

Definitions		
symbol	description	unit
$z$	vertical coordinate	cm
$\epsilon_k$	abundance of element $k$ with respect to H	–
$n_i$	particle density of molecule $i$	$\text{cm}^{-3}$
$n_{\langle\text{H}\rangle}$	total hydrogen nuclei density	$\text{cm}^{-3}$
$\rho = \sum_i n_i m_i = \mu_{\text{H}} n_{\langle\text{H}\rangle} = \mu \sum_i n_i$	gas mass density	$\text{g cm}^{-3}$
$m_i$	mass of particle $i$	g
$m_k$	mass of element $k$	g
$\mu = \sum_i n_i m_i / \sum_i n_i$	mean gas particle mass	g
$\mu_{\text{H}} = \sum_k \epsilon_k m_k$	proportionality constant	g
$T$	gas temperature	K
$p = \frac{\rho}{\mu} kT = \sum_i n_i kT$	gas pressure	$\text{dyn cm}^{-2}$
$D$	diffusion coefficient	$\text{cm}^2 \text{s}^{-1}$

## 1 The Atmospheric Diffusion Problem

To simultaneously model the evolution of the chemical composition of the atmosphere and the crust of a hot rocky planet, we use the implicit/explicit time-dependent second-order diffusion solver DIFFUSE developed by Peter Woitke. At the top of the atmosphere, a modified fixed-flux boundary condition will be applied to allow for the Jeans escape of  $\text{H}_2$  and He (see Sect. 3.1), whereas at the bottom, a modified fixed-concentration boundary condition will be applied to treat the outgasing/deposition of elements from/to the crust (see Sect. 3.2). By book-keeping the element fluxed through the lower boundary, we can also predict how the crust composition changes with time.

In the planet atmosphere between these boundaries, we solve the second-order diffusion problem

$$\frac{\partial(n_{\langle\text{H}\rangle} \epsilon_k)}{\partial t} + \nabla(\vec{v} n_{\langle\text{H}\rangle} \epsilon_k) = \nabla(n_{\langle\text{H}\rangle} D \nabla \epsilon_k) . \quad (1)$$

Assuming a 1-d plane-parallel and static ( $\vec{v} = 0$ ) atmosphere, the equations to solve are

$$\frac{d}{dt}(n_{\langle\text{H}\rangle} \epsilon_k) = \frac{d}{dz} \left( n_{\langle\text{H}\rangle} D \frac{d\epsilon_k}{dz} \right) . \quad (2)$$

Assuming, in addition, a constant density structure  $n_{\langle\text{H}\rangle} = n_{\langle\text{H}\rangle}(z)$  the equations simplify to

$$\frac{d\epsilon_k}{dt} = \frac{1}{n_{\langle\text{H}\rangle}} \frac{d}{dz} \left( n_{\langle\text{H}\rangle} D \frac{d\epsilon_k}{dz} \right) , \quad (3)$$

where  $\epsilon_k(z, t)$  are the height-dependent and time-dependent element abundances in the planet atmosphere we wish to determine. We note that  $n_{\langle\text{H}\rangle} = n_{\langle\text{H}\rangle}(z)$  and  $D = D(z)$  vary by many orders of magnitude throughout the atmosphere, often more than the element abundances we wish to determine, therefore we *cannot* neglect the  $\frac{dn_{\langle\text{H}\rangle}}{dz}$  and  $\frac{dD}{dz}$  terms as

$$\frac{d\epsilon_k}{dt} \neq D \frac{d^2 \epsilon_k}{dz^2} . \quad (4)$$

The diffusion constant  $D(z)$  is determined by (i) the microscopic diffusion which turns out to be important in the uppermost layers  $D_{\text{micro}}$ , and (ii) the turbulent quasi-diffusion  $D_{\text{mix}}$  due to vertical mixing processes excited e.g. by convective or other flow instabilities.

$$D(z) = D_{\text{micro}}(z) + D_{\text{mix}}(z) \quad (5)$$

Since the turbulent diffusion takes place on large spatial scales, we can safely assume that  $D_{\text{mix}}$  does not depend on the molecule (or element) we want to diffuse. Concerning  $D_{\text{micro}}$ , however, there is a small dependence on the size and reduced mass of the molecule with respect to collisions with  $\text{H}_2$ , see Voitke & Helling (2003, Eq. (26) therein), which causes deviations of  $D$  as function of molecule by a factor of about 2 to 3. We will simply neglect these deviations in the following.

