

The atmospheres of rocky exoplanets

I. Outgassing of common rock and the stability of liquid water

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ABSTRACT

Context. Little is known about the interaction between atmospheres and crusts of exoplanets so far, but future space missions and ground-based instruments are expected to detect molecular features in the spectra of hot rocky exoplanets.

Aims. We aim to understand the composition of the gas in an exoplanet atmosphere which is in equilibrium with a planetary crust.

Methods. The molecular composition of the gas above a surface made of a mixture of solid and liquid materials was determined by assuming phase equilibrium for given pressure, temperature, and element abundances. We study total element abundances that represent different parts of the Earth's crust (continental crust, bulk silicate Earth, mid oceanic ridge basalt), CI chondrites and abundances measured in polluted white dwarfs.

Results. For temperatures between ~600 and ~3500 K, the near-crust atmospheres of all considered total element abundances are mainly composed of H₂O, CO₂, and SO₂ and in some cases of O₂ and H₂. For temperatures \lesssim 500 K, only N₂-rich or CH₄-rich atmospheres remain. For \gtrsim 3500 K, the atmospheric gas is mainly composed of atoms (O, Na, Mg, and Fe), metal oxides (SiO, NaO, MgO, CaO, AlO, and FeO), and some metal hydroxides (KOH and NaOH). The inclusion of phyllosilicates as potential condensed species is crucial for lower temperatures, as they can remove water from the gas phase below about 700 K and inhibit the presence of liquid water.

Conclusions. Measurements of the atmospheric composition could, in principle, characterise the rock composition of exoplanet crusts. H₂O, O₂ and CH₄ are natural products from the outgassing of different kinds of rocks that had time to equilibrate. These are discussed as biomarkers, but they do emerge naturally as a result of the thermodynamic interaction between the crust and atmosphere. Only the simultaneous detection of all three molecules might be a sufficient biosignature, as it is inconsistent with chemical equilibrium.

Key words. planets and satellites: terrestrial planets – planets and satellites: composition – planets and satellites: atmospheres – planets and satellites: surfaces – astrochemistry

1. Introduction

After the first detections of exoplanets around the pulsar PSR B1257+12 by [Wolszczan & Frail \(1992\)](#), and the main sequence star 51Peg by [Mayor & Queloz \(1995\)](#), more than 4000 exoplanet detections have been confirmed to date¹. Until recently, the overwhelming majority of the exoplanets found were gaseous giant planets in close orbits to their host stars.

In the last years, it became possible to detect exoplanets of a rocky composition in the habitable zones of their host star, mostly M dwarfs. Notable detections are the planets around our closest star Proxima Centauri ([Anglada-Escudé et al. 2016](#)), Barnard's star ([Ribas et al. 2018](#)), and the seven planet system around Trappist 1 ([Gillon et al. 2017](#)). Even though these planets are in close orbits to their host stars, their equilibrium temperatures are lower than 500 K due to the low effective temperature of their host star. [Turbet et al. \(2016\)](#) showed for Proxima Centauri b that liquid water can be present and might be detectable in the future. On the other hand, rocky exoplanets with short orbital periods around solar-type stars such as 55 Cnc e ([McArthur et al. 2004](#)) or CoRoT-7b ([Léger et al. 2009](#)) have temperatures on the

day side of $T_{\text{eq}} \sim 2400$ K ([Léger et al. 2011](#); [Demory et al. 2016](#)). This temperature is high enough to melt the surface of the planet on the dayside, while the nightside remains solid (magma pond [Kite et al. 2016](#)). During the formation of terrestrial planets, the surface can melt and cause a global magma ocean with a mass dependent depth ([Elkins-Tanton 2012](#)). For short orbital periods and host stars with extensive magnetic fields, this magma ocean can prevail due to inductive heating ([Kislyakova et al. 2017](#)).

To date, it is impossible to determine whether the surface material has been processed by plate tectonics or by radiation and stellar winds on an exposed surface only. For planets with enough heat from stellar irradiation, inductive heating, or tidal forces, for example, an active mantle can prevail that causes active surface processing, such as volcanism or plate tectonics. Planetary structure modelling suggests that hot super-Earths, such as 55 Cnc e, have high atmospheric abundances of refractory elements, such as Ca and Al ([Dorn et al. 2019](#)). These atmospheres are shown to allow the formation of mineral clouds ([Mahapatra et al. 2017](#)).

The number of rocky exoplanets whose atmosphere has already been spectroscopically analysed is very small. However, in the near future, the number of exoplanet atmospheres in reach

¹ <http://exoplanet.eu/catalog/>

for detailed analysis will increase because of spectrographs with high spectral resolution in the near infrared (e.g. CARMENES, Quirrenbach et al. 2012; CRIRES+, Follert et al. 2014), the 30 m telescopes, and space missions, such as TESS, JWST, and PLATO. These instruments will allow for the analysis of the atmospheric composition of nearest rocky exoplanets with unprecedented precision.

Current studies have revealed a large diversity in the composition of rocky exoplanets² and Fig. 1 in Kaltenegger (2017). It seems reasonable to expect a comparably large diversity with respect to their atmospheres (Leconte et al. 2015). The study of exoplanet atmospheres has so far been focused on gas giants (Désert et al. 2008; Snellen et al. 2010; Nikolov et al. 2018; Arcangeli et al. 2018; Salz et al. 2018) due to observational limitations. Kreidberg et al. (2014) observed the super-Earth GJ 1214 b and showed that the analysis of the atmosphere's chemical composition is frustrated by clouds. Atmospheres of exoplanets have been observed to be generally affected by cloud formation (for a recent review see Helling 2019).

In what follows, we investigate the atmospheric gas that forms above a surface ('near-crust atmosphere') made of a mixture of solid and liquid materials under certain thermodynamic conditions and for different sets of element abundances. We assume thermo-chemical equilibrium for the molecules in the gas phase and phase equilibrium for the condensates in contact with that gas. Our approach is to study the atmospheric gas in contact with rocky planet's crust and derive the gas composition immediately above the crust. Schaefer et al. (2012) have presented a similar approach, and Miguel (2019) used the thermo-chemical equilibrium code TEA (Blecic et al. 2016) to discuss the atmospheric gas composition of the potential magma-ocean dayside of 55 Cnc e. All studies assume that the near-crust atmospheric gas had enough time to reach local thermodynamic equilibrium (LTE) with the planetary crust.

We apply the equilibrium code GGCHEM (Woitke et al. 2018) which enables us to calculate the thermo-chemical equilibrium chemistry for gases and condensates in phase equilibrium to temperatures as low as 100 K. GGCHEM has been benchmarked against TEA by Woitke et al. (2018). GGCHEM also allows us to investigate the stability of liquid and solid water at low temperatures. Woitke et al. (2018) have shown that phyllosilicates become stable below about 500 to 700 K in a solar composition gas in phase equilibrium at $p = 1$ bar, which then in fact interferes with the stability of liquid water. Such clay materials can form on the timescales of days on Earth (e.g. Velde 1995, and references therein). We note that such phyllosilicate materials form already in planet-forming discs (Thi et al. 2020) and may contribute substantially to the water delivery to Earth.

We benchmark our code against earlier work by Sharp & Huebner (1990) and compare our results with Schaefer et al. (2012). Different planets in different stellar environments and in different evolutionary states also differ in their elemental composition which is crucial for the composition of the atmosphere. We study the effect of different sets of total element abundances.

We utilise total element abundances informed by geological studies on Earth, continental crust (CC), bulk silicate Earth (BSE), and mid oceanic ridge basalt (MORB), and those informed by astronomical studies, solar abundances, CI chondrites, and abundances deduced from polluted white dwarf (PWD) observations. A wide range of pressures (0.001–100 bar) and temperatures (100–5000 K) is considered. Kinetic effects and geological processes, such as plate tectonics and volcanism,

are not included in our model, and we assume that our system had always enough time to reach the thermo-chemical equilibrium after it may have been affected by momentary disequilibrium events, such as volcanism etc.

In Sect. 2 we briefly describe the GGCHEM code that is used in this work. A detailed comparison to previously published results is provided in Sect. 3 for element abundances of CC and BSE. Section 4 presents additional results for MORB, CI chondrite and PWD abundances. In Sect. 5, the stability of liquid water is studied by modifying the BSE composition to see by how much the content of gaseous atmospheric water needs to increase for liquid water to be present eventually. The effect of the atmospheric pressure on the thermo-chemical equilibrium is discussed in Sect. 6. Section 7 focuses on the estimation of timescales at which the chemical equilibrium is reached. In Sect. 8 we conclude with a discussion. In the appendix a glossary of structural formula for some condensed species is provided (Table A.1).

2. Method: phase equilibrium with GGCHEM

We use the thermo-chemical equilibrium code GGCHEM (Woitke et al. 2018). Based on the principle of minimisation of the total Gibbs free energy the chemical equilibrium for the molecules in the gas phase and phase equilibrium for the condensates is solved. A short summary is provided here. For more details see (Woitke et al. 2018).

Figure 1 shows the basic procedure: A set of elements $k = 1, \dots, K$ is selected, their abundances with respect to hydrogen, ϵ_k^0 , are henceforth called the total element abundances. Based on gas pressure p , gas temperature T and ϵ_k^0 , GGCHEM determines the stable condensates, calculates their abundances (which results in the abundance of condensed elements ϵ_k^{cond}), and calculates the ion, atom, and molecular concentrations in the gas (which results in the element abundances left in the gas phase ϵ_k). Condensates $j = 1, \dots, J$ are considered stable and present if their supersaturation ratios are unity $S_j = 1$, whereas all other condensates are unstable and not present, that is $S_j < 1$. The conservation of elements $\epsilon_k^0 = \epsilon_k + \epsilon_k^{\text{cond}}$ is obeyed for all elements k . The resulting abundances of all gas and condensed phase species obey the conditions of chemical and phase equilibrium.

In many astrophysical objects, such as AGB star winds, brown dwarf atmospheres or protoplanetary discs, the majority of elements remains in the gas phase, that is $\sum \epsilon_k^0 \approx \sum \epsilon_k \gg \sum \epsilon_k$. However, for most applications considered in this paper, such as a gas in contact with a hot planetary crust, only a small fraction of the elements ($10^{-1} \dots 10^{-5}$) actually remain in the gas phase, depending on the temperature, that is $\sum \epsilon_k^0 \approx \sum \epsilon_k^{\text{cond}} \gg \sum \epsilon_k$. Therefore, the vapour pressure of stable condensates is a major component for the composition of the gas.

GGCHEM combines different thermo-chemical data sources. For the molecular equilibrium constants, $k_p(T)$, we use Stock (2008) and Barklem & Collet (2016), complemented by some new fits to the NIST/JANAF database (Chase et al. 1982; Chase 1986, 1998). The condensed phase data $\Delta G_f^0(T)$ is taken from SUPCRTBL (Zimmer et al. 2016) and NIST/JANAF. These datasets allow us to calculate the concentrations of all atoms, ions, molecules and condensed phases in chemical equilibrium for a mixture of up to 41 elements (hydrogen to zirconium, and tungsten). The actual number of gas phase species and condensates depends on the selection of elements and is stated in the corresponding sections for the different calculations.

Phase equilibrium models can generally provide only a very simplified and limited approach to describe the occurrence of

² see <http://exoplanet.eu>

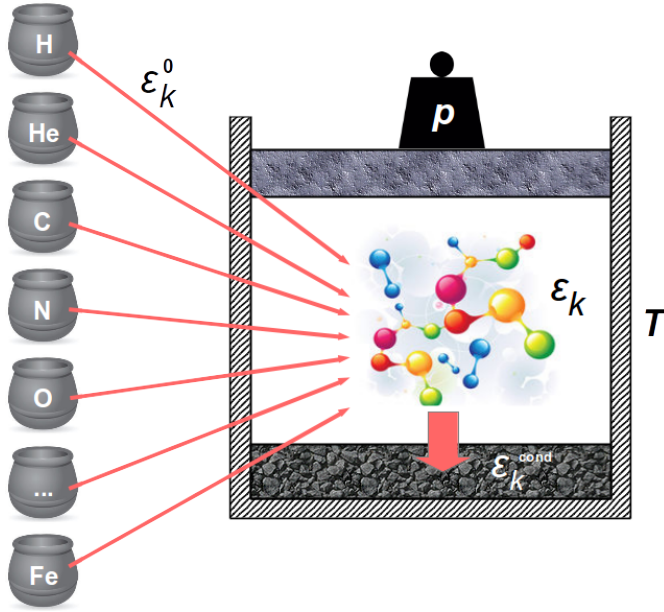


Fig. 1. Principle modelling procedure of GGChem: elements are selected and included with given total abundances ϵ_k^0 . GGChem calculates the equilibrium gas phase and condensate abundances at given gas pressure p and temperature T , providing the element abundances contained in the condensates (ϵ_k^{cond}) and the remaining gas phase (ϵ_k).

condensates in gases, and the nature of gases above solid surfaces, especially when low temperatures are considered, where both the outgassing and the deposition rates are small. No kinetic rates are considered, and the relaxation timescale towards chemical and phase equilibrium cannot easily be discussed. For example, the atmosphere of a rocky planet is in contact with the crust partly on the hot dayside and partly on the cold nightside. Other processes are not considered, such as cloud formation, photodissociation, cosmic ray induced processes, and volcanism, etc. Still, equilibrium models can provide a first understanding and can be used to inform more ambitious kinetic condensation models, for example, about the choice of condensates.

