The condensation temperatures of the elements: A reappraisal

BERNARD J. WOOD1,* DOANE J. SMYTHE1, AND THOMAS HARRISON1

1Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, U.K.

ABSTRACT

As part of a project to investigate the volatilities of so-called “moderately volatile elements” such as Zn, In, Tl, Ga, Ag, Sb, Sb, and Cl during planetary formation, we began by re-calculating the condensation temperatures of these elements from a solar gas at 10−4 bar. Our calculations highlighted three areas where currently available estimates of condensation temperature could be improved. One of these is the nature of mixing behavior of many important trace elements when dissolved in major condensates such as silicates, Fe-rich metals, and sulfides. Nonideal solution of the trace elements can alter (generally lower) condensation temperatures by up to 500 K. Second, recent measurements of the halogen contents of CI chondrites (Clay et al. 2017) indicate that the solar system abundance of chlorine is significantly overestimated, and this affects the stabilities of gaseous complexes of many elements of interest. Finally, we have attempted to improve on previous estimates of the free energies of chlorine-bearing solids since the temperature of chlorine condensation has an important control on the condensation temperatures of many trace elements. Our result for the 50% condensation temperature of chlorine, 472 K is nearly 500 K lower than the result of Lodders (2003), and this means that the HCl content of the solar gas at temperatures <900 K is higher than previously estimated.

We based our calculations on the program PHEQ (Wood and Hashimoto 1993), which we modified to perform condensation calculations for the elements H, O, C, S, Na, Ca, Mg, Al, Si, Fe, F, Cl, P, N, Ni, and K by free energy minimization. Condensation calculations for minor elements were then performed using the output from PHEQ in conjunction with relevant thermodynamic data. We made explicit provision for nonidealities using information from phase diagrams, heat of solution measurements, partitioning data and by using the lattice strain model for FeS and ionic solids and the Miedema model for solutions in solid Fe. We computed the relative stabilities of gaseous chloride, sulfide, oxide, and hydroxide species of the trace elements of interest and used these, as appropriate in our condensation calculations. In general, our new 50% condensation temperatures are similar to or, because of the modifications noted above, lower than those of Lodders (2003).

Keywords: Condensation temperatures, element abundances, solar nebula, thermodynamics

INTRODUCTION

The concept of volatility is an important one in geochemistry and cosmochemistry. During the early evolution of the solar system, there was fractionation of volatile elements between solid, gas, and liquid phases, resulting in the isotopic and chemical fractionations observed between different meteorite groups and planetary bodies. One of the principal tasks in this area is to determine how to interpret the observed chemical and isotopic differences between different bodies in terms of appropriate processes in the solar nebula and during planetary accretion. In this context, it is necessary to consider exactly what is meant by “volatility.” Conventionally, volatility is defined geochemically in a very broad sense as being related to the temperature at which a specific element would condense from a gas of solar composition. Thus, volatile elements are defined as those that condense at relatively low temperature (e.g., < 1100 K) from the putative solar gas while refractory, involatile elements condense at higher temperatures. The utility of the approach lies in the fact that elemental abundances in the bulk silicate Earth (BSE) correlate negatively with condensation temperature when expressed relative to a volatile-rich meteorite group such as CI chondrites.

Figure 1 shows the abundances of a large number of elements in the BSE, expressed relative to abundances in CI chondrites, (and normalized to Mg of 1.0) (Palme and O’Neill 2014) plotted vs. the temperature (Lodders 2003) at which 50% of the element would be condensed from a gas of solar composition at a total pressure of 10−4 bar. As can be seen, refractory lithophile elements such as Ca, Ti, Zr, Sc, and the rare earths (REE) are all present in approximately chondritic proportions one to another in the silicate Earth, while there is a steady decline in abundance of lithophile elements with decreasing condensation temperature beginning at Mg. The latter has a 50% condensation temperature (T50) of 1336 K (Lodders 2003). Lying below the volatility “trend” of lithophile elements are the abundances of siderophile elements that are known to have strong affinities for liquid Fe and are hence believed to be partly partitioned into the core. The so-called highly siderophile elements, encompassing the platinum group, Au and Re are present in approximately chondritic ratio one to another in the BSE, but at <1% of the level of refractory lithophiles. On the left side of Figure 1, we have
grouped together elements that are depleted relative to elements of similar volatility (or condensation temperature) and arbitrarily named them “volatile siderophile” elements. Some of the latter, Sb, Ag, S, and C for example are well-known to partition strongly into Fe-rich metals (Steelmaking Data Sourcebook 1988; Wood 1993; Pei et al. 1995) while others (e.g., Cl) are depleted but not known to partition into liquid Fe, so the reasons for their low abundances are unclear. Note, however, that a recent re-analysis of CI chondrites (Clay et al. 2017) raises the CI normalized concentration of chlorine by a factor of 6.1.

The correlation shown in Figure 1 for lithophile elements is seductive but liable to draw the reader into overinterpretation of geochemical and cosmochemical data because abundances correlate with a process, condensation, which applied only for a brief period in the history of the solar system. The nebular gas of approximately solar composition appears to dissipate within about 3 Ma of the beginning of the solar system (Evans et al. 2009) so that most of the tens of millions of years of planetary growth and even the geological development of small asteroidal bodies such as Vesta (Roszjar et al. 2016) took place in the absence of the H2-rich atmosphere characteristic of the bulk solar system. The nebular gas is, of course, highly reducing (about 7 log fO2 units below the Fe-FeO, IW oxygen buffer) and after it disappeared the atmospheres above protoplanetary bodies would have been established by silicate-gas equilibria under oxygen fugacity conditions governed by the FeO contents of the silicate mantle. If we take the lowest fO2 values plausible, then these would have been controlled, given the presence of metallic cores on the terrestrial planets and many asteroids, by Fe-FeO equilibrium and would thus have been 1–2.5 log units below IW (Righter et al. 1998; Wood et al. 2006).

Despite these observations on the short lifetime of the nebular gas and the inevitable increase in fO2 after it disappeared, the condensation sequence shown in Figure 1 appears to have taken on near-magical significance in the literature. Thus, for example, the difference in abundances of Zn and S in the silicate Earth has been used to infer that the S “missing” from silicate Earth is partitioned into the core and that the difference in Zn/S between CI chondrites and BSE can be used to calculate the S content of the core (Dreibus and Palme 1996). The result is 1.7% S (Dreibus and Palme 1996). The large difference in relative abundance between In and elements of similar volatility such as Tl is often treated as an unexplained anomaly (Witt-Eickschen et al. 2009) an impression enhanced by the fact that In is both more siderophile and more chalcophile than the more depleted Tl (Kiseeva and Wood 2013; Wood et al. 2014). However, In (+3) and Tl (+1) have different oxidation states in many geologic environments so their relative volatilities must depend on oxygen fugacity, with indium becoming, in principle less volatile as fO2 increases. This assertion follows from the idealized equilibrium:

\[ 2\text{In}^0(\text{gas}) + \text{Tl}_2\text{O} (\text{solid}) + O_2 = 2\text{Tl}^0(\text{gas}) + \text{In}_2\text{O}_3 (\text{solid}) \] (1)

Raising fO2 should, in this case, drive the equilibrium to the right, putting Tl into the gas phase and In into the solid.