This neglect allows us to calculate the diffusion of elements rather than the diffusion of individual molecules. The total particle density [ $\text{cm}^{-3}$ ] of element  $k$  is given by

$$n_{\langle\text{H}\rangle} \epsilon_k = \sum_i s_{i,k} n_i \quad (6)$$

where  $s_{i,k}$  is the stoichiometric factor of element  $k$  in molecule  $i$ , for example  $s_{\text{H}_2\text{O},\text{H}} = 2$ . Using Eq. (2), the diffusion of that total nuclei particle density is given by

$$\frac{d}{dt} (n_{\langle\text{H}\rangle} \epsilon_k) = \frac{d}{dt} \sum_i s_{i,k} n_i = \sum_i s_{i,k} \frac{dn_i}{dt} \quad (7)$$

$$= \sum_i s_{i,k} \frac{d}{dz} \left( n_{\langle\text{H}\rangle} D \frac{d}{dz} \left( \frac{n_i}{n_{\langle\text{H}\rangle}} \right) \right) \quad (8)$$

$$= \frac{d}{dz} \left( n_{\langle\text{H}\rangle} D \frac{d}{dz} \left( \sum_i s_{i,k} \frac{n_i}{n_{\langle\text{H}\rangle}} \right) \right) \quad (9)$$

$$= \frac{d}{dz} \left( n_{\langle\text{H}\rangle} D \frac{d\epsilon_k}{dz} \right) \quad (10)$$

## 2 Spatial Grid and Initial Conditions

We use an equidistant grid in  $\{z_i | i = 0, \dots, I\}$  to discretise the 1d-structure of the planetary atmosphere with fixed temperature and pressure points in hydrostatic equilibrium,  $T_i = T(z_i)$  and  $p_i = p(z_i)$ . At the lower boundary ( $z_0 = 0$ ) of the model, the atmospheric gas is in physical contact with the crust. The crust is represented by column densities  $N_j^{\text{cond}}$  for a number of  $j = 1, \dots, J$  condensed species.

At initialisation ( $t = 0$ ), we consider a set of total (gas plus condensed) element abundances  $\{\epsilon_k^0\}$  at temperature  $T_0$  and pressure  $p_0$  in phase equilibrium, using the GGChem-code (Voitke et al., 2017). The total element abundances  $\{\epsilon_k^0\}$  are chosen from one of the sets listed in Table 1. The results of this phase equilibrium computation are

- identification of the  $J$  simultaneously present condensates
- volume density of units of those condensates  $n_j^{\text{cond}}$  ( $j = 1, \dots, J$ ) [ $\text{cm}^{-3}$ ],
- remaining element abundances  $\{\epsilon_k^{\text{gas}}\}$  in the gas phase above the condensates

We define the condensed element abundances as

$$n_{\langle\text{H}\rangle} \epsilon_k^{\text{cond}} = \sum_{j=1}^J s_{j,k} n_j^{\text{cond}} \quad (11)$$

where  $s_{j,k}$  is the stoichiometric factor of element  $k$  in condensate  $j$ , for example  $s_{\text{Al}_2\text{O}_3,\text{O}} = 3$ . The element conservation is then given by

$$\epsilon_k^0 = \epsilon_k^{\text{gas}} + \epsilon_k^{\text{cond}}. \quad (12)$$

At initialisation, we fill the lowest atmospheric cell with the computed gas element composition  $\epsilon_k^{\text{gas}}$ , and use the ratio of identified condensates in phase equilibrium with that gas to initialise the