3. Comparison to previous phase equilibrium models

We compare the phase-equilibrium results obtained with GGChem to previous equilibrium condensation models published by Sharp & Huebner (1990) and Schaefer et al. (2012) in the following Sects. 3.1 and 3.2, respectively. The paper by Sharp & Huebner (1990) includes sufficiently detailed information about the selection of molecules and condensates, and their thermo-chemical data, that allow us to benchmark our results. For Schaefer et al. (2012), we do not exactly know their choice of molecules and condensates, nor their thermo-chemical data applied, so we broadly compare our results, and identify the differences between the two models.

3.1. Sharp & Huebner (1990)

Sharp & Huebner (1990) used a numerical method that directly minimises the total Gibbs free energy of gas phase and condensed phase species. GGChem uses a different numerical method, for details see Woitke et al. (2018), so the aim of this section is mainly to verify our numerical approach. Therefore the chosen elements, element abundances (Table A.2), and the

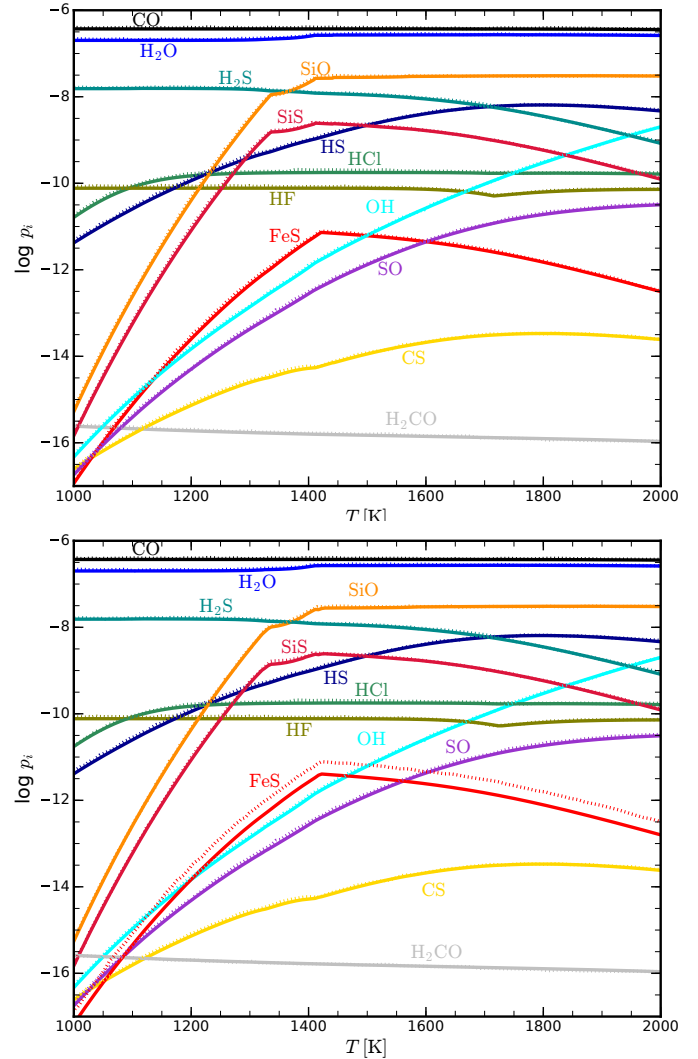


Fig. 2. Comparison of molecular partial pressures computed by GGChem (solid lines) to the results by Sharp & Huebner (1990, dotted lines). Calculations are based on the solar element abundances listed in Sharp & Huebner (1990) for a constant pressure of $p = 0.5$ mbar. The shown elements are chosen to match Fig. 1 in Sharp & Huebner (1990). *Upper panel:* GGChem only uses the molecules and condensates selected by Sharp & Huebner (1990) and applies their thermo-chemical data. *Lower panel:* GGChem uses all molecules and condensates found in its own database and uses its own thermo-chemical data. The agreement is very good. The only visible difference is in FeS, which is slightly depleted in the lower panel.

thermo-chemical data for the gas and condensate species are exactly as described in Sharp & Huebner (1990). Thus both codes use the same 18 elements (H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu and Zr) with 165 gas species and 62 solid condensed species. As in Sharp & Huebner (1990), the pressure is set to 0.5 mbar and the temperature ranges from 1000 to 2000 K.

In Fig. 2, the resulting GGChem molecular partial pressures are shown, with the Sharp & Huebner (1990) results over plotted as dashed lines. The graphs from Sharp & Huebner (1990) Fig. 1 have been digitised from an electronic version of their paper. Within the precision of that digitising process, our results are identical. In addition, the ‘appearance and disappearance temperatures’ of the condensates listed in Table 3 of Sharp & Huebner (1990) agree within ± 1 K with our results.

This demonstrates that our numerical method produces equivalent results for both condensates and molecules.

In the lower panel of Fig. 2, we have applied the full GGChem dataset for molecules and condensed species to the same selection of elements and their abundances, resulting in 388 gas-phase and 204 condensed species, 35 of them being liquids. The results are still very close, with FeS being the only molecule with relevant concentrations that shows a lower concentration compared to the results by Sharp & Huebner (1990). This is caused by the additional occurrence of FeH as a gas phase species, which was not included in Sharp & Huebner (1990). Additional differences in the selection of molecules and condensates are as follows: all gas species and condensates in Sharp & Huebner (1990) are also considered in the full GGChem model. We find that SiO[s], ZrSiO₄[s], CaTiSiO₅[s] and MgCr₂O₄[s] become stable condensates, while MgTi₂O₅[s], and Cr₂O₃[s] are not becoming stable. In the gas phase of these two models, the major difference is that our CrH and CuH concentrations differ by more than one order of magnitude. This is caused by the stability of the additional gas phase species NiCl, TiF₃, TiOF₂, TiOCl₂, TiOCl, AlF₂O, MnF, MnCl, ZrF₃, ZrF₄, CaCl, P₄O₆, PO₂, PCH, FeH, CrS, and TiH, which are all not included in Sharp & Huebner (1990).

3.2. Schaefer et al. (2012)

Two sets of total element abundances were considered by Schaefer et al. (2012) for the calculation of the atmospheric composition above a rocky planet: Continental Crust (CC) and Bulk Silicate Earth (BSE), based on Wedepohl (1995) and Kargel & Lewis (1993), respectively. The corresponding element abundances are listed in Table A.2. The following 18 elements are selected: H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, and Fe, together with their respective single ions. The pressure is kept constant at 100 bar.

The model used in Schaefer et al. (2012) is based on IVTANTHERMO (Belov et al. 1999) with a database including data from Robie & Hemingway (1995) and Holland & Powell (2011). The phyllosilicates present in their dataset were excluded as their focus was on higher temperatures. In order to better compare our model to Schaefer et al. (2012), we computed two models with GGChem, one with and one without phyllosilicates. For the selected elements, GGChem finds 471 gas species in its database and 188 condensates, where 30 of those are liquids and 39 are phyllosilicates.

Phyllosilicates should be an integral part of equilibrium condensation models as they are known in geology to form effectively in a wide temperature range on relatively short timescales as condensates directly from the gas phase, but as alterations in silicate rocks exposed to water vapour (e.g. Velde 1995, and references therein). The effective formation of phyllosilicates is underlined by spectrometric evidence of phyllosilicates on Mars' surface (Poulet et al. 2005). Based on laboratory analysis of different chondrite materials, using backscattered electron micrography, Bischoff (1998) concluded for many carbonaceous chondrites that the aqueous alteration of parent bodies is a fundamental process in their evolution and even argued for pre-accretionary aqueous alteration of distinct components in carbonaceous chondrites. In the cold midplanes of protoplanetary discs, D'Angelo et al. (2019) showed that the hydration of forsterite surfaces by water vapour adsorption should occur within the lifetime of the solar nebula at densities $\sim 10^8 \text{ cm}^{-3}$ and temperatures lower than 500 K, providing between 0.5 and 10 times the amount of water in Earth's oceans to the bulk

composition of Earth, depending on grain size. Thi et al. (2020) argued that the chemisorption sites for OH and H₂O molecules in the silicate cores become occupied at temperatures between 250 and 700 K on timescales shorter than 10^5 yr for 1 mm grains at gas densities of 10^8 cm^{-3} .

3.2.1. Continental crust

Continental crust is a proxy of an SiO₂-rich (felsic) elemental composition which on Earth results from plate tectonics, see e.g. Taylor & McLennan (1995) for a review. The crust of Earth differentiated into two different parts, continental and oceanic crust. The oceanic crust is geologically younger and consists mainly of basalt (SiO₂-poor igneous rock) whereas the continental crust is much older, less dense, and consists mainly of granite, which is a composite material mostly made of SiO₂ (quartz) and feldspar. Plate tectonics on Earth strongly effected the differentiation into the different crust types. Whether other planets have a similar bulk crust composition remains unclear, but planets with Earth-like plate tectonics can be expected to also have a felsic composition, at least in parts of their crusts. Furthermore bulk compositions with high SiO₂ abundances can result in overall felsic compositions. On Venus, spectrometer measurements from the Galileo mission suggest that the highlands are felsic in composition (e.g. Hashimoto et al. 2008), while for Mars, the buried rock underneath the dominant basaltic surface might be of felsic composition (e.g. Cousin et al. 2017). The overall composition of the CC is controversial and leads to different proposed compositions. For further reading, see e.g. Taylor & McLennan (1995), Rudnick & Gao (2003) and Greber et al. (2017). In order to allow a comparison to Schaefer et al. (2012) we use their composition taken from Wedepohl (1995).

Overall, the results of the model by Schaefer et al. (2012) and our GGChem model without phyllosilicates are similar for CC abundances, both showing H₂O and CO₂ as the major gas species between about 570 and 3500 K, with constant particle ratio H₂O:CO₂ = 1.35:1, which is a direct consequence of the assumed total element abundances, since neither hydrogen nor carbon can condense at these temperatures.

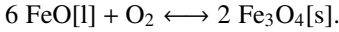
At higher temperatures $\geq 3500 \text{ K}$, O₂ and SiO become the most abundant species, followed by CO, OH, and metal oxides, such as SiO, SiO₂, NaO and AlO, and hydroxides, such as NaOH and KOH, and by the atoms K and Na. Liquid Al₂O₃[l] is found to be stable for temperatures up to 5150 K at 100 bar in our model, where it is the first stable condensate. Other liquid metal oxides are stable at high temperatures as well, in particular MgAl₂O₄[l], CeCaO[l], FeO[l], SiO₂[l], K₂SiO₃[l], Na₂SiO₃[l], with the last liquid solidifying at 1696 K, the melting point of SiO₂.

At lower temperatures, GGChem identifies the following solid compounds as abundant stable condensates (with $\max\{\log_{10}(n_{\text{solid}}/n_{\text{(Si)}})\} > -2$): SiO₂[s] (quartz, by far the most abundant), the three major components of feldspar: CaAl₂Si₂O₈[s] (anorthite), NaAlSi₃O₈[s] (albite) and KAlSi₃O₈[s] (microcline), MgSiO₃[s] (enstatite), Mg₂SiO₄[s] (fosterite), CaMgSi₂O₆[s] (diopside), KAlSi₂O₆[s] (leucite), Fe₂O₃[s] (hematite), Fe₃O₄[s] (magnetite), CaSiO₃[s] (wollastonite), and Ca₂SiO₄[s] (larnite).

At temperatures $\leq 570 \text{ K}$, H₂O gas becomes liquid, and carbon becomes thermally stable as CaMgC₂O₆[s] (dolomite), and so N₂ remains the only abundant gas species. Eventually, at 360 K, nitrogen is found to be stable in form of NH₄Cl (ammonium chloride) and there is no physical solution anymore to produce a $p = 100 \text{ bar}$ gas as all selected elements condense.

Such atmospheres would mainly consist of noble gases, which are not included here.

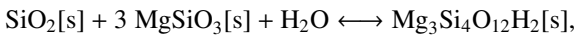
Some deviations between the two models are found for O_2 , SO_2 , and HF. The results by Schaefer et al. (2012) show two major steps in the O_2 concentration at ~ 2600 K and at ~ 1800 K. These changes in O_2 abundances in the gas phase are caused by the chemical stability of different Fe species in the corresponding temperature regimes: $Fe_2SiO_4[l]$ ($T > 2500$ K), $Fe_3O_4[l]$ ($1900 \text{ K} < T < 2500$ K), and $Fe_2O_3[l]$ ($T < 1900$ K). In contrast, in the GGchem-model, there is only one transition, at about 2150 K, where one of the major liquids $FeO[l]$ solidifies to form $Fe_3O_4[s]$ (magnetite), which consumes large amounts of molecular oxygen as



The liquid phases $Fe_2SiO_4[l]$, $Fe_3O_4[l]$, and $Fe_2O_3[l]$ are currently not included in our model. The thermodynamic data for liquids originates mostly from NIST/JANAF, which does not include liquid phases of $Fe_2SiO_4[l]$, $Fe_3O_4[l]$, and $Fe_2O_3[l]$. Towards higher temperatures, the O_2 abundance increases further according to its increasing vapour pressure over the mostly liquid condensates, such as $SiO_2[l]$, $MgSiO_3[l]$, and $FeO[l]$.

Towards lower temperatures, fluorine becomes stable in form of $CaF_2[s]$ (fluorite) around 1500 K, reducing HF in the gas phase. At about 1150 K, sulphur becomes thermally stable in form of $CaSO_4[s]$ (anhydrite) on the expense of $CaMgSi_2O_6[s]$ (diopside). This transition removes sulphur from the gas phase, leading to a fast decrease of the SO_2 concentration below 1150 K. Eventually, in our model without phyllosilicates, $H_2O[l]$ (liquid water) is thermally stable for $T \lesssim 570$ K and leaves behind an N_2 -rich atmosphere.

