Porosity-filling Metamorphic Brines Explain Ceres’s Low Mantle Density

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Abstract

Recent work has sought to constrain the composition and makeup of the dwarf planet Ceres’s mantle, which has a relatively low density, between 2400 and 2800 kg m$^{-3}$, as inferred by observations by the Dawn mission. Explanations for this low density have ranged from a high fraction of porosity-filled brines to a high fraction of organic matter. We present a series of numerical thermodynamic models that yield the mineralogy and fluid composition in the mantle as a function of Ceres’s thermal evolution. We find that the resulting phase assemblage could have changed drastically since the formation of Ceres, as volatile-bearing minerals such as serpentinite and carbonates would partially destabilize and release their volatiles as temperatures in the mantle reach their maximum about 3 Gyr after Ceres’s formation. These volatiles consist mainly of aqueous fluids containing Na$^+$ and HS$^-$ throughout the metamorphic evolution of Ceres and, in addition, high concentrations of CO$_2$ at high temperatures relatively recently. The predicted present-day phase assemblage in the mantle, consisting of partially devolatilized minerals and 13–30 vol% fluid-filled porosity, is consistent with the mantle densities inferred from Dawn. The metamorphic fluids generated in Ceres’s mantle may have replenished an ocean at the base of the crust and may even be the source of the Na$_2$CO$_3$ and NaHCO$_3$ mineral deposits observed at Ceres’s surface.

Unified Astronomy Thesaurus concepts: Ceres (219); Mantle (1005); Planetary interior (1248)

1. Introduction

Dwarf planet Ceres is the largest asteroid in the main belt and the only dwarf planet in the inner solar system. NASA’s Dawn mission returned geophysical observations (gravity, topography relaxation) that yielded constraints on Ceres’s global interior structure and regional-scale variations. From admittance inversion under the assumption of isostasy, Ermakov et al. (2017) derived an average mantle density of about 2430 kg m$^{-3}$. Accounting for a possible fossil shape responsible for a slight departure from hydrostatic equilibrium (Park et al. 2016), Mao & McKinnon (2018) inferred a mantle density of about 2700–2800 kg m$^{-3}$. Both models require an overlying crust with a density close to that of water ice with a small fraction of salts and rock. As shown below, this range is lower than the densities predicted from geochemical and thermal modeling (e.g., Castillo-Rogez et al. 2018). In particular, the Ermakov et al. (2017) density estimate suggests the presence of a large fraction of porosity ($\sim$25%), similar to the porosity inferred from Enceladus’s low rocky mantle density (Choblet et al. 2017). The presence of porosity at least in the upper part of the mantle is supported by gravity observations (Raymond et al. 2020). However, no rigorous modeling of Ceres’s mantle density has been performed yet. The Ermakov et al. (2017) estimate for Ceres’s mantle was interpreted by Fu et al. (2017) to be consistent with a carbonaceous chondrite composition modified by minor heating. The low viscosity inferred by these authors for the upper mantle was interpreted as evidence for pore fluids. Zolotov (2020) also suggested that this low mantle density indicates a porous mantle and the presence of a high fraction of organic matter, whose density is relatively low ($<2000$ kg m$^{-3}$).