Table 1: Different sets of element abundances normalised to hydrogen (need citations).  $A(-B)$  means  $A \times 10^{-B}$ .

	solar	Earth crust	meteoritic
H	1.00(+0)	1.00(+0)	1.00(+0)
He	8.51(-2)	1.08(-6)	—
Li	1.12(-11)	2.07(-3)	1.03(-5)
C	2.69(-4)	1.20(-2)	5.25(-2)
N	6.76(-5)	9.76(-4)	4.20(-3)
O	4.90(-4)	2.07(+1)	1.05(+0)
Na	1.74(-6)	7.39(-1)	1.00(-2)
Mg	3.98(-5)	6.90(-1)	2.07(-1)
Al	2.82(-6)	2.20(+0)	1.42(-2)
Si	3.24(-5)	7.23(+0)	2.09(-1)
P	2.57(-7)	2.44(-2)	1.49(-3)
S	1.32(-5)	7.86(-3)	5.24(-2)
Cl	3.16(-7)	2.94(-3)	4.38(-4)
K	1.07(-7)	3.85(-1)	7.52(-4)
Ca	2.19(-6)	7.45(-1)	1.15(-2)
Ti	8.91(-8)	8.42(-2)	4.74(-4)
Cr	4.37(-7)	1.41(-3)	2.42(-3)
Mn	2.69(-7)	1.24(-2)	2.06(-3)
Fe	3.16(-5)	7.26(-1)	1.65(-1)
Ni	1.66(-6)	1.03(-3)	9.30(-3)

crust. At given pressure, there is a free constant in phase equilibrium, namely the total amount of condensates. We can add an arbitrary amount of the stable mixture of condensates as

$$\tilde{\epsilon}_k^0 = \epsilon_k^{\text{gas}} + X \epsilon_k^{\text{cond}} . \quad (13)$$

and re-run the phase equilibrium computation at the same pressure and temperature, but now with  $\{\tilde{\epsilon}_k^0\}$  instead of  $\{\epsilon_k^0\}$  – all resulting gas properties including  $\epsilon_k^{\text{gas}}$  will stay the same. This property of phase equilibrium allows us to introduce the “thickness of the active crust”  $D$  as a free parameter of the model. From the condensed species densities  $n_j^{\text{cond}}$  and the monomer volumes  $V_j$  we find the crust volume composition as

$$\beta_j = \frac{n_j^{\text{cond}} V_j}{\sum_j n_j^{\text{cond}} V_j} . \quad (14)$$

The volume  $V$  of an area  $A$  of crust of thickness  $D$  is given by

$$V = A \cdot D = \sum_j \beta_j V = \sum_j A N_j^{\text{cond}} V_j \quad (15)$$

from which we can calculate the initial material column densities in the active crust as

$$N_j^{\text{cond}} = D \frac{\beta_j}{V_j} . \quad (16)$$

All other atmospheric cells above the bottom cell ( $i = 1, \dots, I$ ) are initially filled with a gas of another chosen set of element abundances, for example solar abundances.

### 3 Boundary Conditions

#### 3.1 Upper boundary condition

We specify the escaping element fluxes from the top of the atmosphere by applying the formula for Jeans escape  $\rightarrow$  Tian (2015) as upper boundary condition of the model.

Where to apply that formula?  $\rightarrow$  exobase  $\rightarrow$  Volkov et al. (2011).

Here, we need to decompose the elements into molecules, apply the Jeans escape to each molecule, and lump the escaping fluxes together to get the escaping element fluxes.