When we do include phyllosilicates in our model (lower panel of Fig. 3), the atmospheric composition does not change at higher temperatures, however, at $T < 720$ K, phyllosilicates become stable and have a profound influence on both the molecular and solid composition. We find two phyllosilicates in our CC model, $Mg_3Si_4O_{12}H_2[s]$ (talc) at $T < 720$ K, and $Ca_2FeAl_2Si_3O_{13}H[s]$ (epidote) at $T < 410$ K. These are very effective in removing water from the gas phase, for example



thereby inhibiting the stability of liquid water on the surface. Since hydrogen disappears sooner than carbon from the gas phase in the model including phyllosilicates, there is in fact a narrow temperature interval 600 K – 720 K where CO_2 is the most abundant molecule.

3.2.2. Bulk silicate Earth

Bulk silicate Earth is an approximation for the composition of the Earth excluding its core. This leads to a composition that is rich in MgO and FeO-bearing silicates (mafic), but relatively poor in C, N, F, P, S, Cl, and K. For the model comparison we use the same total element abundance as Schaefer et al. (2012) taken from Kargel & Lewis (1993).

Relevant liquids at high temperatures in our GGchem-model are $SiO_2[l]$, $FeO[l]$, $MgSiO_3[l]$, $Mg_2SiO_4[l]$, $MgAl_2O_4[l]$, $MgO[l]$, and $CaO[l]$, with the first stable condensate being $MgAl_2O_4[l]$ at 4900 K. The relevant solid composition at lower temperatures includes $Mg_2SiO_4[s]$ (fosterite), $MgSiO_3[s]$ (enstatite), $FeO[s]$ (ferropericline), $CaMgSi_2O_6[s]$ (diopside), $MgAl_2O_4[s]$ (spinel), $NaAlSi_3O_8[s]$ (nepheline), $Fe_2SiO_4[s]$ (fayalite), $Fe_3O_4[s]$ (magnetite), $FeAl_2O_4[s]$ (hercynite),

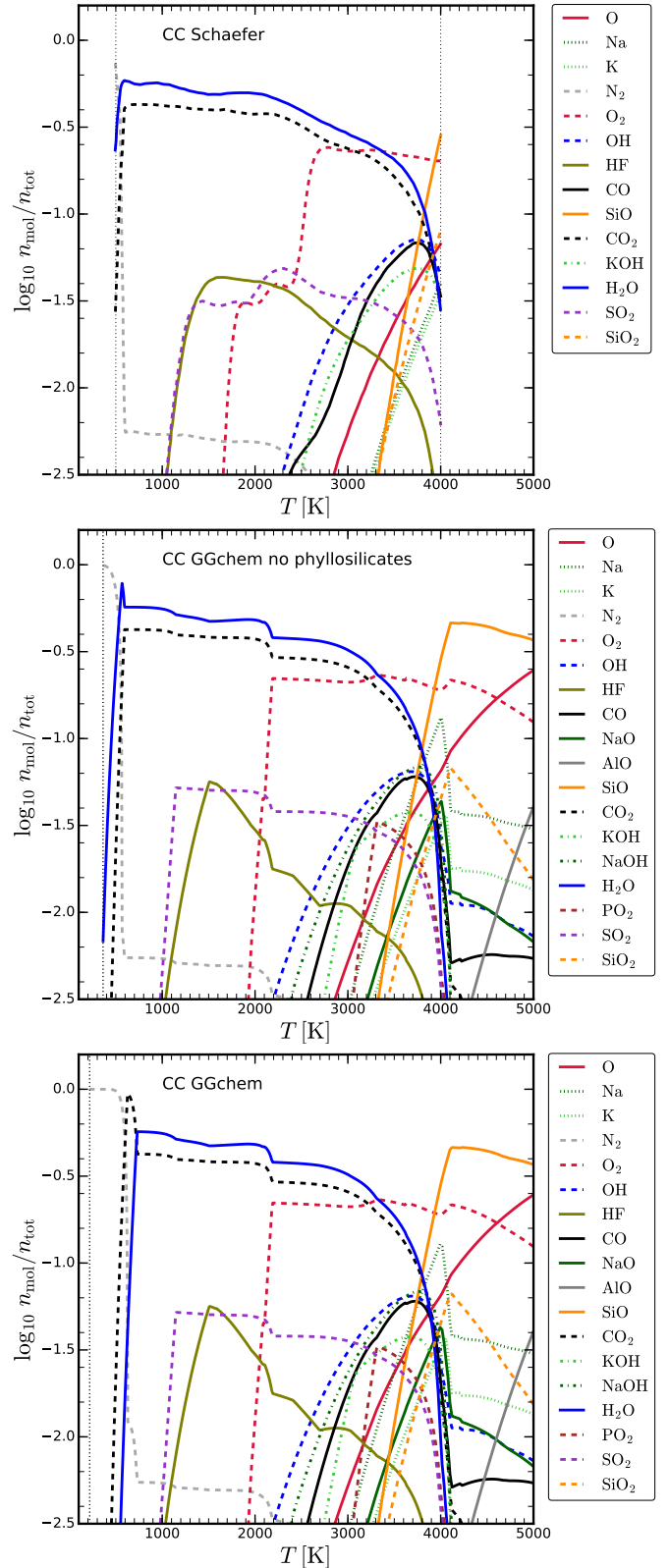
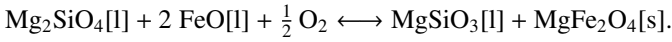


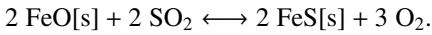
Fig. 3. Comparing the molecular concentrations ($n_{\text{mol}}/n_{\text{tot}}$) over Continental Crust (CC) at $P = 100$ bar predicted by GGchem with the results obtained by Schaefer et al. (2012). *Top panel:* results by Schaefer et al. (2012) scanned from their Fig. 1. *Middle panel:* results from GGchem disregarding phyllosilicates. *Bottom panel:* results from GGchem for the full dataset. All species with $\log n_{\text{mol}}/n_{\text{tot}} > 1.5$ are shown. The thin, vertical dotted lines indicate the upper and lower limits of the models. For the GGchem models this means that all elements are condensed below the corresponding temperature.

CaAl₂Si₂O₈[s] (anorthite), NaAlSi₃O₈[s] (albite), NaAlSi₂O₆[s] (jadeite), MgFe₂O₄[s] (magnetoferrite), Ca₃Al₂Si₃O₁₂[s] (grossular), Ca₂MgSi₂O₇[s] (åkermanite), and Ca₂SiO₄[s] (larnite).

Concerning the gas phase abundances, both the [Schaefer et al. \(2012\)](#) model and our GGChem-model show that H₂O and O₂ are the most abundant gas species in a wide temperature range, but the deviations between the models are more pronounced for BSE abundances. For high temperatures ≥ 4200 K, both models find the gas phase to be mostly composed of O, Na, Mg, Fe, SiO, and MgO, in addition to O₂. The most obvious deviation is the concentration of O₂, which dominates the gas phase in our GGChem-model between about 2300 K and 4200 K, whereas it drops already at 3100 K in the model by [Schaefer et al. \(2012\)](#). Similar to the model for CC abundances, the disappearance of O₂ in our model for BSE abundances is caused by the solidification of FeO[l] around 2300 K, which consumes oxygen as



Once O₂ has disappeared, H₂O becomes the most abundant and SO₂ the second most abundant species. At $T \approx 1300$ K, sulphur condenses in form of FeS[s] (troilite), for example as



This removes SO₂ and hence sulphur from the gas phase, making CO₂ the second most abundant gas species after H₂O.

For $T \lesssim 550$ K, H₂O is thermally stable as liquid water H₂O[l]. Both our GGChem model and the [Schaefer et al. \(2012\)](#) model suggest that, after water is stable as a liquid, the atmosphere becomes rich in CH₄, with some traces of H₂. At even lower temperatures, the GGChem model predicts that NH₄Cl (ammonium chloride) becomes stable at 330 K and CH₄[s] (methane ice) at 220 K, below which there is no solution anymore for a 100 bar atmosphere.

At temperatures below about 1000 K, the inclusion of phyllosilicates (lower panel in Fig. 4) again leads to substantial differences between our model and [Schaefer et al. \(2012\)](#). As the phyllosilicates KMg₃AlSi₃O₁₂H₂[s] (phlogopite) and NaMg₃AlSi₃O₁₂H₂[s] (sodaphlogopite) become stable at temperatures of 970 and 930 K, respectively, the water in the atmosphere is removed. This removal leads to an earlier domination of CO₂ and subsequently to the formation of solid C[s] (graphite) at about 800 K, and the development of an N₂-rich atmosphere, in contrast to the model without phyllosilicates. In fact, nitrogen stays in the atmosphere down to 100 K and does not condense in form of NH₄Cl as in our CC model.

Our models without phyllosilicates match those of [Schaefer et al. \(2012\)](#), which do not include phyllosilicates. The inclusion of phyllosilicates as condensed species causes strong deviations in the gas phases for temperatures below ~ 1000 K. This underlines the importance of phyllosilicates for the investigation of atmospheres of rocky exoplanets.

4. Other total element abundances

One of the major aims and challenges of exoplanet research is to determine the element composition of surfaces and atmospheres, for the purpose of characterisation. After having studied the theoretical predictions for Continental Crust (CC) and Bulk Silicate Earth (BSE) element abundances in the previous section, where we also have checked our results against previously published results, we now explore three additional sets of total

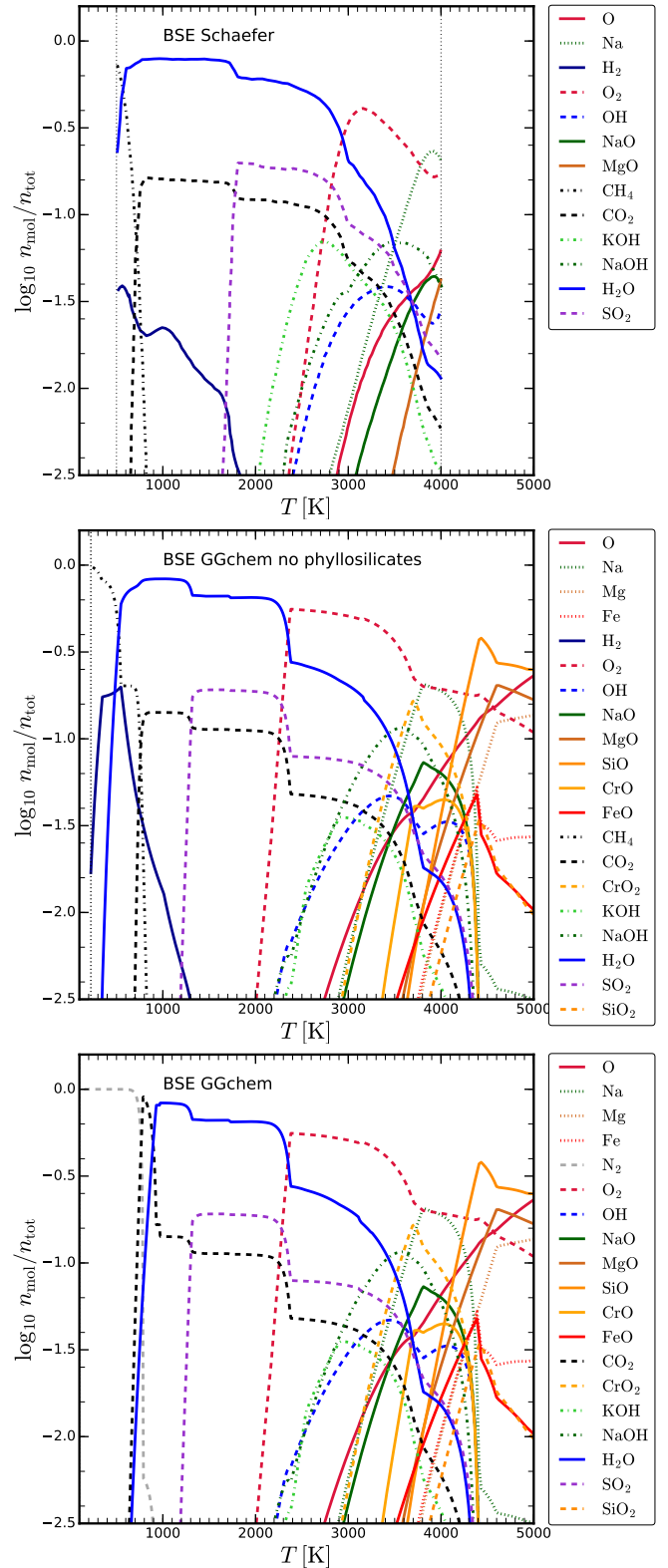


Fig. 4. Similar to Fig. 3, but for bulk silicate Earth (BSE) total element abundances.

element abundances for our phase equilibrium models: (1) mid oceanic ridge basalt (MORB) elemental abundances, (2) measured elemental abundances of carbonaceous chondrites (CI), and (3) exoplanet elemental abundances deduced from spectral analyses of polluted white dwarfs. In Fig. 5, we plot these element abundances in units of the silicon abundance, the dominant

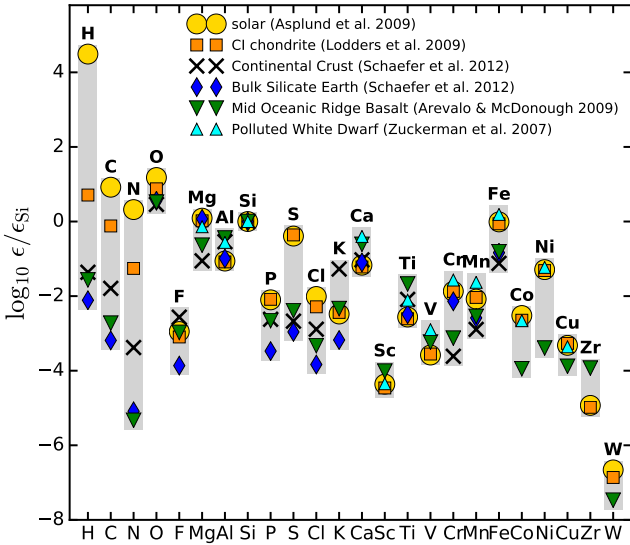


Fig. 5. Element abundances relative to silicon (nuclei particle ratios) for different materials and astronomical sources.

rock-forming element, and compare them to the element abundances discussed earlier in this paper.