Our study started from the question “Are the calculated condensation temperatures from a solar gas relevant to elemental abundances in silicate Earth?” We began by performing condensation calculations for 30 of the more volatile elements. These convinced us that the results are very sensitive to the wide range of possible assumptions for the properties of the trace elements dissolved in the major phases. For example, we are able to reproduce the result of Lodders (2003) for Ag and Pb dissolved in solid Fe assuming ideal solution, but when we take account of the likely nonidealities of Ag and Pb in Fe, the condensation temperatures drop by several hundred degrees Kelvin. As we progressed through most of the naturally occurring elements we found that the behavior of Cl in the solar gas has major influences on the properties of many of the elements and that the recently re-determined halogen contents of the solar system (as in CI chondrites, Clay et al. 2017) should change condensation temperatures significantly. We, therefore, determined to revise the published values to take account of the new measurements.

**Calculation strategy: Condensation from a solar gas**

Many of the calculations discussed below can be and were performed in a spreadsheet. The first step, however, is to determine the stabilities of the solids and gaseous species of the major elements. To do this, we used the computer program PHEQ (Wood and Hashimoto 1993) that performs free energy minimization for fixed total gas pressure and temperature and provides the number of moles of each species for a known starting composition. It was written specifically for performing condensation calculations and, as initially configured, uses free energy data for 93 gaseous and 148 solid species of the elements H, O, C, S, Na, Ca, Mg, Al, Si, and Fe. These are tabulated in 100 K intervals in the form:

\[ \frac{\mu^0}{RT} = \frac{H^0 - H^0_{298} - TS^0 + \Delta H^0_{298}}{RT} \] (2)

In Equation 2, \( H^0 \) and \( S^0 \) refer to enthalpy and entropy of the pure phase at the subscripted temperature and \( \Delta H^0_{298} \) to the...
Figure 2. (a) Fractions of different phases present in the stable solid assemblage as a function of temperature at total pressure = 10^{-4} bar. Corundum is the first phase to appear at about 1675 K and is joined by small amounts of hibonite and melilite before the major phase of condensation begins at ~1380 K. (b) Concentrations of major elements in the gas phase (normalized to the initial Mg content of the solar gas) as a function of temperature at 10^{-4} bar.

enthalpy of formation from the elements at 298 K. For reasons that will become clear as we continue, we have added solid and gas data for species of the elements F, Cl, P, N, Ni, and K. Other updates and modifications of PHEQ described in the literature include the GRAINS code of Petaev (2009). Although the PHEQ program, as initially configured, assumes ideal solution for olivines, orthopyroxenes, clinopyroxenes, plagioclases, metals, spinels, and melilite this assumption introduces only small errors in $T_{50}$ for the major elements Na, Ca, Mg, Al, Si, and Fe that all, except for Na, condense above 1300 K. The calculated condensation temperatures for these elements agree well with those of Lodders (2003) and of earlier workers on this subject (Table 1). Most of the minor elements of interest condense into Fe metal or iron sulfide, however, and we have made explicit provision for nonideal solution in these cases as detailed below.

Calculations were performed at a total pressure of 10^{-4} bar, and we followed normal convention of re-equilibrating solids and gases at each step in the condensation process as temperature declined. Although there are several estimates of solar system abundances of the elements, we opted, apart from the halogens, to use those of Lodders (2003) to facilitate comparison with her calculations of condensation temperature. Figure 2 shows the abundances of the important solid phases and gas components as functions of temperature at 10^{-4} bar. Small amounts of corundum appear at about 1675 K, followed by hibonite at 1630 K, melilite at 1550 K, and spinel at 1410 K. Major forsteritic olivine and Fe-rich metal start precipitating at 1380–1360 K, followed by other silicates, clinopyroxene, plagioclase, and orthopyroxene at 1350, 1305, and 1285 K, respectively. With declining temperature, the proportions of these phases change as they react with one another and with the solar gas. The other major phase to appear is iron sulfide at 710 K, and this increases in proportion at the expense of Fe metal as the temperature falls further (Fig. 2). Table 2 gives the major solid and gaseous species in 50° intervals from 1700 down to 350 K together with the fugacities of H$_2$O, O$_2$, HCl, and H$_2$S at each temperature. We reiterate that these are equilibrium calculations, however, and that it has been shown that some of the expected reactions, notably the reduction of N$_2$ and CO to NH$_3$ and CH$_4$ are kinetically inhibited at low temperatures (Lewis and Prinn 1980).

Trace and minor element condensation

Our general approach to condensation can be carried out for most elements in a spreadsheet. Let us suppose that our trace element M is present in the gas phase predominantly as monatomic M$^0$ and that it condenses to oxide MO$_{1.5}$. The condensation equilibrium can be represented as follows:

$$M^0 (\text{gas}) + 0.75O_2 (\text{gas}) = MO_{1.5} (\text{solid}) \quad (3)$$

The logarithm of the equilibrium constant for the reaction (log $K_r$) is calculated from the tabulated equilibrium constants of formation of the species involved from their constituent elements:

$$\log K_r = \log K^{M^{0.5}}_{O_2} - \log K^{-0.75}_{O_2} - 0.75\log K^{O_2}_{O_2} \quad (4)$$

We fit log $K_r$ as a function of temperature or reciprocal temperature. Then, from the equilibrium constant for reaction 3 we have:

$$\log P_{M^0} = \log a^{\text{solid}}_{MO_{1.5}} - \log K_r - 0.75\log P_{O_2} \quad (5)$$

where $P_{M^0}$ and $P_{O_2}$ are the partial pressures of M$^0$ and O$_2$ in the gas phase, respectively, and $a^{\text{solid}}_{MO_{1.5}}$ is the activity of the metal oxide in the condensing solid. We obtain log$P_{O_2}$ as a function of temperature from the PHEQ program and as a starting point assume that MO$_{1.5}$ is a pure oxide with $a_{MO_{1.5}}$ equal to 1. We fix $P_{M^0}$ at the value expected at a total gas pressure of 10^{-4} bar when 50% of the solar abundance of M is in the gas phase. We then vary temperature until the left- and right-hand sides of Equation 5 are equal. This gives us $T_{50}$. Exactly the same approach is used if, for example, the most stable gaseous species is MCl or MS or MOH. In these cases, however, the equilibrium must also use appropriate log K and partial pressure data for HCl, H$_2$S, H$_2$O, and H$_2$. If two or more gaseous species are present in similar amounts, we simply reduce
log $P$, for the most stable species by an appropriate amount to take account of the fractions of these additional species.