#### 3.2 Lower boundary condition

At the bottom of the atmosphere, the atmospheric gas is in physical contact with the crust. At pressures of the order of a few tens of milli-bars to several bars, the collision rates of gas particles with the crust are huge, leading to a fast relaxation between gas and crust towards phase equilibrium. We will therefore assume that the gas at the bottom of the atmosphere is saturated (i.e. in phase equilibrium) with respect to the solid/liquid materials present in the crust.

$$S_j(\epsilon_k) \Big|_{z=0} = 1 \quad (17)$$

As shown in Appendix B of (Woitke et al., 2017), the number of simultaneously present condensates in phase equilibrium  $J$  is limited by the number of elements  $K$  contained in them,

$$\begin{aligned} J &= \text{number of condensates in crust } j = 1, \dots, J \\ K &= \text{number of condensed elements in crust } k = 1, \dots, J, J+1, \dots, K \end{aligned}$$

i.e. the number of condensing elements can (and usually will) exceed the number of condensates in the crust ( $K \geq J$ ). To quantify our phase equilibrium inner boundary condition for the diffusion experiment, we need to solve Eq. (17) for the unknown  $K$  gas element abundances in contact with the crust. As the diffusion experiment progresses, however, we have to make sure that the element fluxes through the inner boundary are consistent with the stoichiometry of a linear combination of the currently stable  $J$  crust condensates. We achieve this in two steps. First, we make a case differentiation between “limiting” and “non-limiting” elements and determine the element fluxes of the limiting elements. Second, we then use the stoichiometry of the condensates in the crust as an additional constraint to determine the element fluxes of the non-limiting elements. Our inner boundary condition is formulated as follows:

$$\begin{aligned} 1) \text{ element not affected by condensation} &: \text{ zero-flux boundary condition } j_k = 0, \\ 2) \text{ limiting element} &: \text{ fixed concentration } \epsilon_k \text{ from Eq. (17),} \\ 3) \text{ non-limiting element} &: \text{ derived element flux } j_k \neq 0. \end{aligned} \quad (18)$$

The distinction between “limiting” and “non-limiting” elements is based on the gas phase abundances in the bottom atmospheric cell. We sort all  $K$  elements involved in the condensation process by their abundance. The  $1, \dots, J$  elements with lowest abundances are identified as limiting elements. All others  $J+1, \dots, K$  are non-limiting elements.

We first run the diffusion solver for the non-affected elements, with zero flux boundary condition, and for the limiting elements with fixed  $\epsilon_k$  boundary condition, resulting in the fluxes of the limiting elements through the inner boundary:

$$\text{limiting element } k = 1, \dots, J: \quad j_k = -n_{\langle H \rangle} D \frac{d\epsilon_k}{dz} \Big|_{z=0}. \quad (19)$$

Next, we reconstruct the changes of the crust column densities  $N_j^{\text{cond}}$  from these fluxes by solving the following system of linear equations

$$\sum_{j=1}^J s_{j,k} \frac{dN_j^{\text{cond}}}{dt} = j_k, \quad (20)$$

which are  $J$  equations for  $J$  unknowns. Finally, we derive the non-limiting element fluxes by using the stoichiometry of the crust condensates

$$\text{non-limiting element } k = J + 1, \dots, K: \quad j_k = \sum_j s_{j,k} \frac{dN_j^{\text{cond}}}{dt} \quad (21)$$

For example, let's assume we have  $\text{MgSiO}_3[\text{s}]$  and  $\text{Mg}_2\text{SiO}_4[\text{s}]$  as condensates ( $J = 2$ ), which are made of elements Mg, Si and O ( $K = 3$ ). The least abundant elements in the gas phase will limit the growth of these condensates, here Mg and Si, whereas there is plenty of O available, so there is one non-limiting element, namely O. Applying the condition of phase equilibrium at the bottom of the atmosphere, we calculate the element abundances  $\epsilon_{\text{Mg}}$  and  $\epsilon_{\text{Si}}$  in phase equilibrium over the crust, and use these values as boundary conditions for the diffusion solver. As a result, the element fluxes through the inner boundary  $j_{\text{Mg}}$  and  $j_{\text{Si}}$  are determined via the diffusion experiment (Eq. 19). To calculate the respective changes of crust column densities, we solve

$$\begin{pmatrix} 1 & 2 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} dN_{\text{MgSiO}_3}^{\text{cond}}/dt \\ dN_{\text{Mg}_2\text{SiO}_4}^{\text{cond}}/dt \end{pmatrix} = \begin{pmatrix} j_{\text{Mg}} \\ j_{\text{Si}} \end{pmatrix} \quad (22)$$