4.1. Mid Oceanic Ridge Basalt

Measurements by probes and orbiter missions infer that rocks of basaltic composition are very common in the solar system as they can also be found on Mars, Venus, Mercury, and on our Moon (e.g. Grotzinger 2013; Gilmore et al. 2017; Wang et al. 2019b). The major difference of these rock compositions is the Fe content, which is related to the planetary mass, causing a different degree of differentiation (Elkins-Tanton 2012). Another factor is the accretion history of the planet as well as the interior chemistry, causing different interior redox states. On Earth, basalt is most common in the oceanic crust. Therefore, we use the mean composition of the MORB from Arevalo & McDonough (2010) for our analysis.

Figure 5 and Table A.2 show that MORB, in general, has element abundances similar to CC and BSE, but is enriched in S, Ca, and Ti, and poor in N. The abundance of Mg in MORB is significantly larger than in CC, but less than in BSE. We restrict our model to the same elements as in the previous section (H, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, and their corresponding ions).

The results of this model are shown in Fig. 6. Important liquids at high temperatures are found to be $\text{SiO}_2[\text{l}]$, $\text{FeO}[\text{l}]$, $\text{MgSiO}_3[\text{l}]$, $\text{Al}_2\text{O}_3[\text{l}]$, $\text{Na}_2\text{SiO}_3[\text{l}]$, $\text{MgTi}_2\text{O}_5[\text{l}]$, $\text{CaO}[\text{l}]$, and $\text{MgAl}_2\text{O}_4[\text{l}]$, with the first condensate being $\text{Al}_2\text{O}_3[\text{l}]$ at 5150 K in this model. At lower temperatures, MORB shows a particularity rich solid composition in our model, including $\text{SiO}_2[\text{s}]$ (quartz), $\text{MgSiO}_3[\text{s}]$ (enstatite), $\text{FeTiO}_3[\text{s}]$ (ilmenite), $\text{Fe}_2\text{SiO}_4[\text{s}]$ (fayalite), $\text{NaAlSi}_3\text{O}_8[\text{s}]$ (albite), $\text{CaTiSiO}_5[\text{s}]$ (sphene), $\text{CaMgSi}_2\text{O}_6[\text{s}]$ (diopside), $\text{Fe}_3\text{O}_4[\text{s}]$ (magnetite), $\text{CaAl}_2\text{Si}_2\text{O}_8[\text{s}]$ (anorthite), $\text{Al}_2\text{SiO}_5[\text{s}]$ (kyanite), $\text{FeO}[\text{s}]$ (ferropericlyase), $\text{Mg}_2\text{SiO}_4[\text{s}]$ (fosterite), $\text{NaAlSi}_2\text{O}_6[\text{s}]$ (jadeite), $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}[\text{s}]$ (grossular), $\text{CaSiO}_3[\text{s}]$ (wollastonite), $\text{Fe}_2\text{TiO}_4[\text{s}]$ (ulvospinel), $\text{Ca}_2\text{SiO}_4[\text{s}]$ (larnite), $\text{FeS}[\text{s}]$ (troilite), and $\text{C}[\text{s}]$ (graphite).

The atmosphere over MORB is predicted to be more reducing than over CC and BSE, with O_2 only playing a minor role. Between temperatures of about 1300 and 3500 K, the atmosphere consists mainly of H_2O and SO_2 with a particle ratio

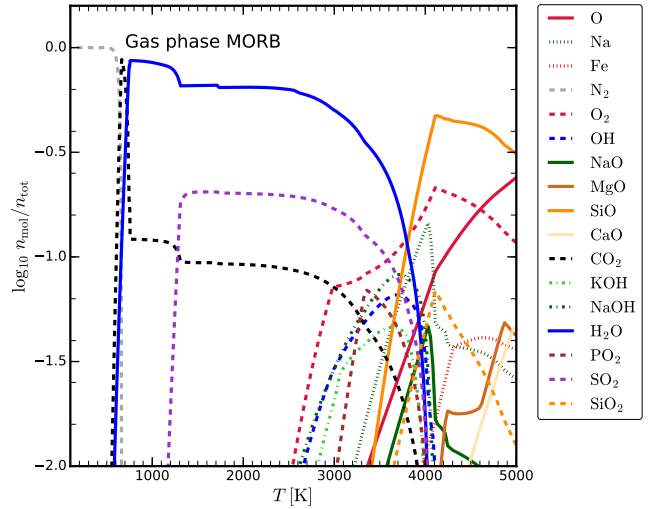


Fig. 6. Molecular concentrations $n_{\text{mol}}/n_{\text{tot}}$ for Mid Oceanic Ridge Basalt (MORB) element abundances as function of temperature for a constant pressure of $p = 100$ bar. Phyllosilicates are included in this model. All species with maximum log concentration > -1.4 are shown.

of about 6:1, according to the assumed element abundances of H and S. At higher temperatures, the gas mainly consists of SiO molecules and O atoms. At lower temperatures, $\text{FeS}[\text{s}]$ condenses at $T < 1300$ K, removing SO_2 from the gas phase. The following phyllosilicates become stable below about 750 K: $\text{Mg}_3\text{Si}_4\text{O}_{12}\text{H}_2[\text{s}]$ (talca), $\text{FeAl}_2\text{SiO}_7\text{H}_2[\text{s}]$ (Fe-chloritoid), and $\text{KMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2[\text{s}]$ (phlogopite). These phyllosilicates remove the water from the atmosphere and lead to a narrow temperature interval within which CO_2 becomes the most abundant gas species. They also prevent the formation of liquid water at lower temperatures. At $T < 650$ K, $\text{C}[\text{s}]$ (graphite) condenses, leaving behind an N_2 -rich atmosphere.

4.2. CI chondrite abundances

Chondrites are believed to be remainders of the formation period of the planets and thus can provide insights into the composition of the planets at very early stages. It remains a matter of debate whether it is still possible today to find meteorites that resemble the building blocks of Earth, since their isotope ratios do not match those on Earth (see e.g. Drake & Righter 2002; Yoshizaki et al. 2018). However, the isotope ratios of the planets can be explained by a mixture of different types of chondrites.

In order to investigate potential atmospheres based on these primitive remainders of the planet formation, Fig. 7 shows the results for CI chondrite element abundances, based on the *Orgueil* meteorite (see Lodders et al. 2009, and Table A.2). This meteorite has an extraordinarily primitive composition, which is rich in Fe, Mg, and S, but has only little Si, Ca, and Al. The volatile elements H, C, and N are significantly more abundant than for CC, BSE, and MORB (see Fig. 5).

Due to these differences, the liquid and solid composition is very different from all other cases studied so far. The first condensate $\text{MgAl}_2\text{O}_4[\text{l}]$ appears at $T \approx 4500$ K at 100 bar, while other abundant liquids are $\text{SiO}_2[\text{l}]$, $\text{FeO}[\text{l}]$, $\text{FeS}[\text{l}]$, $\text{MgSiO}_3[\text{l}]$, $\text{Mg}_2\text{SiO}_4[\text{l}]$, and $\text{MgO}[\text{l}]$. The most important solid condensates are $\text{SiO}_2[\text{s}]$ (quartz), $\text{FeS}[\text{s}]$ (troilite), $\text{MgSiO}_3[\text{s}]$ (enstatite), $\text{NaAlSi}_3\text{O}_8[\text{s}]$ (albite), $\text{C}[\text{s}]$ (graphite), $\text{FeS}_2[\text{s}]$ (pyrite), $\text{Fe}_3\text{O}_4[\text{s}]$ (magnetite), $\text{FeO}[\text{s}]$ (ferropericlyase), $\text{Fe}_2\text{SiO}_4[\text{s}]$ (fayalite), and $\text{NaAlSiO}_4[\text{s}]$ (nepheline). A number of carbonates becomes stable below about 500 K, among them $\text{FeCO}_3[\text{s}]$ (siderite), $\text{MgCO}_3[\text{s}]$ (magnesite), and $\text{MnCO}_3[\text{s}]$ (rhodochrosite). At

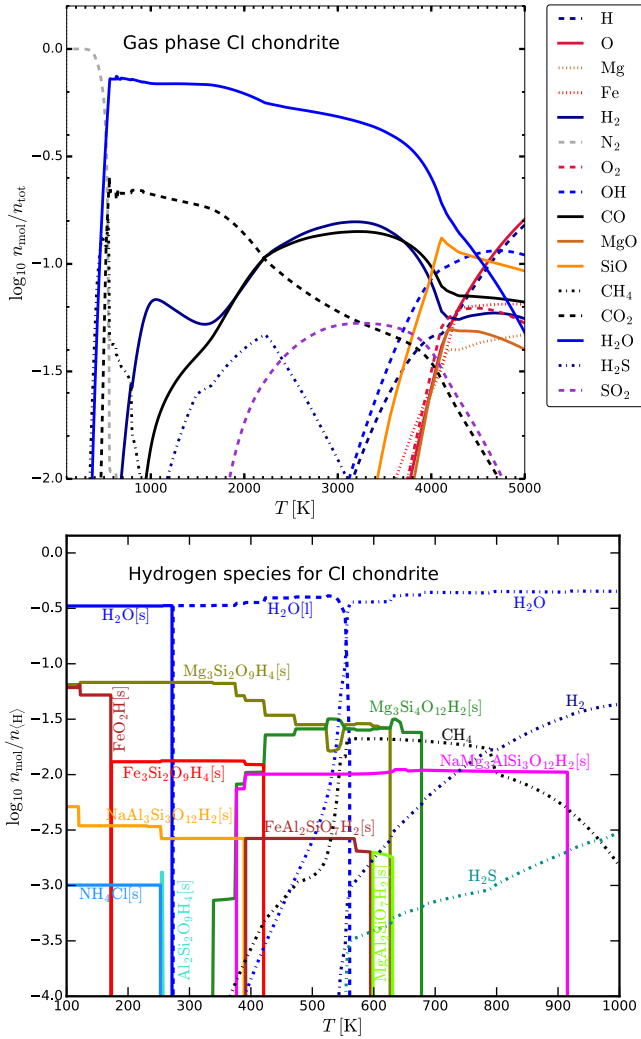


Fig. 7. Results for carbonaceous chondrite (CI) total element abundances at constant pressure $p = 100$ bar. Phyllosilicates are included in the model. *Top panel:* gas phase concentrations ($n_{\text{mol}}/n_{\text{tot}}$) between 100 and 5000 K. All species with maximum log concentration > -1.4 are shown. *Bottom panel:* gaseous and condensed species that contain hydrogen per H-nucleus (n/n_{H}) between 100 and 1000 K, we note the different scaling. The linestyles correspond to the different categories of condensates: silicates (solid), liquids (dotted), phyllosilicates (short dashed), other H-bearing species (long dashed), and other condensates (dash dotted).

temperatures below 400–900 K, hydration is very common, to the formation of phyllosilicates as $\text{Mg}_3\text{Si}_4\text{O}_{12}\text{H}_2[\text{s}]$ (talca), $\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2[\text{s}]$ (sodaphlogopite), $\text{Mg}_3\text{Si}_2\text{O}_9\text{H}_4[\text{s}]$ (lizardite), and $\text{Fe}_3\text{Si}_2\text{O}_9\text{H}_4[\text{s}]$ (greenalite). Despite the formation of those phyllosilicates, there is still enough hydrogen available for liquid and solid water to become thermally stable in this model, $\text{H}_2\text{O}[\text{l}]$ at 560 K and $\text{H}_2\text{O}[\text{s}]$ at 271 K. Interestingly, $\text{FeO}_2\text{H}[\text{s}]$ (goethite) becomes stable at about 170 K.

The gas phase mainly consists of H_2O for almost all temperatures considered, followed by CO_2 , CO and H_2 , and the sulphur molecules H_2S and SO_2 . At very high temperatures, $T > 4500$ K, O, H, OH, SiO, and CO become more abundant. Once the phyllosilicates, graphite and the carbonates have formed around 500 K, the gas phase is dominated by N_2 . Although NH_4Cl (ammonium chloride) becomes stable around 250 K in this model, the chlorine abundance is not large enough here to exhaustively consume N_2 .

In the bottom panel of Fig. 7 we show the hydrogen bearing species between 100 and 1000 K. The different H phases of H_2O incorporate most of the H atoms. The first H bearing condensate is $\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2[\text{s}]$ (sodaphlogopite) at about 910 K, followed by $\text{Mg}_3\text{Si}_4\text{O}_{12}\text{H}_2[\text{s}]$ (talca), $\text{MgAl}_2\text{SiO}_7\text{H}_2[\text{s}]$ (Mg-chloritoid), $\text{Mg}_3\text{Si}_2\text{O}_9\text{H}_4[\text{s}]$ (lizardite), and $\text{FeAl}_2\text{SiO}_7\text{H}_2[\text{s}]$ (Fe-chloritoid), before $\text{H}_2\text{O}[\text{l}]$ condenses at about 550 K. The amount of H kept in phyllosilicates increases steadily to lower temperatures, but is insufficient to suppress the thermal stability of liquid water.

