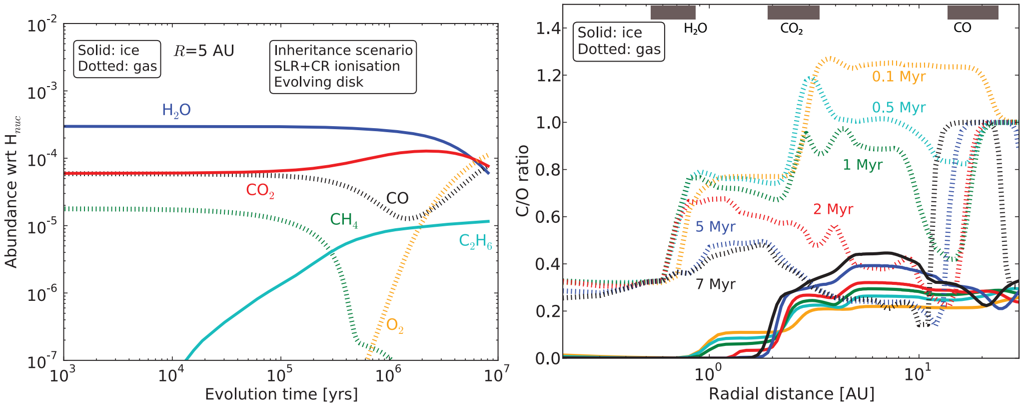

Figure 3. Left panel: time evolution of key volatile species at 5 AU in the disk midplane. Right panel: evolution of the elemental C/O ratios in gas and ice caused by the evolution in the chemistry, at different timesteps. The grey boxes in the right panel indicate the radial regions that the iceline of a volatile move over due to the evolution of the physical conditions.

References

Alibert, Y., Carron, F., Fortier, A., *et al.* 2013, *A&A*, 558, A109
Ali-Dib, M., Mousis, O., Petit, J.-M., *et al.* 2014, *ApJ*, 785, 125
Birkby, J. L., de Kok, R. J., Brogi, M., *et al.* 2013, *MNRAS*, 436, L35
Bitsch, B. & Johansen, A. 2016, *A&A*, 590, A101
Crossfield, I. J. M. 2015, *PASP*, 127, 941
Eistrup, C., Walsh, C., & van Dishoeck, E. F. 2016, *A&A*, 595, A83
Fraine, J., Deming, D., Benneke, B., *et al.* 2014, *Nature*, 513, 526
Walsh, C., Nomura, H., & van Dishoeck, E. 2015, *A&A*, 582, A88
Williams, J. P. & Cieza, L. A. 2011, *ARA&A*, 49, 67
Öberg, K. I., Murray-Clay, R., & Bergin, E. A. 2011, *ApJL*, 743, L16
Lambrechts, M. & Johansen, A. 2012, *A&A*, 544, A32
Madhusudhan, N., Amin, M. A., Kennedy, G. M. 2014, *ApJL*, 794, L12
McElroy, D., Walsh, C., Markwick, A. J., *et al.* 2013, *A&A*, 550, A36
Seager, S. & Deming, D. 2010, *AR&A*, 48, 631
Sing, D. K., Fortney, J. J., Nikolov, N., *et al.* 2016, *Nature*, 529, 59
Snellen, I. A. G., de Kok, R. J., de Mooij, , *et al.* 2010, *Nature*, 465, 1049