The simplified case above describes condensation into a pure solid phase of element M to MO$_{1.5}$. Higher condensation temperatures are obtained, however, if we consider the fact that trace elements will, in general, dissolve in one or more of the major phases described above and illustrated in Figure 2. This is because the activity of any component $i$ is generally lowered relative to that of pure $i$ ($a_i = 1$) if $i$ is dissolved in a major element phase $P$:

$$\log a_i = n \log (X_i) + n \log (\gamma_i)$$  \hspace{1cm} (6)

In Equation 6, $n$ refers to the number of sites in phase P on which $i$ substitutes, $X_i$ is the mole fraction of $i$ on those sites, and $(\gamma_i)_r$ is the activity coefficient of $i$ in phase P. Mole fraction $X_i$ comes from having 50% of element $i$ in the solid phase. If the solid solution is ideal $(\gamma_i)_r = 1.0$ and $i$ will condense into P so long as the sum of the second and third terms on the right-hand side is less than zero i.e.,

IF: $\log (X_i)_p + \log (\gamma_i)_r < 0$, condensation of $i$ is into phase P
ELSE: $i$ condenses into pure $i$ at a lower temperature.

To calculate activities and condensation temperatures in cases of dissolution in a major phase, we started with the phases nominated by Lodders (2003) as the hosts and searched for other solutions in cases where it seemed likely that such existed.

**Activity coefficients of trace elements**

We used a combination of phase equilibria, thermodynamic data, and crystallographic measurements to make estimates of the activity coefficients of trace elements in the major solid phases in the condensation sequence.

**Activity coefficients in solid Fe from solubility.** At temperatures below 1185 K, the stable form of Fe is body-centered-cubic $\alpha$-Fe while face-centered cubic $\gamma$-Fe is stable between 1185 and 1667 K. For elements such as Ag and Pb that are almost insoluble in solid Fe we estimate activity coefficients from known solubility at a fixed temperature. Thus, for example, in equilibrium with pure Ag the maximum mole fraction of Ag dissolved in $\gamma$-Fe at 1366 K is $3.7 \times 10^{-5}$ (Wriedt et al. 1973). A first estimate of the activity coefficient at this temperature would then be:

$$\gamma_{Ag} = 1/X_{Ag} = 1/(3.7 \times 10^{-5}) = 27027$$

At this temperature the Ag is liquid, however, so we should make a correction for the free energy of the liquid-solid transformation in pure Ag. This makes $\gamma_{Ag}$ larger by a factor $f_{Ag}$:

**Table 1. 50% condensation temperatures and major host phases at $10^{-4}$ bar**

| Element | $T_m$ (K) | This study Phase | Activity coefficient (%) | Lodders (2003) Phase | $T_m$ (K) | Wasson (1985) $T_m$ (K) |
|---------|-----------|-----------------|--------------------------|----------------------|-----------|-----------------------|
| Li      | 1148      | En              | 5.0 [1]                  | Fo + En              | 1142      | 1225                  |
| Be      | 1551      | MII             | Iny = 1000 ln(16)/T [2]  | MII                   | 1452      |                       |
| B       | 740       | PI              | Iny = 0.64; $\gamma$ > 0.56 [3] |                       | 908       | Fsp                   |
| C       | 40        | CH$_4$·H$_2$O + CH$_4$ ice |                       |                       | 123       |                       |
| N       | 183       | Rock + Water ice |                       |                       | 180       |                       |
| O       | 674       | F-Ap            | 1 (assumed ideal)       | F-Ap                 | 734       |                       |
| Ne      | 1035      | PI              | Iny = 0.64; $\gamma$ > 0.56 [3] |                       | 958       | Fsp                   |
| Mg      | 1343      | Fo + Cpx        | 1 (pure)                 | Fo                    | 1336      | 1340                  |
| Al      | 1652      | Crn             | 1 (pure)                 | Hbn                   | 1633      | 1650                  |
| Si      | 1314      | Fo + Cpx        | 1 (pure)                 | Fo + En               | 1310      | 1311                  |
| P       | 1287      | Scb             | 1 (pure)                 | Scb                   | 1229      | 1151                  |
| S       | 672       | Tro             | 1 (pure)                 | Tro                   | 664       | 648                   |
| Cl      | 472       | Cl-Ap           | 1 (assumed ideal)        | Sdl                   | 948       | 863                   |
| K       | 993       | PI              | Iny = 1100 ln(9.57)/T [2] |                       | 1006      | Fsp                   |
| Ca      | 1535      | MII             | 1 (pure)                 | Hbn + MII             | 1517      | 1518                  |
| Sc      | 1541      | Prv + MII       | 1 (assumed ideal)        | Hbn                   | 1659      | 1644                  |
| Ti      | 1565      | Prv             | 1 (pure)                 | Prv                   | 1582      | 1549                  |
| V       | 1370      | Fe alloy + Prv  | Iny = 29000/(8.314·T) [4] | Prv                  | 1429      | 1450                  |
| Cr      | 1291      | Fe alloy        | Iny = 60000/(8.314·T) [4] | Fe alloy              | 1296      | 1277                  |
| Mn      | 1123      | Fo + En         | 1 (close to ideal) [1]   | Fo + En               | 1158      | 1190                  |
| Fe      | 1338      | Fe alloy        | 1 (assumed ideal)        | Fe alloy              | 1334      | 1336                  |
| Co      | 1354      | Fe alloy        | 0.85 [4]                 | Fe alloy              | 1352      | 1351                  |
| Ni      | 1363      | Fe alloy        | 0.68 [5]                 | Fe alloy              | 1353      | 1354                  |
| Cu      | 1034      | Fe alloy        | Iny = 1000 ln(117)/T [7] | Fe alloy              | 1037      | 1037                  |
| Zn      | 704       | Fe alloy        | Iny = 1123 ln(1.86)/T [8] |                       | 726       | 660                   |
| Ga      | 1010      | Fe alloy        | Iny = –7043/T [9]        | Fe alloy + Fsp        | 968       | 918                   |
| Ge      | 830       | Fe alloy        | Iny = –52000/(8.314·T) [10] |                       | 883       | 825                   |
| As      | 1235      | Fe alloy        | Iny = 60000/(8.314·T) [4] |                       | 1065      | 1157                  |
| Se      | 701       | Fe alloy        | Iny = 1293 ln(1.67)/T [2] |                       | 697       | 684                   |
| Br      | 412       | Syl             | Iny = 420 ln(3.36)/T [2] |                       | 546       | –690                  |
| Kr      | 752       | Sa              | Iny = 1000 ln(1.43)/T [2] |                       | 52        | Kr·HfO                 |
| Rb      | 1548      | Prv             | Iny = 1100 ln(1.53)/T [2] |                       | 1464      | Ca-titanate            |
| Sr      | 1551      | MII + Prv       | 1 (assumed ideal)        | Hbn                   | 1659      | 1592                  |
| Zr      | 1722      | ZrO$_2$        | 1 (pure)                 | ZrO$_2$               | 1741      | 1780                  |
| Nb      | 1561      | Prv             | 1 (assumed ideal)        | Ca-titanate           | 1559      | –1550                 |
| Mo      | 1520      | Mo metal        | 1 (pure)                 | Refractory metal alloy | 1590      | 1608                  |