The CI chondrite composition is the only rocky element composition considered in this paper that produces liquid and solid water without the need for additional hydrogen and oxygen. Although other rock compositions produce large amounts of gaseous water as well, phyllosilicates are thermodynamically more favourable than the liquid water, and hence inhibits the stability of liquid water for those other element abundances in phase equilibrium. However, the CI chondrites are hydrated so much that even after the formation of the phyllosilicates, there is still some water left to condense.

4.3. Polluted white dwarf abundances

The bulk composition of an exoplanet can be studied in terms of its mean density, which is determined by the planet’s mass and diameter. These quantities can be measured by a combination of radial velocity and transit observations (e.g. Weiss & Marcy 2014; Rice et al. 2019). A new, powerful and potentially more direct approach to measure the bulk composition of exoplanets is to determine the element composition in the atmospheres of polluted white dwarfs.

White dwarfs (WDs), the burnt-out cores of low-mass stars which become visible only after the terminal ejection of a planetary nebulae, usually have pure hydrogen or helium atmospheres, because all elements heavier than He settle down quickly ($\sim 10^5$ yr) in the extremely strong gravitational field of the object (see e.g. Paquette et al. 1986; Koester 2009). Nevertheless, some WDs show an enrichment in elements like O, Mg, Al, Si, Ca, Fe, Si, and C (e.g. Wilson et al. 2016; Farihi et al. 2016). These white dwarfs with metal absorption line features are hence called polluted white dwarfs (PWDs). The observed relative metal abundances in these PWDs are comparable to the Earth’s composition with some deviations, see references in Wilson et al. (2019) and Fig. 5. The most plausible reason for such enrichment with heavy elements in a white dwarf’s atmosphere is the accretion of planetesimals or planets from the white dwarf’s planetary system. The challenge is, however, that the datasets from PWDs are lacking some important elements as their detection is presently very challenging.

In Table A.2 we list the measurements for the WD GD 362 by Zuckerman et al. (2007), which shows a composition that is particularly Fe-rich, see Fig. 5. Unfortunately, the abundances of H and He as pollutant are impossible to derive this way, since these elements originate from the WD atmosphere itself. Thus, we excluded He from our calculations. Furthermore the values for C, N, and O are only provided as upper limits. In our model, we have therefore used averaged abundances for elements H, C, N, and O, computed from mean values of the logarithmic abundances from the columns denoted by “CC Schaefer”, “BSE Schaefer”, “MORB” and “CI meteorite” in Table A.2. This results in $\epsilon_{\text{H}} = 6.218$, $\epsilon_{\text{C}} = 5.344$, $\epsilon_{\text{N}} = 3.5365$ and $\epsilon_{\text{O}} = 7.903$. In this work, we only investigate element abundances from a single PWD which has inferred abundances for a large number of elements allowing a more diverse atmosphere and condensate

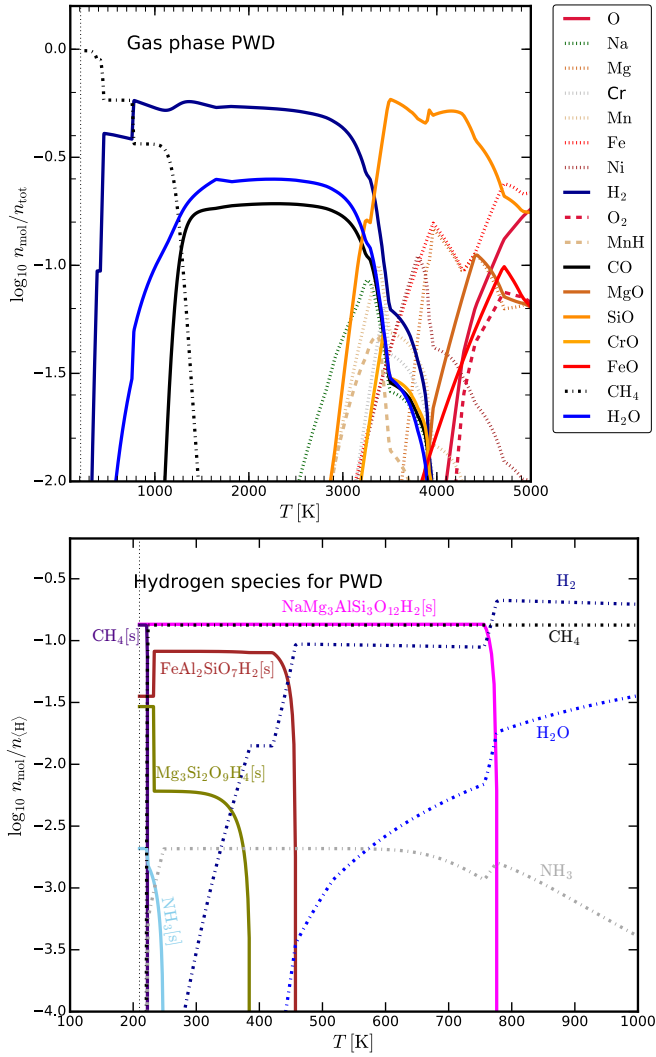


Fig. 8. Results for Polluted White Dwarf (PWD) total element abundances at constant pressure $p = 100$ bar. Phyllosilicates are included as possible condensates. *Top panel:* gas phase concentrations ($n_{\text{mol}}/n_{\text{tot}}$) between 100 and 5000 K. All species with maximum $\log n_{\text{mol}}/n_{\text{tot}} > -1.4$ are shown. *Bottom panel:* gaseous and condensed species that contain hydrogen are plotted with their concentration per H-nucleus n/n_{H} between 100 and 1000 K (we note the different scalings).

composition. An in-depth analysis of multiple elemental abundances inferred from PWD is beyond the scope of this paper. The origin of the pollutant material range from complete planets, stripped planetary cores, comets to gas giants (see e.g. Harrison et al. 2018; Bonsor et al. 2020).

We have included 17 elements in our model (H, C, N, O, Na, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Ni, and Cu). Some important elements have been disregarded, because their element abundances are not available, in particular F, P, S, Cl, and K. We also excluded Sc and Co because the condensate data in our model is not reliable for these elements. GGChem finds 194 gas species and 142 condensed species in its database, 23 of them being liquids, for the included 17 elements.

The results of our phase-equilibrium model are shown in Fig. 8. At $T \geq 3700$ K, Fe is the most abundant gas species, followed by SiO and O. Additionally, O_2 , FeO, Mg and MgO are abundant in the gas, but oxygen never becomes the dominant gas species as it is kept in large quantities in FeO[l].

At $T \sim 4900$ K, CaO[l] and MgAl_2O_4 [l] are the first condensates. Other relevant liquids are FeO[l], MgO[l], MgSiO_3 [l],

MgTiO_3 [l], and Fe[l], before CaO[l] solidifies as Ca_2SiO_4 [s] at $T \sim 3900$ K. Further condensates are Ni[l] and Ti_4O_7 [s], before the condensation of SiO₂[l], CaSiO₃[s], Ca_2SiO_4 [s], Mn_2SiO_4 [s], Na_2SiO_3 [l], and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ [s] in the temperature range $2900 \text{ K} < T < 3400 \text{ K}$ causes the atmospheric composition to change from an SiO dominated atmosphere to an H₂ dominated atmosphere with H₂O and CO being further abundant gas species.

At $T \lesssim 1300$ K, CO transforms into CH₄, which causes the H₂O concentration to decrease, which leaves an atmosphere rich in H₂, CH₄ and H₂O. The thermal stability of the phyllosilicates $\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2$ [s] (sodaphlogopite) at $T \lesssim 770$ K, $\text{FeAl}_2\text{SiO}_7\text{H}_2$ [s] (iron-chloritoid) at $T \lesssim 460$ K, and $\text{Mg}_3\text{Si}_2\text{O}_9\text{H}_4$ [s] (lizardite) at $T \lesssim 380$ K removes H₂ and H₂O from the gas phase, eventually leading to a pure CH₄ atmosphere. The trace gas NH₃ condenses at $T \lesssim 250$ K. The last gas species to become stable as a condensate is CH₄ at $T \lesssim 220$ K. For even lower temperatures, no species remain stable in the gas, and therefore no physical solution is possible for a $p = 100$ bar atmosphere. The formation of phyllosilicates inhibits once again the formation of water as a condensate.

The PWD element abundances are particularly rich in Fe, which binds oxygen from the atmosphere to form additional Fe-bearing solid compounds. Hence, increasing the total Fe abundance causes a more reducing atmosphere. The same effect can be achieved by increasing the Fe content in other element mixtures. For example, considering BSE abundances, an increase for the Fe abundance by 1 wt % causes the atmosphere to change from a mixture of H₂O, CO₂, and SO₂ to a mixture of H₂, H₂O, and CH₄ (see Fig. A.2). The results for Fe-enriched BSE abundances and PWD abundances are indeed very similar. Thus, a reducing atmosphere is expected for planets with increased total iron abundance in the crust, or could be caused by the late delivery of iron-rich bodies to the planet surface.

5. Stability of condensed water

The occurrence of surface water is believed to be one of the necessary conditions for the emergence of life as we know it (e.g. Westall & Brack 2018). Therefore, we investigate the potential stability of water in an equilibrium crust-atmosphere model.

The results of our models, as discussed in the previous sections, show that the formation of phyllosilicates can inhibit the formation of liquid and solid water for most rock compositions, except for the CI chondrite abundances. This raises the question by how much we need to change the total element abundances in order to allow for water to condense. We therefore have carried out additional simulations with altered element abundances based on the Bulk Silicate Earth (BSE) dataset.

Crucial for the water formation is the presence of hydrogen. We have therefore tested two approaches: (i) increasing the H abundance, and (ii) increasing the H and O abundances with particle ratio 2:1. The respective elements are added to the BSE abundances before normalising them to 1. Figure 9 shows our results for temperatures between 100 and 1000 K for these models.

The two top panels once again demonstrate the effect of the phyllosilicates. Only if the phyllosilicates are artificially removed from our list of condensates, we find liquid water to be thermally stable between about 350 and 550 K. If the phyllosilicates are included, however, in particular $\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2$ [s] (sodaphlogopite) and $\text{KMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2$ [s] (phlogopite), hydrogen is very efficiently removed from the gas phase, and liquid water cannot become thermally stable (upper right panel of Fig. 9).

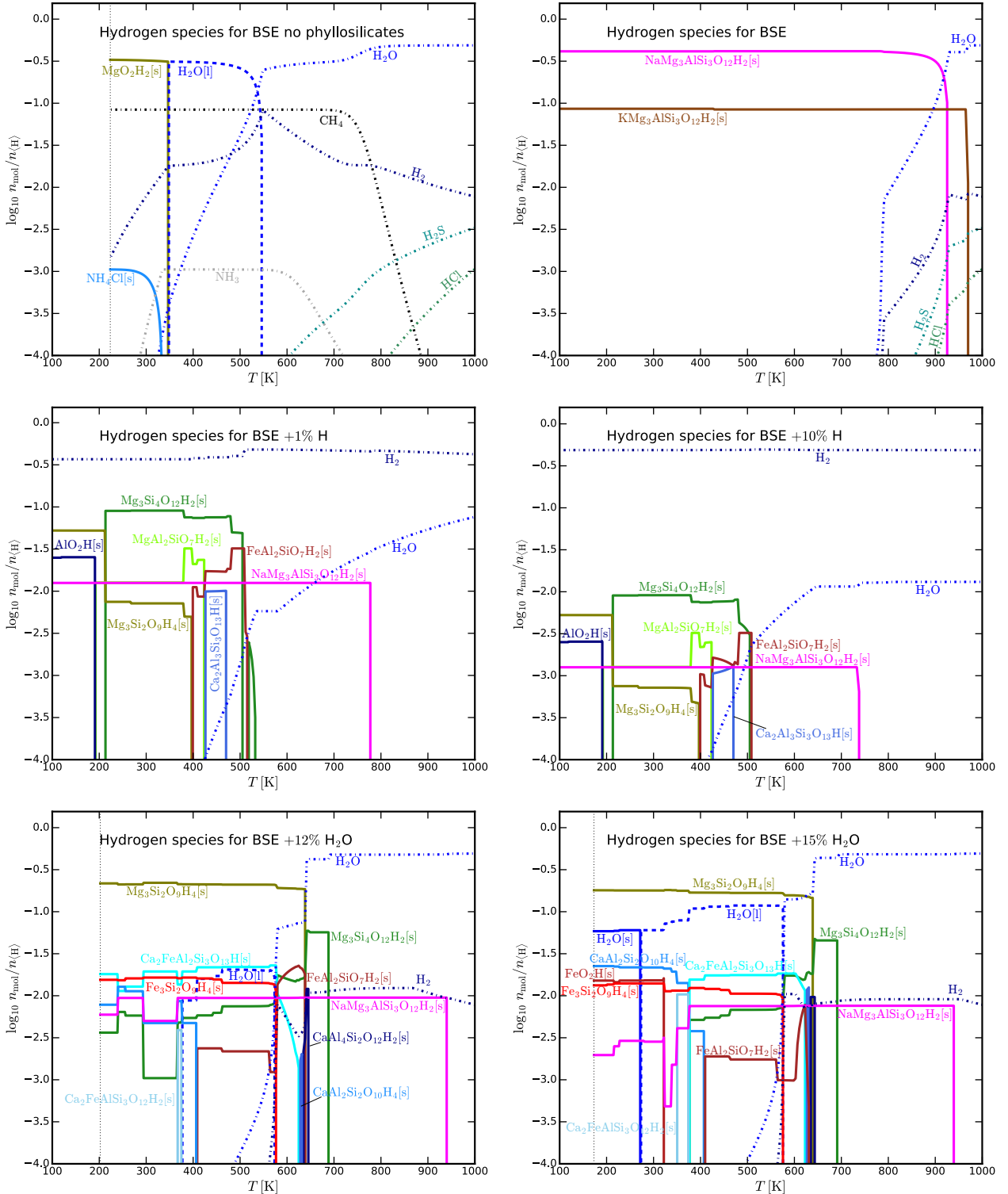


Fig. 9. Distribution of hydrogen among the different gas and condensed species. All models are run at 100 bar and for the following abundances: *top left panel:* BSE without phyllosilicates; *top right panel:* BSE; *middle left panel:* BSE + 1.339 wt% H; *middle right panel:* BSE + 15 wt% H; *bottom left panel:* BSE + 12 wt% H_2O ; *bottom right panel:* BSE + 15 wt% H_2O . The threshold concentration for species to be shown is set to 10^{-3} for all abundances except for BSE + 10% H ($10^{-3.5}$).