We investigate the thermal evolution of Ceres’s mantle in order to interpret the density data inferred from the Dawn observations and test the stability of organic matter. We show, similar to previous studies, that even for a mildly warm internal evolution, Ceres’s rocky material releases fluids as a consequence of low-grade thermal metamorphism (e.g., Castillo-Rogez 2011; Neveu et al. 2015). However, previous studies have assumed thermal metamorphism and fluid release from the mantle in a single step (around 750–850 K). In practice, Melwani Daswani et al. (2021) showed that petrological changes due to temperature excursions develop continuously with increasing temperature, in addition to several discrete fluid-releasing events. Metamorphic reactions lead to the dehydration and devolatilization of minerals and the release of volatiles at the surface with the overall effect of compacting pores and increasing the density of the interior. For example, the reaction antigorite $\rightarrow$ olivine + talc + water proceeds in various steps from about 670 to 970 K, releasing varying amounts of water as the structure and composition of antigorite changes with increasing temperature (e.g., Wunder et al. 2001). This study builds on the previous work by Melwani Daswani et al. (2021) to explore the equilibrium phase changes and fluids released in Ceres’s mantle for a broad parametric space. This leads to identifying conditions that can explain observational constraints during the thermal evolution of Ceres and yield new insights into Ceres’s mantle composition and structure (e.g., porosity). Thermodynamic models derived from experimental phase relations (e.g., Padrón-Navarta et al. 2011, 2013, 2010) allow us to constrain the volumes of the fluids involved and their composition. Coupled to various scenarios of global fluid transport or the long-term stability of deep fluid reservoirs, we can constrain the volatiles retained in the interior, as well as those lost to space, in line with present-day estimations of a transient exosphere formed by sublimation of crustal water ice (e.g., Formisano et al. 2016; Landis et al. 2017; Schorghofer et al. 2017; Villarreal et al. 2017). The methodology is described in Section 2 and the results in Section 3, and we discuss the implications and comparisons to constraints from Dawn and the models in Section 4.
2. Methods

We test the hypothesis that Ceres’s low-density mantle could reflect a large porosity fraction in the form of a mixture of rock particles, brines, and organic matter. The central pressure in Ceres is ~150 MPa, so while porosity likely decreases gradually with depth, pore close-off pressures may not be reached, and significant porosity could still be retained. Neveu & Desch (2015) suggested that the faster sinking of dense particles (e.g., chondrules and calcium-aluminum-rich inclusions; CAIs) could lead to a “core,” on top of which finer particles would sediment. However, as noted by these authors, the particle size distribution of primordial rock is not well constrained. In this study, we assume homogeneous particles in terms of size and composition. Different particle sizes would have no effect on the equilibrium thermodynamic models we carry out, but a compositionally heterogenous interior is likely to change the resulting fluid and mineral composition, particularly because the densest, most volatile-poor particles settling in the deeper interior are the ones that experience the highest temperature but yield lower fluid volumes during Ceres’s thermal evolution. We partially offset this by specifying the maximum fluid volumes allowed to exist in equilibrium at various depths within the interior (see Section 2.2).

2.1. Parameters Controlling Bulk Density

Two main parameters control the density of Ceres: composition ($X$) and porosity ($\Phi$). Composition is inherited from the chemical makeup of Ceres’s accreting material, whereas porosity refers to the percentage of fluid-infilled volume containing no solid. It is also convenient to define the maximum porosity threshold ($\Phi_{\text{max}}$), which is the maximum volume capacity for a material to retain free fluids. Fluids in excess of $\Phi_{\text{max}}$ are displaced; they cannot be accommodated in the available pore space. We discuss the role and control of porosity in Section 2.2.

Based on Ceres’s surface composition, its bulk composition has most often been approximated as similar to carbonaceous chondrites, particularly CI and CM chondrites, with varying degrees of additional water or carbon (e.g., McSween et al. 2018; Zolotov 2020). A cometary composition is also relevant based on the large fraction of carbon found on Ceres’s surface, assuming it has not been concentrated during Ceres’s evolution (e.g., Prettyman et al. 2019).

We test CI chondrites, CM chondrites, and comets as initial bulk compositions for Ceres and add 0, 10, and 25 wt% water to the chondrite compositions, in addition to the water that is structurally bound in minerals and organics (~20 and ~13 wt% in CI and CM chondrites, respectively; Garenne et al. 2014). We also explore an organic-enriched mixture (25 wt% cometary and 75 wt% CI chondrite material) of material formed at >15 au (Desch et al. 2018) from the Sun in the early solar system. A summary of the initial bulk compositions used here is shown in Table 1.