(Continued on next page)


\[ f_{c} = \exp[\Delta S_{m}(T - T_{M})/(RT)] \]

where \( \Delta S_{m} \) is the entropy of melting at the melting temperature of 1234 K, \( T \) is the temperature of interest, and \( R \) is the gas constant.

To extrapolate a known (or estimated) value of \( \gamma_{l} \) up and down temperature we make the usual assumption that activity coefficients approach 1 at infinite temperature. This leads to a calculated \( \gamma_{l} \) at temperature \( T \) from \( \gamma_{TM} \) measured at temperature \( T_{M} \).

\[ \ln(\gamma_{l}) = (T_{M}/T) \ln(\gamma_{TM}) \]

**Activity coefficients in Fe from Miedema model.** Where the Fe - M (M being the minor element of interest) phase diagram is complex such that extraction of activity coefficients is difficult, we have used the semi-empirical Miedema model (Boom et al. 1983; Miedema et al. 1980) to estimate activity coefficients in the solid Fe alloy. This model for the energetics of mixing of binary alloys has 3 parameters for each element, an electron density parameter, the work function of the metal and the atomic surface area. It has been found to successfully predict alloying behavior in a large number of cases. We did not re-calculate heats of mixing using the Miedema model but have simply adopted published values calculated for binary alloys with Fe (Boom et al. 1983).

**Activity coefficients from lattice strain theory.** Insertion of a “foreign” ion into a crystal lattice generally requires that the lattice relaxes to accommodate the ion that will, in general, have a different radius and sometimes charge from those of the major ion that it is replacing. Thus, for example, in the case of chalcophile elements such as Pb, Cd, or Zn dissolving in FeS, the differences in ionic radius between Fe and the substituent trace element leads to a positive free energy of strain around the cation defect. If we treat the lattice as elastically isotropic, the strain-free energy per mole of substituent can be shown to be (Brice 1975; Blundy and Wood 1994):

\[ \Delta G_{\text{strain}} = 4\pi E_{s}N_{u} \left( \frac{r_{s} - r_{c}}{2} \right)^{2} \left( \frac{r_{s} - r_{c}}{3} \right)^{1/2} \]

In Equation 8, \( E_{s} \) is the Young’s modulus of the host, \( N_{u} \) is Avogadro’s number, \( r_{s} \) is the radius of the substituent (Pb, Cd, or Zn in this case), and \( r_{c} \) is the radius of the cation that fits without
strain into the lattice. In the case of FeS, $r_e$ is assumed to be the ionic radius of Fe$^{2+}$. In cases where the Young’s modulus is unknown we use the bulk modulus for the crystal $K$ and convert assuming a Poisson’s ratio of 0.25 yielding $E_b = 1.5$ $K$ (Blundy and Wood 1994).

The strain-free energy leads to an activity coefficient of:

$$\gamma_i = \exp \frac{\Delta G_{\text{strain}}}{RT}$$  \hfill (10)

We used this approach for substitution of elements into phases (other than Fe) for which no thermodynamic, partitioning, or solubility data were available.

Activity coefficients from thermodynamic or partitioning data. In some cases, there have been direct measurements of the thermodynamic properties of the minor elements of interest and these yield estimates of the activity coefficients. There are, for example, measurements of the enthalpies of mixing of the systems Fe–Ga and Fe–Ge (Predel and Vogelbein 1975, 1979) and these can be turned into partial molar enthalpies of solution of Ge and Ga in solid Fe. These partial molar enthalpies $H_i$ are then converted into activity coefficients using an analog of Equation 10.

$$\gamma_i = \exp \frac{H_i}{RT}$$  \hfill (11)

A final method of estimating $\gamma_i$ is from partitioning between liquid and crystals. In this case, we assume that the ratio of crystal–liquid partition coefficients $D_c$ and $D_l$, for the tracce ion of interest (i) and the major ion of the host crystal (o) can be inverted to give activity coefficient (Davis et al. 2018), i.e.,

$$\frac{D_c}{D_l} = \frac{1}{\gamma_i}$$  \hfill (12)

High-temperature condensation (>1300 K) of metals and oxides

Elements forming simple alloys or metals: Os, Ir, Ru, W, Re, Mo. At high temperatures (>1300 K) in a solar gas, the dominant species of many elements is the uncharged atom M$. This makes the calculation of condensation temperature into one of the stable phases of Figure 2 relatively straightforward, or even easier in the cases of elements that condense at higher temperatures into pure metal or oxide. Os is calculated to condense to Os metal at 1806 K. Ir would be expected to form a solid solution with Os, and we assumed it dissolves ideally in Os-Ir alloy, giving a $T_\text{50}$ of 1566 K. Ru should also alloy with osmiridium and making this assumption yields $T_\text{50}$ of 1533 K for Ru.

The dominant gas species of W is calculated to be WO and W is calculated to form an alloy with Re with $T_\text{50}$ of 1736 K for both

| $T$ (K) | Major solid and gaseous species present at different temperatures and fugacities of $O_2$, $H_2O$, $H_2S$, and $HCl$ | Major solid phases |
|---------|-------------------------------------------------|------------------|
| 1700    | Al, CO, Ca, Fe, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1650    | Al, CO, Ca, Fe, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1600    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1550    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1500    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1450    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1400    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1350    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1300    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1250    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1200    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1150    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1100    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1050    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 1000    | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 950     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 900     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 850     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 800     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 750     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 700     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 650     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 600     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 550     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 500     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 450     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 400     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |
| 350     | CO, Fe, H, H, H, O, H, S, Mg, Na, SIO, S, SiS, SH, Ni, Ni | Crn |

Notes: Crn = corundum; Hbn = hibonite; Mill = melilitite; Spl = spinel; Ol = olivine; Cpx = clinopyroxene; Pl = plagioclase; Opx = orthopyroxene; Scb = schreibersite; Tro = troilite; Ap = apatite; Sdl = sodalite; Sa = sanidene; Tr = tremolite.