With additional H only, we have been unable to find models where liquid water would be thermally stable. We depict the concentrations of the hydrogen species in the middle panels of Fig. 9 after increasing the hydrogen abundance by 1 and 10 wt%, respectively. The dominant H bearing species in both cases is found to be H_2 . In comparison to the unaltered BSE model, however, a larger variety of phyllosilicates is found to form:

$\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2[\text{s}]$ (sodaphlogopite), $\text{FeAl}_2\text{SiO}_7\text{H}_2[\text{s}]$ (iron-chloritoid), $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{13}\text{H}[\text{s}]$ (clinozoisite), $\text{Mg}_3\text{Si}_4\text{O}_{12}\text{H}_2[\text{s}]$ (talca), $\text{MgAl}_2\text{SiO}_7\text{H}_2[\text{s}]$ (Mg-chloritoid), $\text{Mg}_3\text{Si}_2\text{O}_9\text{H}_4[\text{s}]$ (lizardite), and AlO_2H (diaspore).

With additional H and O, the formation of liquid and solid water succeeds in our models, see lower panels of Fig. 9. Since the mass ratio O:H is 16:1, the inclusion of 1 wt% water results

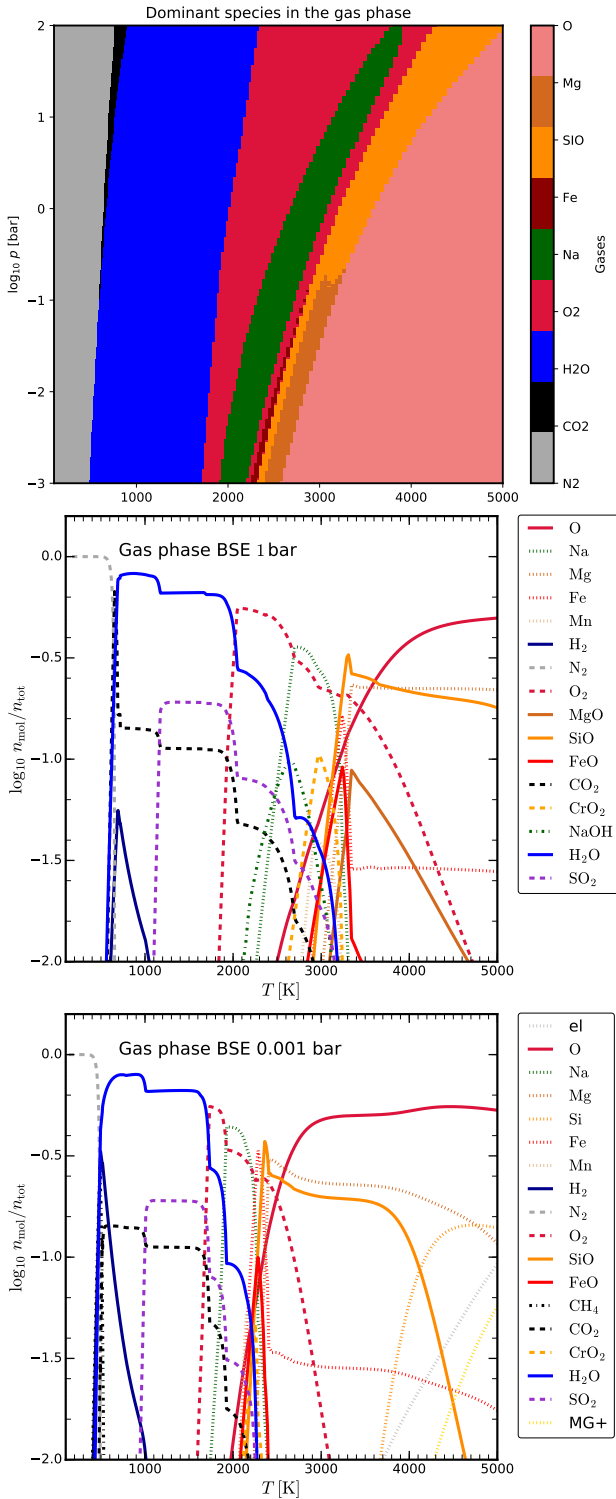


Fig. 10. Results for BSE total abundances at different pressures. *Upper panel:* dominant gas species with respect to the highest concentration in the p - T plane. *Middle panel:* gas concentrations ($n_{\text{mol}}/n_{\text{tot}}$) at $p=1$ bar. *Lower panel:* gas concentrations ($n_{\text{mol}}/n_{\text{tot}}$) at $p=0.001$ bar. The transitions in composition are caused by phase changes as listed in Table A.3. Further pressure levels are shown in Fig. A.1.

in an increase of 1/9 wt% for H and 8/9 wt% for O. We find that liquid water becomes stable after adding about 12 wt% of H_2O to the total BSE element abundances, whereas 15 wt% are required for the stability of solid water. The diversity of phyllosilicates increases again. In addition we find

$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{13}\text{H}[\text{s}]$ (epidote), $\text{CaAl}_2\text{Si}_2\text{O}_{10}\text{H}_4[\text{s}]$ (lawsonite), $\text{Ca}_2\text{FeAlSi}_3\text{O}_{12}\text{H}_2[\text{s}]$ (ferri-prehnite), $\text{CaAl}_4\text{Si}_2\text{O}_{12}\text{H}_2[\text{s}]$ (margarite), and $\text{Fe}_3\text{Si}_2\text{O}_9\text{H}_4[\text{s}]$ (greenalite). For $T < 200$ K, no atmosphere is found to be stable, since all included elements are thermally stable in condensates.

This analysis shows that phyllosilicates can act as a reservoir for capturing a certain amount of water. By adding sufficient hydrogen and oxygen, it is possible to saturate the phyllosilicates and to have liquid and solid water as stable condensates. The added water in our model could be an indicative of an additional delivery of water to the planet, for example via the incorporation of icy comets. However, there are other possible explanations. For example, the existence of phyllosilicates is thermodynamically impossible in the hot core and the overwhelming part of the mantle. The large amount of water that had once been present in this matter is likely to have been driven out into the crust and atmosphere during planet evolution. This way, there is plenty of water available to saturate the phyllosilicates in the crust and to have excess water to form an ocean.

6. Pressure variation

In the previous sections only a particular, fixed pressure of 100 bar was considered. However, the atmospheric pressures at the bottom of rocky planets can vary by orders magnitude, from several mbars to about 100 bars, comparable to our Solar System planets Mars and Venus, respectively. The hot atmospheres of very young rocky exoplanets might even have atmospheric pressures of multiple 100 bars (e.g. [Dhaliwal et al. 2018](#); [Olson & Sharp 2018](#)), following the general trend of increased vapour pressures for higher temperatures. Therefore, we investigate the influence of the atmospheric pressure on the atmospheric and crust composition in this section. This analysis is based on the BSE total element abundances.

In Fig. 10 we show the most abundant gas species in the p - T plane between 0.001 bar and 100 bar, and between 100 and 5000 K. The middle and lower panels show the atmospheric compositions at selected, constant pressures of 1 bar and at 0.001 bar, respectively. The plot for $p = 100$ bar was already shown in Fig. 4, lower panel. Additional pressure levels (10 bar and 0.1 bar) are available in the Appendix, see Fig. A.1.

Generally speaking, the phase changes occurring in the atmosphere are the same, but shift to lower temperatures for lower pressures. In particular, the temperature window in which O_2 is the dominant gas species becomes narrower for lower pressures. At 100 bar this range is roughly 2000–4000 K, whereas at 0.001 bar it narrows down to about 1600–1900 K. The temperatures where the various condensates appear and disappear are shifted likewise, see Table A.3.

7. Timescales

All calculations presented assumed that our systems have reached chemical equilibrium. We address this assumption by investigating three timescales. First, the timescale for the condensation from the gas phase to form the different condensates. Second, an annealing timescale that rearranges the condensate phase towards the thermodynamically favoured phase. Last, we investigate the chemisorption timescale, describing the formation of phyllosilicates.

We consider the relaxation of a state $y(t)$ towards equilibrium y_0 via the first-order ordinary differential equation $dy/dt = f(y)$, where f is the given time derivative. The relaxation timescale is found by considering small deviations from the

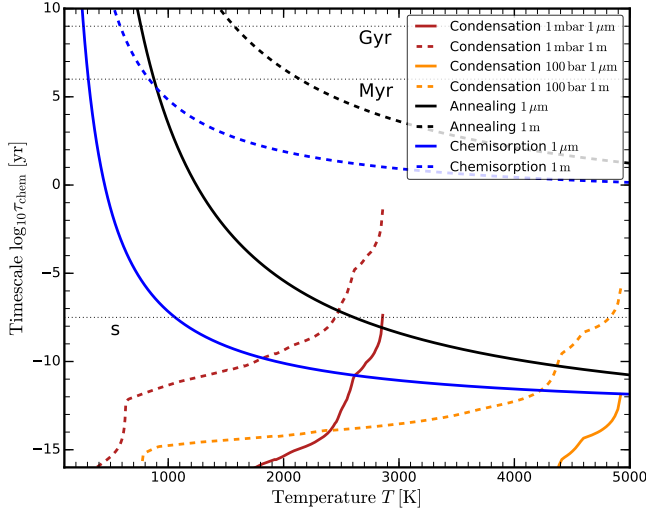


Fig. 11. Timescale estimates for the BSE total element abundances. The condensation timescale is shown for different pressures and length scales of $1 \mu\text{m}$ and 1m . The timescales for annealing and chemisorption are shown for scales of $1 \mu\text{m}$ and 1m each. The horizontal dotted lines illustrate times of 1s , 1Myr and 1Gyr , respectively.

equilibrium state as

$$\frac{dy}{dt} \approx f(y_0) + \frac{df}{dy}(y - y_0), \quad (1)$$

where $f(y_0) = 0$. The relaxation timescale is $(y - y_0)/(dy/dt)$, hence

$$\tau_{\text{relax}} = \left(\frac{\partial f}{\partial y} \Big|_{y_0} \right)^{-1}. \quad (2)$$

Close to the equilibrium state, the system relaxes as

$$y(t) = y_0 + (y(0) - y_0) \exp(-t/\tau_{\text{relax}}). \quad (3)$$

equilibrium. For the gas-condensed phase transition we have $y = V_s$ and

$$f(V_s) = (n - n_0)v_{\text{th}}A_{\text{tot}}V_1\alpha \quad (4)$$

$$= (V_{s0} - V_s)v_{\text{th}}A_{\text{tot}}\alpha. \quad (5)$$

where V_s is the volume of a condensate s per cm^3 , V_{s0} its value in phase equilibrium, n the number of key molecules in the gas phase forming the condensate, and n_0 its value in phase equilibrium. n and V are connected as

$$V_1(n - n_0) = -(V_s - V_{s0}), \quad (6)$$

in other words, an excess of key molecules in the gas phase means that the condensation is momentarily not complete. V_1 is the monomer volume. A_{tot} is the total surface of all condensates and α the sticking coefficient, assumed to be unity. v_{th} is the thermal velocity calculated by

$$v_{\text{th}} = \sqrt{\frac{8k_{\text{B}}T_{\text{g}}}{\pi m}}. \quad (7)$$

with the mass m of the gas species containing most of the limiting element. The limiting element is the least abundant element in the gas phase that is included in the considered condensate. When computing Eq. (8), we consider the longest timescale of all active condensates. The identifications of the slowest condensate, its limiting element and key species have little effect

on the results as they only enter via the thermal velocity which requires a species mass. k_{B} is the Boltzmann constant and T_{g} the gas temperature. Inserting Eq. (5) in (2) the condensation timescale τ_{cond} follows as

$$\tau_{\text{cond}} = (v_{\text{th}}A_{\text{tot}}\alpha)^{-1} = \left(v_{\text{th}} \frac{A_{\text{tot}}}{V_{\text{tot}}} V_{\text{tot}}\alpha \right)^{-1}. \quad (8)$$

V_{tot} is the total volume of all condensates. Equation (8) expresses the time it takes for the key molecule of the slowest condensate to collide with an existing surface. We approximate the surface-volume fraction $A_{\text{tot}}/V_{\text{tot}}$ by the dimension ratio

$$\frac{A_{\text{tot}}}{V_{\text{tot}}} \propto \frac{a^2}{a^3} = \frac{1}{a}, \quad (9)$$

with a length scale of a . The inclusion of different scales introduces factors of the order of 10^0 . For example, spherical symmetric grains with a radius of a have a surface-volume ratio of

$$\frac{A_{\text{tot}}}{V_{\text{tot}}} = \frac{4\pi a^2}{\frac{4}{3}\pi a^3} = \frac{3}{a}. \quad (10)$$

In Fig. 11, the condensation timescale for BSE abundances is shown for pressures of 100bar and 1mbar as well as for different length scales of $1 \mu\text{m}$ and 1m . For the 1mbar calculation, no condensates are stable for $T \gtrsim 2900 \text{K}$, thus the condensation timescale cannot be calculated. In case of the 100bar atmosphere, this threshold is at $T \approx 4900 \text{K}$.