for the unknowns  $dN_{\text{MgSiO}_3}^{\text{cond}}/dt$  and  $dN_{\text{Mg}_2\text{SiO}_4}^{\text{cond}}/dt$ . Finally the matching oxygen flux through the inner boundary is found from the stoichiometry of the crust condensates as

$$j_{\text{O}} = 3 \frac{dN_{\text{MgSiO}_3}^{\text{cond}}}{dt} + 4 \frac{dN_{\text{Mg}_2\text{SiO}_4}^{\text{cond}}}{dt} \quad (23)$$

which is then finally used as inner boundary condition to simulate the diffusion of oxygen in the atmosphere. Equation (23) demonstrates that non-limiting elements must be treated separately. If the three element fluxes ( $j_{\text{Mg}}$ ,  $j_{\text{Si}}$  and  $j_{\text{O}}$ ) were all determined by independent diffusion experiments, it would generally be impossible to convert them into only two condensates ( $\text{MgSiO}_3$  and  $\text{Mg}_2\text{SiO}_4$ ).

This inner phase-equilibrium boundary condition (Eq. 18) can be used to simulate the deposit of new condensates on top of the crust as well as the outgasing of crust materials into the atmosphere. It can be applied to an arbitrary mixture of elements, where some of them (like hydrogen and carbon) are not directly involved in the condensation process, but change the molecular abundances in the gas above the crust. It is also possible to model mixed cases, where for example one condensate outgases whereas others, at the same time, grow on top of the crust.

### 3.3 Updating the crust thickness and composition

The diffusion experiment as described in Sections (3.1) and (3.2) is carried out for a limited timestep  $\Delta t$ , during which the crust column densities  $N_j^{\text{cond}}$  can change, but we assume that the selection and number of condensates in the crust stays the same during  $\Delta t$ . After each time step, however, we re-examine whether this is still the case. We first invert and then redo the procedure as described in Sect. 2.

We first decompose all condensates in the crust and all molecules in the lowest atmospheric cell into their constituting elements as

$$N_k = n_{\langle \text{H} \rangle} \epsilon_k^{\text{gas}} \Delta z + \sum_{j=1}^J s_{j,k} N_j^{\text{cond}} , \quad (24)$$

where  $\Delta z$  is the vertical extent of the lowest atmospheric cell and  $N_k$  are the element column densities in crust and lowest cell. These elements are “uploaded” into the lowest atmospheric cell which then has element abundances

$$\epsilon_k^0 = \frac{N_k}{n_{\langle \text{H} \rangle} \Delta z} . \quad (25)$$

At temperatures above about 400 K (Woitke et al., 2017), hydrogen cannot yet be incorporated in any stable condensates in phase equilibrium, in which case we have  $N_{\text{H}} = n_{\langle\text{H}\rangle}\Delta z$  and  $\epsilon_{\text{H}}^0 = \epsilon_{\text{H}} = 1$ , but in general, for example when the crust includes phyllosilicates,  $\epsilon_{\text{H}}^0 > \epsilon_{\text{H}} = 1$  is possible according to Eq. (25).

We then re-run the phase-equilibrium solver for  $\{\epsilon_k^0\}, p_0, T_0$ . Most of the elements will fall out as condensates again, and only a small fraction will remain in the gas phase. Normally, these results are identical to the pre-update states. However, under certain circumstances some condensates can get exhausted as they outgas, some new ones can appear, or phase transitions between condensates in the crust can occur as the gas above it changes composition with time. The results of this procedure are used to update the crust column densities  $N_j^{\text{cond}}$  and the gas element abundances in the bottom atmospheric cell  $\epsilon_k^{\text{gas}}$ . The updated crust column densities and thickness are

$$N_j^{\text{cond}} = n_j^{\text{cond}} \Delta z \quad (26)$$

$$D = \sum_j N_j^{\text{cond}} V_j . \quad (27)$$

## 4 Element Conservation

### References

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