Table 2. Major solid and gaseous species present at different temperatures and fugacities of $O_2$, $H_2O$, $H_2S$, and $HCl$.
elements. Similarly, Mo metal should form at high temperature with $T_{\text{so}}$ of 1520 K.

**Elements condensing into Fe metal**

As soon as metallic Fe appears (1380 K) Rh, Pt, Pd, and V, which have very low activity coefficients (<<1) in Fe, begin to dissolve in it. We used the Miedema model for activity coefficients (Boom et al. 1983) and calculated $T_{\text{so}}$ values of 1370, 1370, 1330, and 1370 K for these four elements. Ni also dissolves into Fe with a $T_{\text{so}}$ value of 1363 K followed by Co at 1354 and Cr (1291) all condensing from M$^0$ in the gas to the Fe-rich metal with small nonidealities (Table 1).

For phosphorus we followed Lodders (2003) and assumed that (Fe,Ni)$_3$P is a potentially stable phase. The most stable gas species at high temperatures are P$_2$, PO, and PS. We used experimental data on P$_2$ partial pressures above phosphides (Zaitsev et al. 1995) to calculate the thermodynamic properties of Fe,P that were added to the PHEQ database. The properties of Ni,P were taken from Barin et al. (1989). (Fe,Ni)$_3$P was found to appear at 1310 K with a $T_{\text{so}}$ of 1287 K for phosphorus.

**Refractory lithophiles: Y, Sc, Ti, Nb, Ta, U, Th, Zr, Hf, and the lanthanides**

Most of these elements are so oxophile that the most stable gas species, even in the reducing solar gas is MO or MO$_2$ rather than M$^0$. Ti is calculated to condense from TiO in the gas into CaTiO$_3$ perovskite, starting at 1583 K with a $T_{\text{so}}$ of 1565 K. Many of these refractory lithophiles are very compatible in perovskite (Corgne and Wood 2005) and will, depending on their properties, condense into it (below 1583 K) or into hibonite (at temperatures below its appearance at 1630 K). The lanthanides are also very compatible in gehlenite-rich melilite (Nagasawa et al. 1980), so we can assume that this also becomes a host for the REE at temperatures below its appearance at 1550 K. For the lanthanides we used thermodynamic data on the gaseous oxides (Konings et al. 2014) and the gaseous element (Barin et al. 1989) to compute the stable gas species and the temperature of condensation of the oxide, which was assumed to dissolve into hibonite, perovskite, and/or melilite as discussed above. For the elements Sm, Eu, Tm, and Yb the most stable gaseous species is M$^0$. For all the other REE except Ce it is MO while for Ce it is CeO$_2$. Several elements are calculated to dissolve in hibonite almost as soon as it appears at 1630 K (La, Nd, Gd, Tb, Dy, Ho, Er, Tm, and Lu). This is largely because their mole fractions are so low relative to Ca in the gas that their activities, taking account of the activity coefficients of Davis et al. (2018) (Eq. 6) in the solid are <10$^{-4}$. Three lanthanides—Sm, Pr, and Yb—dissolve in hibonite together with perovskite and melilite at slightly lower temperatures. The two elements that are not M$^0$, Eu$^{2+}$, and Ce$^{4+}$ should condense primarily into melilite and perovskite at 1491 and 1454 K, respectively. For yttrium, we used data on the properties of YO gas (Pedley and Marshall 1983) to calculate condensation into melilite, hibonite, and perovskite with $T_{\text{so}}$ of 1551 K. The stable ScO gas species is calculated to similarly condense into melilite and perovskite with $T_{\text{so}}$ of 1541 K.

In a solar gas, the dominant Zr species at high temperatures are ZrO and ZrO$_2$, and these condense to form solid ZrO$_2$ with $T_{\text{so}}$ of 1722 K. For Hf, we obtained the thermodynamic properties of HfO (gas) from Pedley and Marshall (1983) and calculated condensation to the pure HfO$_2$ solid (Barin et al. 1989) at 1720 K ($T_{\text{so}}$). Assuming ZrO$_2$ and HfO$_2$ form a solid solution has insignificant effect because the condensation temperatures are virtually identical.

Ta has stable gas species of TaO and TaO$_2$ and 50% condensation as Ta$_2$O$_5$ is calculated to occur at 1546 K if Ta dissolves ideally in perovskite. A value of 1561 K is obtained for Nb condensing as NbO and NbO$_2$ into perovskite.

The most stable gaseous species of Th is ThO$_2$ in the solar gas. Assuming ideal solution of Th in hibonite, perovskite, and melilite we obtain $T_{\text{so}}$ for Th of 1630 K with hibonite as the principal host. For U we obtained the thermodynamic properties of the gaseous oxides from Konings et al. (2014) and obtained a similar result to Th for condensation into hibonite ($T_{\text{so}} = 1609$ K), given the properties of UO$_2$ (solid) from Barin et al. (1989).

Ba and Sr are also refractory and potentially stabilized by solution in perovskite. We used thermodynamic data for BaTiO$_3$ and SrTiO$_3$ (Barin et al. 1989) and used the elastic strain model with $r_0$ of 1.18 Å and $E_0$ of 130 GPa (Corgne and Wood 2005) to calculate activity coefficients using the eightfold-coordinated ionic radii of Shannon (1976). This leads to $T_{\text{so}}$ values of 1548 and 1423 K for Sr and Ba, respectively.

Finally, Be condensation was treated using the thermodynamic data for BeO (solid), BeO (gas), and Be (gas) and, assuming condensation into melilite, $T_{\text{so}}$ is 1550 K, essentially at the point of melilite appearance.

### Condensation at temperatures $<$1300 K

**Condensation of Cl, F, Br, and I**

Cl is cosmochemically abundant and forms stable gas species with many of the elements of interest, predominantly at temperatures below 1100 K. Figure 3 shows calculated MCl/M$^0$ ratios for several elements of interest as a function of temperature at 10$^{-4}$ bar in the solar composition gas. Because of the stabilizing effect of gaseous Cl (as HCl) on other gas species at low temperatures, the temperature of condensation of Cl into solid phases is critical to the calculation of condensation temperature for several of the other elements of interest. If, for example, in the regime below 800 K Cl is uncondensed, then elements such as In are stabilized in the gas relative to the solid by the presence of gaseous chlorides.