The timescale based on reorganisation of condensates in the lattice structure itself is based on the transfer of sub groups of molecules from one point in the lattice to another by solid diffusion. This annealing process is described by Duschl et al. (1996) and Gail & Sedlmayr (1999) and the timescale can be calculated by

$$\tau_{\text{annealing}} = \frac{(\Delta a)^2}{\frac{1}{3}\lambda^2\nu \exp\left(\frac{-E_a}{k_{\text{B}}T}\right)}. \quad (11)$$

λ is the step length, ν the oscillation frequency, E_a the activation energy that needs to be overcome in order to move from one to an adjacent lattice place, k_{B} the Boltzmann constant and T the temperature. Δa is the total distance that the particle needs to travel in the lattice structures by random walk.

The black lines in Fig. 11 show the annealing timescales for different annealing distances Δa of $1 \mu\text{m}$ and 1m . As Gail & Sedlmayr (1999), we use the typical SiO_4 vibration frequency $\nu = 2 \times 10^{13} \text{s}^{-1}$ for the annealing process. SiO nucleation experiments from Nuth & Donn (1982) resulted in a characteristic activation energies for silicates of $E_a/k_{\text{B}} = 41\,000 \text{K}$. We assume a step size of $\lambda = 1 \text{nm}$, based on the order of magnitude of the monomer size calculated by $\lambda = \sqrt[3]{V_1}$ for monomer volumes V_1 .

For the formation of phyllosilicates, the chemisorption of H_2O in silicates is of importance (Thi et al. 2020). The formula to calculate these timescales is also given by Eq. (11). Thi et al. (2020) calculate the oscillation frequency for H_2O a surface sight as $\nu = 10^{12} \text{s}^{-1}$. The activation energy for a chemisorbed H_2O at the surface to occupy a free silicate core chemisorption site is $E_a/k_{\text{B}} = 13\,470 \text{K}$ (Okumura & Nakashima 2004). The chemisorption timescales for different thicknesses of 1m and $1 \mu\text{m}$ are shown in Fig. 11 as blue lines.

The timescales in Fig. 11 show that the formation of new condensates from the gas phase is quicker than 1yr for all temperatures and pressures considered. However, the formation

of the thermodynamically most favourable lattice structure by rearrangement via solid diffusion may take a long time. For μm -sized particles, the silicate rearrangement (annealing) timescale exceeds 1 Myr at about 900 K. In comparison, the chemisorption timescale for the diffusion of water into the rock structure is faster, exceeding 1 Myr at about 300 K for μm -sized particles.

The comparison of condensation timescales and annealing timescales provides a first order insight to the structure of the condensates. The condensate is crystalline if $\tau_{\text{cond}} > \tau_{\text{annealing}}$, because the condensates can rearrange quick enough to form the crystalline structure. For $\tau_{\text{cond}} \ll \tau_{\text{annealing}}$ the condensation occurs much faster and the formed condensate is amorphous (Gail & Sedlmayr 1999).

Especially the timescales for the phyllosilicate formation are very interesting as small rocks can be hydrated on timescales of planetary evolution which is in agreement to the conclusions of Thi et al. (2020). This underlines the importance of the inclusion of phyllosilicates to atmosphere-crust models.

8. Summary and discussion

The composition of the near-crust atmosphere of a rocky planet depends on the composition of the crust, and vice versa, as the atmosphere and the crust form a coupled thermo-chemical system. The gas in such near-crust atmospheres diffuses (or is transported) into the higher, low-pressure atmospheric regions where it may become, for example, subject to cloud-formation and/or mass loss. In our model we investigate the composition of the atmospheric gas directly in contact with the crust based on chemical phase equilibrium. The assumed total element abundances, and the thermo-chemical data of the condensed species included, are crucial factors for the determination of the composition of crust and atmosphere. All temperature values correspond to an atmospheric pressure of 100 bar.

Near-crust gas composition regimes. The near-crust atmospheres of the investigated rocky compositions (CC, BSE, MORB and CI chondrite) fall roughly into three regimes:

- (i) near-crust atmospheres with $T \lesssim 600$ K are dominated by N_2 or CH_4 ,
- (ii) near-crust atmospheres with $600 \text{ K} \lesssim T \lesssim 3000$ K are dominated by H_2O , CO_2 and SO_2 , but O_2 dominates for a BSE-crust for $T \gtrsim 2000$ K,
- (iii) near-crust atmospheres with $T \gtrsim 3000$ K consist of a combination of O_2 , metal atoms, oxides, and hydroxides.

The resulting near-crust atmospheric composition at lower temperatures ($T \lesssim 700$ K) depends on whether or not phyllosilicates are included. This can result in a shift from CH_4 as a dominant gas species to N_2 , as the hydrogen is consumed by condensates in the form of phyllosilicates. The model results for the CI chondrite abundances are the only ones that produces CO in gas concentrations higher than 10%, due to the relatively high C abundance.

The near-crust atmosphere for a rocky surface according to the polluted white dwarfs metal abundance remains inconclusive with respect to P, S, and K species as they are not measured in the PWD spectra. Nevertheless, our results for PWD abundances provide insight into the atmospheric composition of a potential iron rich planet. The major species of the corresponding near-crust gas phase would be CH_4 ($T \lesssim 750$ K), H_2 ($750 \text{ K} \lesssim T \lesssim 3300$ K), SiO ($330 \text{ K} \lesssim T \lesssim 4700$ K), and Fe ($4700 \text{ K} \lesssim T$).

Implications on magma oceans. We observe in our models that liquids start to play a role at temperatures $T \gtrsim 1700$ K, where

parts of the crust are molten for all total element abundances considered. For hot super Earth planets like 55 Cnc e or CoRoT-7b with dayside temperatures in the range from about 2500–3000 K the crust is mainly liquid, but also contains some solids. The crust composition can be grouped into two regimes, correlating with the difference in the Mg/Si ratio:

- (i) BSE/CI: melt consisting of mainly $\text{MgSiO}_3[\text{l}]$, $\text{FeO}[\text{l}]$, and $\text{MgSiO}_4[\text{l}]$ while the main solids are $\text{Ca}_2\text{MgSi}_2\text{O}_7[\text{s}]$ (åkermanite), $\text{MgCr}_2\text{O}_4[\text{s}]$ (picrochromite), and $\text{MnO}[\text{s}]$ (manganosite).
- (ii) CC/MORB: melt consisting of mainly $\text{SiO}_2[\text{l}]$, $\text{MgTi}_2\text{O}_5[\text{l}]$ and $\text{FeO}[\text{l}]$ while the solids contain $\text{MnSiO}_4[\text{s}]$ (tephroite), $\text{Cr}_2\text{O}_3[\text{s}]$ (eskolaite), and $\text{CaSiO}_3[\text{s}]$ (wollastonite).

The near-crust atmosphere above a magma ocean consists, in all cases, mainly of H_2O , O_2 , CO_2 , and SO_2 . The major differences are the dominance of O_2 over H_2O for the BSE abundances and the occurrence of H_2 and CO as the second and third most abundant gases in case of the CI chondrite element abundances.

Water stability. Phyllosilicates inhibit the thermal stability of liquid and solid water. The CI chondrite total element abundance is the only case for which the thermal stability of water as a condensate is not inhibited by phyllosilicates. In fact, water is abundant enough to overcome the stability of phyllosilicates in the CI chondrite case. Similarly, we are able to force the BSE composition to have liquid water as a thermally stable condensate by adding 12 wt% H_2O to the total element abundance. An additional 3 wt% H_2O allow solid water to be thermally stable. This shows the importance of phyllosilicates for the search for planets with potential liquid water. The role of phyllosilicates for the water content of exoplanets is further emphasised by their continuous formation on Earth's surface on short timescales. On the other hand, it is hypothesised, that most of the Earth's water is trapped in phyllosilicates in the wet mantle transition zone (Wang et al. 2019a). But this zone is not saturated with water and is believed to be able to take up all of Earth's water.

Timescale investigations show that hydration of small rocks occurs on evolutionary timescales also for temperatures as low as 300 K underlining the importance of phyllosilicates to the system. The rearrangement in refractory condensates towards the thermodynamically most favourable state is only valid for small scales and temperatures above 900 K. However, the major changes of the atmospheric composition at temperatures below 1000 K are caused by the formation of phyllosilicates and ices.

Implication for habitability. The search for habitable and inhabited planets is one of astrophysics ultimate goals. The occurrence of life alters the atmosphere and produce some gas species that can be used as biotracers. Earlier studies suggest that O_2 and O_3 would be a good biosignature, but more recent studies show that also abiotic sources can produce sufficient levels of O_2 in atmospheres (Domagal-Goldman et al. 2014; Harman et al. 2015, 2018; Luger & Barnes 2015). This underlines the necessity of understanding the difference between biosignatures and false positives. Previous studies show that various gas species can be used as biotracers (O_2 , O_3 , N_2O , CH_4 , CH_3Cl , NH_3 , C_2H_6 , and sulphur hazes (Domagal-Goldman et al. 2011; Lammer et al. 2019, and references therein)). In this study we find that some of these species are consistent with equilibrium models, but the occurrence of multiple of these species can be a sign for non equilibrium chemistry. While O_2 is a major constituent of the atmosphere at $T < 2000$ K, we are unable to produce stable O_2 at lower temperatures ($T \lesssim 1500$ K). Some further gas species that might be linked to life, especially N_2 and CH_4 , only occur at low temperatures. According to our model and the element

abundances analysed in this work, we conclude that the following gas compositions as possible signs for non-equilibrium and potential signature of life, ordered by the strength of argument

- (i) O₂ as abundant gas species for $T \lesssim 1500$ K,
- (ii) N₂ and O₂ at the same time for $T \lesssim 1500$ K (see also Stüeken et al. 2016),
- (iii) NO or NO₂ for $T \lesssim 1500$ K,
- (iv) CH₄ and O₂ at the same time.

The simultaneous occurrence of N₂ and O₂ with high concentrations is also possible for sufficiently high N abundances. N₂ is usually outgassing as a volatile whereas O₂ is produced from molten rock at high temperatures, but if we simply assume a much higher N-abundance, both O₂ and N₂ can coexist also at high temperatures in equilibrium. We note, however, that the detection of N₂ can be affected by lightning in cloudy atmospheres Ardaseva et al. (2017).

One of the crucial aspects in the formation of life as we know it is the occurrence of liquid water. From the results of this work, the upper crust of a (cooling) planet needs to be saturated in phyllosilicates in order to allow for the stability of liquid water on the surface. The detection of gaseous water in the atmosphere is not conclusive for the existence of liquid water, as the phyllosilicates are able to incorporate all potential liquid water in phase equilibrium.

Other conclusions about the crust composition on the basis of observations of the atmospheric composition can be ambiguous. However, the use of equilibrium models can provide the first steps to characterise the conditions on the surface of terrestrial exoplanets based on observations of atmospheric species.

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Appendix A: Additional figures and tables
Table A.1. Glossary for different condensed species.

Name	Sum formula	Structural formula
Dolomite	CaMgC_2O_6	$\text{CaMg}(\text{CO}_3)_2$
Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
Phlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2$	} $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{F}, \text{OH})_2$
Flourophlogopite	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$	
Sodaphlogopite	$\text{NaMg}_3\text{AlSi}_3\text{O}_{12}\text{H}_2$	$\text{NaMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{12}\text{H}_2$	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$
Fe-Chloritoid	$\text{FeAl}_2\text{SiO}_7\text{H}_2$	} $(\text{Fe}, \text{Mg}, \text{Mn})_2\text{Al}_4\text{Si}_2\text{O}_{10}(\text{OH})_4$
Mg-Chloritoid	$\text{MgAl}_2\text{SiO}_7\text{H}_2$	
Mn-Chloritoid	$\text{MnAl}_2\text{SiO}_7\text{H}_2$	
Lizardite	$\text{Mg}_3\text{Si}_2\text{O}_9\text{H}_4$	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Greanalite	$\text{Fe}_3\text{Si}_2\text{O}_9\text{H}_4$	$\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Goethite	FeO_2H	$\text{FeO}(\text{OH})$
Epidote	$\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{13}\text{H}$	$\text{Ca}_2(\text{FeAl}_2)(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$
Lawsonite	$\text{CaAl}_2\text{Si}_2\text{O}_{10}\text{H}_4$	$\text{CaAl}_2(\text{Si}_2\text{O}_7)(\text{OH})_2(\text{H}_2\text{O})$
Prehnite	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{12}\text{H}_2$	$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$
Ferri-Prehnite	$\text{Ca}_2\text{FeAlSi}_3\text{O}_{12}\text{H}_2$	$\text{Ca}_2\text{FeAlSi}_3\text{O}_{10}(\text{OH})_2$
Margarite	$\text{CaAl}_4\text{Si}_2\text{O}_{12}\text{H}_2$	$\text{CaAl}_2\text{Al}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$