Lodders (2003) notes that the condensation temperatures of the halogens are uncertain and gives $T_{\text{so}}$ for F, Cl, Br, and I of 734, 948, 546, and 535 K, respectively. The relatively abundant Cl was considered to condense into sodalite (Na$_4$Al$_2$Si$_2$O$_8$Cl), at 948 K, this phase occurring in some carbonaceous chondrites. Sodalite is also a stable phase at high temperatures in some alkali-silica-undersaturated rocks (Stormer and Carmichael 1971).

To derive thermodynamic data for sodalite, we used calorimetric measurements of third law entropies, heat capacities and enthalpy of formation (Komada et al. 1995). We then tested these against the reversed phase-equilibrium experiments of Sharp et al. (1989) who determined the equilibrium boundary for the breakdown of sodalite to β-nepheline plus sodium chloride:

$$Na_4Al_2Si_2O_8Cl = 3NaAlSiO_4 + NaCl$$

(13)
Sodalite was determined to be the stable assemblage at pressures up to about 0.8 GPa in the temperature range 900–1100 K (Sharp et al. 1989). Using the equations of state of Sharp et al. (1989) we used the phase equilibrium results to estimate that the free energy change of reaction 13 at 1 bar lies in the range 16.0 to 16.9 kJ at 923–1073 K. To reproduce these values and to generate the apparent change in P-T slope of the reaction from negative to positive above about 1000 K we followed Sharp et al. in adding entropy of Al-Si disorder in sodalite above 800 K. We find that adding 35 J/K of additional entropy (Sharp et al. 1989) lead to higher Cl50 values for Cl. This is because the activity of KI dissolved in KCl would be depressed by several hundred degrees Kelvin. Frequently, however, the effect is lessened by the precipitation of another phase, by the insolubility of, for example, Ag, Pb, and Bi in solid iron.

Paradoxically, the new, lower solar abundance abundances of Cl (Clay et al. 2017) lead to higher T50 values for Cl. This is because Cl begins to condense into fluorapatite soon after it appears at 675 K if the original high Cl abundances (Lodders 2003) are used. In this case about a third of the Cl condenses as chlorapatite until all P is consumed, but T50 for Cl is not reached until NaCl and KCl start to precipitate at 410 K. When we revert to the new lower Cl abundances, more than 50% of the Cl condenses into fluorapatite-chlorapatite solutions before halides or sodalite become stable. This, therefore, increases T50 for Cl, which becomes dependent on the thermodynamic properties of chlorapatite. To perform these calculations, we added to the PHEQ database thermodynamic data for fluorapatite (Hovis and Harlov 2010; Robie et al. 1978), hydroxypapatite, and chlorapatite (Drouet 2015) together with the properties of a large number of gaseous species from Barin et al. (1989), detailed in Supplemental Table S1, combined with those of PH, PN, PH3 (Lodders 1999), and PS (Lodders 2004). P begins to condense into (Fe,Ni)3P at 1310 K (discussed above) but this phosphide starts being consumed when fluorapatite appears (675 K) and is completely lost at 590 K. The enthalpy of formation of chlorapatite, Ca5(PO4)3Cl, has been measured several times, with a spread from −6639 to −6548 kJ (Drouet 2015) that produces considerable uncertainty in the condensation temperature of this component of apatite. Hovis and Harlov (2010) also determined large apparent nonidealities in fluoro-chlorapatite solid solutions, which, if applied at face value would substantially lower the condensation temperature of Cl. These authors suggested, however, that their calorimetric measurements were influenced by anion vacancy defects in their synthetic apatite crystals and that the fluorapatite-chlorapatite series is essentially ideal. We commenced with an enthalpy of formation (−6580.35 kJ) in the middle of the measured range and assumed ideal solution. In this case chlorapatite appears in solid solution in fluorapatite (which itself condenses rapidly at 675 K) at about 610 K. The chlorapatite component then condenses over an extended temperature interval with T50 of 472 K. Lowering the enthalpy of formation to that determined by Cruz et al. (2005) (−6615.5 kJ) has little effect on the initial temperature of Cl condensation, but T50 is reached much more rapidly, at about 600 K. To put these values in context, if chlorapatite is completely destabilised then T50 into KCl is about 420 K, while we would need to go to the lower limit of measured heats of formation to push T50 significantly above 620 K.

We used bromapatite heat of formation data from Cruz et al. (2005) and estimated the heat capacity and entropy of this phase from the values for fluorapatite, CaF2 and CaBr2. Based on these estimates, Br should not condense above 350 K in apatite. We instead calculate condensation at about 420 K into K(Cl,Br) solid solution. Activity coefficients for KBr, based on the low bulk modulus of KCl (Vijay and Verma 2000) should be about 3.36 at 420 K. Using the same elasticity data, KI should have an activity coefficient of ~7000 in KCl under these conditions, which means that the activity of KI dissolved in KCl would be much greater than 1. KI should, therefore, condense as a pure phase with T50 of 390 K.

**Low-temperature condensation into Fe and FeS**

**Nonideality issues.** Lodders (2003) groups Ag, As, Au, Bi, Cu, Ge, P, Pb, Sb, Sn, and Te as siderophile elements condensing into the Fe alloy. We began by assuming ideal solution of most of these elements in the metal and found good agreement with Lodders’ T50 values (in parentheses), as follows As 1030 K (1065); Pb 739 K (727); Bi 751 K (746); Ag 997 K (996); Sb 930 K (979); Sn 725 K (704). The problem with these values, however, is that there are demonstrable nonidealities evidenced by the insolubility of, for example, Ag, Pb, and Bi in solid iron. When the activity coefficients implied by the low extents of solubility, as exemplified by Ag, discussed above, are added to the thermodynamic data, the condensation temperatures are depressed by several hundred degrees Kelvin. Frequently, however, the effect is lessened by the precipitation of another phase, generally FeS, into which the trace element dissolves.

**Condensation into iron: Au, As, Cu, Ge, Ga, Sb, and Bi.** Au, which has AuS as the dominant gas species, has large activ-
ity coefficients in solid Fe (Boom et al. 1983). Nevertheless, we find condensation into Fe with $T_{50}$ of 967 K. Arsenic dissolves into Fe with strong negative deviations from ideality. Both the Miedema model and a more recent thermodynamic assessment (Pei et al. 1994) lead to essentially the same $T_{50}$ of 1235 K. Cu has small positive deviations from ideality when dissolved in Fe (Arita et al. 1981). We obtain virtually identical $T_{50}$ to that of Lodders (2003) (1035 K) when the nonidealities are accounted for. The condensation temperature of Ge into Fe is influenced by large negative deviations from ideal solution. We estimated the enthalpy of solution of Ge in Fe from the results of Predel and Vogelbein (1979) and converted this [−52 kJ/(gm·atom)] to activity coefficients using Equation 11. The result is similar to that of Wai and Wasson (1979), a calculated $T_{50}$ temperature of 830 K. Ga also dissolves in Fe with strong negative deviations from ideality. The most stable gaseous species at low temperatures are GaCl, GaF, and GaOH (Wai and Wasson 1979) although the free energy of GaOH is fairly uncertain (Battat et al. 1974).