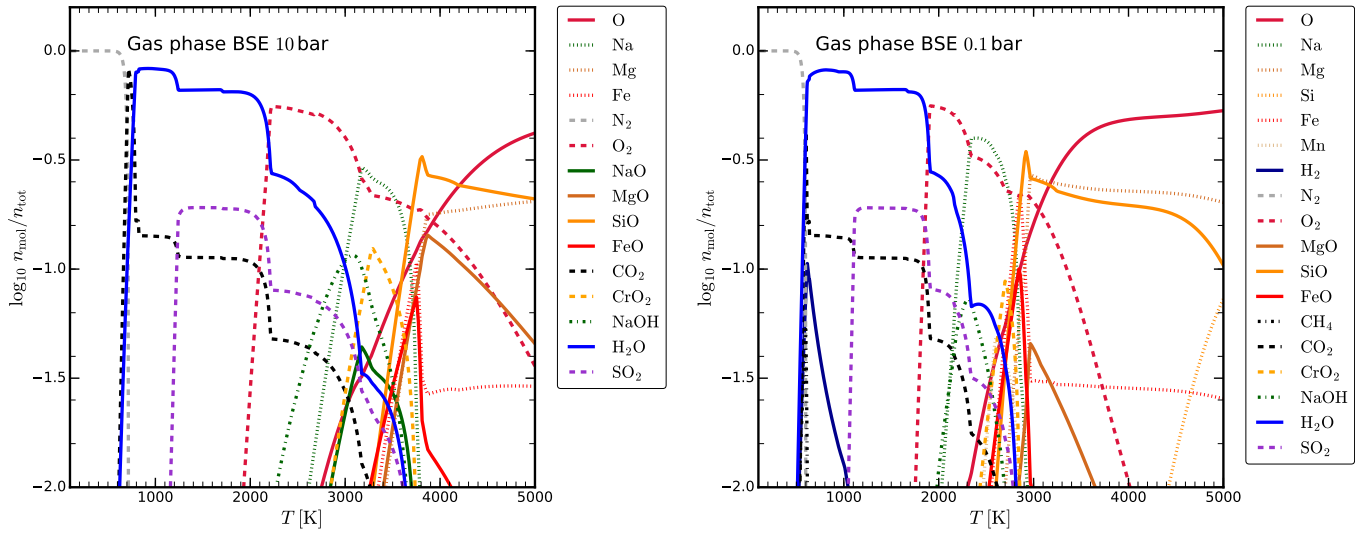

Fig. A.1. Two further pressure profiles for the pressure levels of 10 bar and 0.1 bar are shown as described in Fig. 10.

Table A.2. Element abundances from different astronomical and geological sources.

Element	Solar	CC schaefer	BSE schaefer	MORB	CI meteorite	Polluted white dwarf
References	1 H normalised	2 mfrac [%]	2 mfrac [%]	3 mfrac [%]	4 mfrac[%]	5 H normalised
H	12	0.045	0.006	0.045	1.97	12
He				0.000006	0.00000917	13.14
Li				0.00065	0.000147	
Be				0.000076	0.0000021	
B				0.00016	0.0000775	
C	8.5695	0.199	0.006	1.5	3.48	<7.5
N	8.0704	0.006	8.8E-05	0.14	0.295	<9
O	8.83	47.2	44.42	43.94564	45.9	<8
F	4.8867	0.053	0.002	0.0087	0.00582	
Ne					0.000000018	
Na	6.2757	2.36	0.29	2.06978	0.499	5.35 ± 0.20
Mg	7.5233	2.2	22.01	4.57101	9.68	7.16 ± 0.25
Al	6.427	7.96	2.12	7.77999	0.85	6.74 ± 0.20
Si	7.4976	28.8	21.61	23.59144	10.7	7.3 ± 0.30
P	5.4798	0.076	0.008	0.08030	0.0967	
S	7.1965	0.07	0.027	4	5.35	
Cl	5.2534	0.047	0.004	0.037	0.0698	
Ar					0.000000133	
K	5.1208	2.14	0.02	0.13282	0.0544	
Ca	6.3555	3.85	2.46	8.14033	0.922	6.9 ± 0.10
Sc	3.0416			0.00398	0.00059	2.95 ± 0.30
Ti	4.9408	0.401	0.12	1.00690	0.0451	5.19 ± 0.10
V	3.9159			0.0309	0.00543	4.4 ± 0.30
Cr	5.6014	0.013	0.29	0.0249	0.265	5.73 ± 0.10
Mn	5.4661	0.072	0.11	0.14250	0.193	5.67 ± 0.10
Fe	7.4167	4.32	6.27	8.10729	18.5	7.49 ± 0.10
Co	6.1788			0.0043	0.0506	4.64 ± 0.40
Ni				0.0092	1.08	6.07 ± 0.15
Cu	4.23			0.0074	0.0131	3.94 ± 0.40
Zn				0.00913	0.0323	
Ga				0.00175	0.000971	
Ge				0.0021	0.00326	
As				0.00018	0.000174	
Se				0.0013	0.00203	
Br	2.6279			0.00012	0.000326	
Kr					0.0000000522	
Rb				0.000288	0.000231	
Sr	2.9273			0.0129	0.000781	2.72 ± 0.30
Y	2.1788			0.00368	0.000253	
Zr	2.9447			0.01169	0.000362	
W				0.000012	0.0000096	
Sum		99.812	99.773	105.423	100.066	

Notes. “H normalised” means \log_{10} of nuclei particle ratio with respect to hydrogen, where H is normalised to 12, and “mfrac [%]” means mass fraction in the condensate.

References. (1) [Sharp & Huebner \(1990\)](#); (2) [Schaefer et al. \(2012\)](#); (3) [Gale et al. \(2013\)](#); (4) [Lodders et al. \(2009\)](#); (5) [Zuckerman et al. \(2007\)](#).

Table A.3. Temperatures where different condensed species appear (T_{high}) and disappear (T_{low}) in phase equilibrium for BSE abundances.

Condensates	Name	T_{high} [K]	T_{low} [K]	T_{high} [K]	T_{low} [K]	T_{high} [K]	T_{low} [K]
		$p = 100$ bar		$p = 1$ bar		$p = 1$ mbar	
MgAl ₂ O ₄ [l]		4871	2403	3653	2403	2532	2403
MgO [l]		4562	3849				
CaO [l]		4562	3799				
MgSiO ₃ [l]		4387	1850	3290	1850	2341	1850
FeO [l]		4387	1644	3247	1644	2281	1644
MgTiO ₃ [l]		4330	2499	3205	2499		
Mg ₂ SiO ₄ [l]		3849	2164	3333	2164	2403	2164
MnO	Manganosite	3849	2341	2924	2341		
Na ₂ SiO ₃ [l]		3799	2193	2703	2193		
Ca ₂ SiO ₄	Larnite	3799	3205	3421	3205		
Cr ₂ O ₃	Eskolaite	3701	3701				
Mg ₃ P ₂ O ₈		3512	3247				
MgCr ₂ O ₄	Picrochomite	3377	320	2963	320	2251	320
Ca ₃ P ₃ O ₁₃ H	Hydroxyaoatite	3247	3081	2532	2372		
Ca ₂ MgSi ₂ O ₇	Åkermanite	3205	1975	3205	1975	2403	1975
P ₂ O ₁₀		3122	1688	2372	1666	1850	1581
K ₂ SiO ₃ [l]		2886	2532				
Al ₂ O ₃ [l]						2668	2532
Ca ₂ Al ₂ SiO ₇	Gehlenite					2532	2435
KAlSiO ₄	Kalsilite	2532	2081	2341	2081		
MgTi ₂ O ₅ [l]		2499	2001	2499	2001	2311	2001
Ca ₃ MgSi ₂ O ₈	Merwinite					2435	2403
MgAl ₂ O ₄	Spinel	2403	2136	2403	2136	2403	2136
MgFe ₂ O ₄	Magnesioferrite	2372	1924	2027	1924		
MnTiO ₃	Pyrophanite	2341	1850	2341	1850	2136	1850
NaAlSiO ₄	Nepheline	2193	1949	2193	1949	380	277
Mg ₂ SiO ₄	Forsterite	2164		2164		2164	
CaAl ₂ Si ₂ O ₈	Anorthite	2136	570	2136	570	2136	570
KAlSi ₂ O ₆	Leucite	2081	1155	2081	1155	1874	1155
Fe ₂ TiO ₄	Ulvöspinel	2001	1233	2001	1233	2001	1233
CaMgSi ₂ O ₆	Diopside	1975	347	1975	347	1975	347
NaAlSi ₃ O ₈	Albite	1949	380	1949	380	1924	380
Fe ₃ O ₄	Magnetite	1924		1924		1733	
SiO ₂ [l]		1850	1826	1850	1826	1850	1826
MnSiO ₃	Pyroxmangite	1850	1581	1850	1581	1850	1581
MgSiO ₃	Enstatite	1826		1826		1826	
Ca ₅ P ₃ O ₁₂ F	Flourapatite	1710				1623	
FeO	Ferropericlaase	1644	1000	1644	1000	1644	1000
Mn ₂ SiO ₄	Tephroite	1581	1560	1581	1560	1581	1560
MnTiO ₃ (*)	Pyrophanite	1560	1170	1560	1170	1560	1170
NaCl [l]		1462	1068				
FeS	Troilite	1316		1170		1000	
FeTiO ₃	Ilmenite	1233		1233		1233	
Mn ₃ Al ₂ Si ₃ O ₁₂	Spessartine	1170		1170		1170	
KAlSi ₃ O ₈	Microcline	1155	962	1155	712	1155	513
KMg ₃ AlSi ₃ O ₁₀ F ₂	Flourophlogopite	1140	427	925	427	731	427
NaCl	Halite	1068		1054		780	
Fe ₂ SiO ₄	Fayalite	1000	150	1000	150	1000	150
KMg ₃ AlSi ₃ O ₁₂ H ₂	Phlogopite	962		712		513	
NaMg ₃ AlSi ₃ O ₁₂ H ₂	Sodaphlogopite	925		684		493	
C	Graphite	780		649		487	
FeAl ₂ O ₄	Hercynite	570		570		570	
MgF ₂		427	187	427	187	427	187
NaAlSiO ₄ (*)	Nepheline	380	277	380	277	380	277
Ca ₃ Al ₂ Si ₃ O ₁₂	Grossular	347		347		347	
Cr ₂ O ₃ (*)	Eskolaite	320		320		320	
NaAlSi ₂ O ₆	Jadeite	277		277		277	
CaF ₂		187	100	187	100	187	100
Fe	Iron	150		150		150	
MgF ₂ (*)		100		100		100	

Notes. Three different pressure levels are considered as indicated. The condensates are ordered by the temperature of their first appearance at $p = 100$ bar. The (*) indicates species, that are stable at a second temperature range.

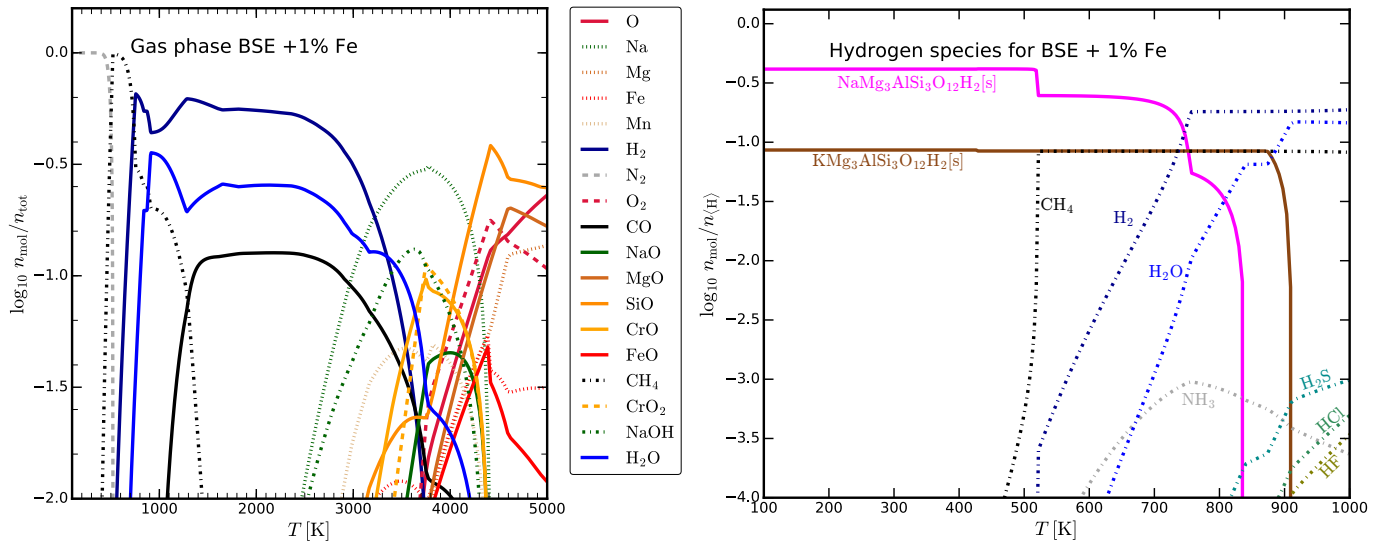


Fig. A.2. Results for BSE total element abundances at constant pressure $p = 100$ bar. Phyllosilicates are included as possible condensates. *Left panel:* gas phase concentrations ($n_{\text{mol}}/n_{\text{tot}}$) between 100 K and 5000 K. All species with maximum $\log n_{\text{mol}}/n_{\text{tot}} > -1.4$ are shown. *Right panel:* gaseous and condensed species that contain hydrogen are plotted with their concentration per H-nucleus n/n_{H} between 100 and 1000 K (we note the different scalings).