For antimony, SbS should, given Knudsen cell mass spectrometric data (Hino et al. 1986), be an important gas species in the temperature range of interest, with $S_{b}$, $S_{b}^{0}$, $S_{a}$, and $S_{b}Cl$ all present in proportions that are strongly temperature-dependent. We find that the activity coefficients estimated from phase relations (Pei et al. 1995) Sb condenses into iron at around 890 K. Use of the lower activity coefficients adopted by Wai and Wasson (1979) estimate for $\gamma_{Ga}$. This would lower $T_{50}$ by about 200 K.

Sn may condense either into Fe metal or into FeS depending on activity coefficients. For the metal, we estimate a minimum activity coefficient of 45 at 873 K based on the Fe-Sn phase diagram (Hari Kumar et al. 1996) while in FeS an activity coefficient of 1060 is obtained at 700 K from the lattice strain model given an $E_{\gamma}$ of 81 GPa (discussed below). The most stable gas species is SnS and the condensation temperature into Fe is 604 K while condensation into sulfide is calculated to be at about 50 K lower temperature.

There is essentially complete immiscibility in the Bi-Fe system with activity coefficients of the order of 2500 even in liquid Fe at 1873 K (Boa et al. 2008). Extrapolating this value down to 750 K or using the Miedema model results in either case of Bi activity >1 in Fe. Hence Bi should precipitate as Bi metal rather than in solution in Fe. We obtain $T_{50}$ of 485 K for Bi metal.

**Condensation into FeS and as sulfide.** S, Se, and Te all condense primarily into FeS. The PHEQ program has thermodynamic data for both pyrrhotite Fe$_{0.877}$S and troilite FeS that are treated as separate phases. Using the data as given, pyrrhotite should precipitate first from a solar gas. This has been shown, however, to be inconsistent with more recent thermodynamic data (Grønvold and Stølen 1992; Lauretta et al. 1996). Lauretta et al. (1996) showed that, at the H$_{2}$S/H$_{2}$ ratio of the solar nebula, the thermodynamic data of Grønvold and Stølen (1992) indicate that FeS, troilite should be the most stable sulfide and hence should appear first. We, therefore, used the data of Grønvold and Stølen (1992) for FeS and Fe$_{0.877}$S to calculate that troilite appears at 710 K with $T_{50}$ for S of 672 K, virtually identical to the Lodders (2003) value for S.

We have measured (unpublished) partition coefficients of Se between solid FeS and sulfide liquid of about 0.6 at 1293 K. We assume that this corresponds to the reciprocal of the activity coefficient that is therefore 1.67 at 1293 K. The stable gas species H$_{2}$Se condenses FeSe into FeS with $T_{50}$ of 701 K. We used the same approach for Te and adopted an activity coefficient of 40 at 1293 K based on our partitioning experiments. This results in $T_{50}$ of 665 K.

For Ag we assumed nonideal solution with activity coefficients obtained from the lattice strain model and $E_{\gamma}$ of 81 GPa, which is in reasonable agreement with the bulk moduli of the different FeS polymorphs (Kusaba et al. 1997) and with $r_{5}$ the sixfold radius of Fe$^{2+}$ (Shannon 1976). These parameters were also constrained to be in accord with our measured (unpublished) solid sulfide-liquid sulfide partition coefficient $D_{Ag}$ of $\approx$0.03 at 1323 K. Ag is calculated to condense into iron sulfide with $T_{50}$ of 699 K.

The most stable gaseous species of Cd should be Cd$^{2+}$ and this condenses into FeS with a $T_{50}$ of 502 K. Activity coefficients were obtained from the lattice strain model with Cd$^{2+}$ radius from Shannon (1976).

ZnS mixes with only small nonidealities into FeS (Fleet 1975), and we find that incorporating Fleet’s results, Zn condenses into FeS essentially as soon as it appears, with $T_{50}$ of 704 K.

Indium has several important gaseous species in the temperature range of interest, including InOH (Skulan et al. 2006) and InCl (Barin et al. 1989). The latter dominates before Cl condenses. Indium has stable sulfides InS and In$_{2}$S$_{3}$ and the former should be more stable at the H$_{2}$S fugacities of the solar nebula. Assuming that InS dissolves ideally in FeS, we obtain a $T_{50}$ of 580 K. In$^{2+}$ is, however significantly larger than Fe$^{2+}$ and InS has metal-metal bonds (Schwarz 2002; Schwarz et al. 1995) so is unlikely to dissolve ideally in FeS. The low-pressure structure (Schwarz et al. 1995) has a very distorted coordination polyhedron around In, with average In-S distances of 2.92 Å, which, taking the S$^{2-}$ radius from Shannon (1976) leads to an In$^{2+}$ radius of 1.08 Å. The polyhedron becomes much less distorted by 4.3 GPa however (Schwarz et al. 1995), and performing the same calculation leads to an In$^{2+}$ radius of 0.92 Å. We averaged these 2 values and used the lattice strain model to estimate an activity coefficient of 5.2 at 1000 K in FeS. We hence calculate that In will condense as InS into FeS at 492 K ($T_{50}$) from the solar gas.

This means that, at solar system abundances, PbS activities in FeS would be >1 below 530 K. At lower temperatures, Pb would condense from Pb$^{4+}$ and H$_{2}$S as pure PbS. We thus obtain condensation of pure PbS at 495 K.
Tl behaves similarly to Pb. The lattice strain model gives activity coefficients on the order of $10^9$ at 1000 K for dissolution into FeS while the Miedema model gives activity coefficients of about $10^8$ for dissolution into Fe metal at the same temperature. These large values mean that Tl should condense into a Tl phase, either Tl$_2$S or Tl metal and the temperatures are of the order of 400 K or lower depending on the stability of the TICI gaseous species (Fig. 3). We find that the $T_{50}$ temperatures for Tl condensing into both Tl metal and Tl$_2$S are virtually identical, at 365 K.

Condensation into silicates: K, Rb, Cs, Li, Mn, and B

The alkalis—K, Rb, and Cs—were all assumed to condense into the phases with which they are most associated in nature, the feldspars. For K we assumed condensation into either the albitic plagioclase present in the major element condensation sequence or into a separate sanidine feldspar. We calculated activity coefficients in plagioclase using lattice strain parameters derived from plagioclase-liquid partitioning experiments (Blundy and Wood 1994) and obtained a $T_{50}$ temperature of 993 K into plagioclase with K$^+$ as the dominant gas species. Given an activity coefficient of 35 from the lattice strain model at 700 K however, KAlSi$_3$O$_8$ should exsolve from plagioclase at lower temperatures. Cs and Rb will then condense into sanidine. We modeled the properties of Rb and Cs feldspar by assuming that the log K of formation of RbAlSi$_3$O$_8$ minus that of KAlSi$_3$O$_8$ and of CsAlSi$_3$O$_8$ minus KAlSi$_3$O$_8$ are the same as the differences in log K of formation of RbO$_{0.5}$ minus KO$_{0.5}$ and of CsO$_{0.5}$ minus KO$_{0.5}$. Then we used the lattice strain model data (Blundy and Wood 1994) to calculate activity coefficients for dissolution into sanidine. This yields $T_{50}$ values of 752 K for Rb and 593 K for Cs.

The dominant gas species of Li close to the condensation temperature is LiCl. We used the orthopyroxene-liquid partition coefficient data (Frei et al. 2009) to estimate an activity coefficient of $\sim$5. Assuming that Li dissolves in pyroxene as Li$_2$SiO$_3$, we obtain $T_{50}$ of 1148 K. If we were to treat Li$_2$SiO$_3$ dissolution into olivine in a similar manner, we would obtain a lower condensation temperature. According to the partitioning data of Frei et al. (2009) Mn$^{2+}$ fits into the M2 site of orthopyroxene without strain ($\gamma = 1.0$) and will fit into the M1 site with an activity coefficient of 1.5 at 1673 K. Given the close approach to ideality and $D_{\text{Mn}}$, (liquid/crystal) values close to 1.0 (. Labbier et al. 2014; Le Roux et al. 2015) for both orthopyroxene and olivine we assumed that Mn mixes ideally in olivine and Mg-pyroxene during condensation. We obtain virtually identical temperatures for condensation into pyroxene and olivine (1123 K). This is reduced by 11 K if we make explicit provision for the small nonidealities mentioned above.

In the low-temperature region of interest B$_2$O$_3$ is calculated to be the most stable form of B in both gas and solid phases and, assuming, following Lodders (2003), that B replaces Al in plagioclase feldspar, then, if the solution is ideal, we obtain $T_{50}$ of 740 K.

**DISCUSSION**

The results of our calculations are given in Table 1 together with a summary of the activity coefficient expressions discussed above. Figure 4 shows silicate Earth abundances of the elements plotted, in the same manner as in Figure 1, vs. the $T_{50}$ condensation temperatures generated in this study. One might argue that, with the exception of the elements S, Se, and Te, the “volatility trend” is better defined by our results than by those of Lodders (2003). This would require either the “eye of faith” or a statistical analysis that we do not consider worth performing, since there is no physical or chemical reason we are aware of that the volatile elements should all fall on the same line in a plot of this kind. Planetary and protoplanetary processes such as melting, core formation, and silicate differentiation must obviously have exerted considerable influence on the final abundances of elements in silicate Earth.

Figure 5a shows the differences between our values of $T_{50}$ and those of Lodders (2003). As can be seen, agreement is good for the relatively refractory elements that condense above 1300 K. Principal differences are found at temperatures below 900 K where we find Cl-species stable in the gas phase and strong nonidealities in the solid phases for most elements. Both these effects reduce condensation temperature leading to a positive difference between Lodders’ condensation temperatures and ours.

**IMPLICATIONS AND CONCLUDING REMARKS**

We have attempted to update the generally accepted equilibrium condensation temperatures of Lodders (2003) by making what we believe are realistic assumptions about activity coefficients for trace elements dissolved in the major phases, Fe, FeS, pyroxene, olivine, and plagioclase. In the course of this re-analysis, we also found based on reversed phase-equilibrium experiments (Sharp et al. 1989) that the stability of sodalite during the condensation sequence is much lower than was proposed in the earlier study. This means that the $T_{50}$ temperature for Cl is 472 K rather than 948 K. The presence of significant amounts of cosmochemically abundant CI (as HCl) in the gas phase between 1000 and 400 K stabilizes gaseous chlorides such as KCl, RbCl, CsCl, GaCl, TICI, and InCl and...
lowers condensation temperatures for these minor elements.

One important point to note is that some earlier authors (Larimer 1967; Grossman 1972; Grossman and Larimer 1974; Wai and Wasson 1979) made solid solution assumptions and used gaseous species that are similar to the ones we find to be most appropriate. Hence their results are often similar to ours, as can be seen in Figure 5b and Table 2. These authors only studied small subsets of the periodic table, however, and the more recent all-encompassing study of Lodders (2003) has superseded their work in the minds of most geochemists. We believe that our critique and discussion here will provide more context for condensation results and give the reader some idea of where there are significant uncertainties or errors in the calculations.

In conclusion, we must recognize that it is impossible to generate a list of exact condensation temperatures of the elements from a solar gas. There are uncertainties in solar abundances, uncertainties in the thermodynamic data that we use and, at low temperatures at least, in the assumption that perfect equilibrium is maintained and that all stable solids have been considered. However, given the equilibrium assumption, we do assert that

**Figure 5.** A comparison of our results for 50% condensation temperatures of the elements ($T_{50}$) to those of (a) Lodders (2003) and (b) Wasson (1985). Principal differences arise for the volatile elements because of the stabilities of Cl complexes in the gas phase and the nonidealities of trace elements in Fe(metal) and iron sulfide (see text).
we have a robust list. We await with interest future updates and comments on our work.

ACKNOWLEDGMENTS AND FUNDING

This work would have been much more arduous if John Wood had not provided B.J.W. with the source code and database for PHEQ about 25 yr ago. He is gratefully acknowledged. T.H. commenced this work as a fourth year undergraduate project. We received funding from the European Research Council grant 267764 and from the Natural Environment Research Council (U.K.) grant NE/M000427/1 and 000370/1. We acknowledge with thanks the detailed and constructive reviews of Andrew Davis, Denton Ebel, Mikhail Petkev, and Laura Schaefer, particularly the fact that the last two reviewers repeated and checked some of our calculations. Any remaining errors and omissions are of course entirely our responsibility.

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ACKNOWLEDGMENTS AND FUNDING

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**Endnote:**

1Deposit item AM-19-66852, Supplemental Table. Deposit items are free to all readers and found on the MSA website, via the specific issue’s Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2019Jun2019_data/ Jun2019_data.html).