2.2. Ocean Buildup by Prograde Metamorphism

To determine the mass and composition of fluids produced during heating and devolatilization of the interior, we use the Perple X Gibbs free energy minimization program, which computes stable phase assemblages using experimental and modeled thermodynamic data, including molecular and electrolytic fluid models optimized for computing aqueous fluid speciation (Connolly 2009; Galvez et al. 2015; Connolly 2005; Connolly & Galvez 2018). Details about the solution models and thermodynamic database are given in the Appendix. For each initial bulk composition (Table 1), we model a zero-dimensional heating pathway throughout the deep interior using Rcrust (Mayne et al. 2016), which provides an interface for Perple X to set up specific phase fractionation models. To elaborate, we construct a 1D column spanning the radius of Ceres discretized into a number of vertical points that experience isobaric heating steps and track the composition and mass of the equilibrium mineral-plus-fluid assemblage. At each heating step ($\Delta T$), the Gibbs free energy of the assemblage in each point is minimized, resulting in a new equilibrium assemblage that depends on the heating step directly prior to it but is not affected by the adjacent vertical points.

We simulate the buildup of the ocean by imposing a limit on the fraction of volatiles retained in the assemblage as porosity-filling free fluid at each heating step. That is, fluids (except silicate melt; see below) are fractionated and irreversibly removed from the equilibrium assemblage of the particular point (shown as cells in Figure 1) to go into the growing ocean reservoir when they become thermodynamically stable and if they exceed a predefined porosity threshold ($\Phi_{\text{max}}$). As a limiting case, for each bulk composition computed (Section 2.1), all fluids (including gases, liquids, and their dissolved species) produced during heating are extracted from the interior (i.e., $\Phi = 0$). Buoyancy drives fluids upward, with transport being particularly rapid in permeable materials in the direction of maximum compressive stress (e.g., Richard et al. 2007). Retention of fluids at depth would lead to an unstable solution that is out of hydrostatic equilibrium. Thus, the only path for free fluids should, a priori, always be up in a spherically symmetric body. However, the efficient extraction of volatiles from Ceres’s interior is not a guarantee, particularly since Ceres’s shape and gravity suggest a deviation from hydrostatic equilibrium (Park et al. 2016), so we also explore solutions in which free fluids are retained in pore space of their own production; sufficient overburden pressure and low gravity may effectively prevent the escape of volatiles from the mantle. Simulating the precise migration of fluids would require a dedicated study, perhaps using finite element modeling; our approach explores the bounding scenarios and rigorous geochemical and petrologic constraints at the expense of physically realistic fluid transport.

For each bulk composition, we test the effect of retaining a fixed volume of fluid in the rocky interior by up to 10 or 30 vol% fluid and extracting any fluid in excess (i.e., specifying a maximum porosity threshold $\Phi_{\text{max}}$ of 10 or 30 vol%), analogous to how a magma chamber reaches a critical size threshold prior to eruption (e.g., Townsend & Huber 2020). Finally, for select compositions, we explore two two-layer structure models and two three-layer models with varying $\Phi_{\text{max}}$ dependent on overburden pressure. We denote the maximum porosity in multilayer models with the symbols $\Phi_{\text{max}1}$, $\Phi_{\text{max}2}$, and $\Phi_{\text{max}3}$, if applicable, from the top of the mantle to the bottom. A summary of the differences between the models is shown in Table 2. A total of 40 models encompassing the ranges of compositions and porosities were performed.

The thermal evolution of Ceres’s interior is modeled after the approach described in Castillo-Rogez et al. (2019). Ceres’s assumed to have formed about 3.5 Myr after the CAIs aken as a time reference for the decay of $^{26}$Al (see...
compressibility on rock density likely prohibits convection onset in the rocky mantle, porosity decreases with depth, and the impact of fluids produced. We describe the extraction of silicate melt is not consequential because upwelling following release is not accounted for. The retention or extraction of silicate melt is not consequential because temperatures in the thermal evolution of Ceres never reach the solidus of chondritic rocks (Figure 2; see Agee et al. 1995; Andraut et al. 2011).

3. Results

3.1. Evolution of Ceres’s Density and Porosity

Ceres’s average density changes during its thermal evolution over 4.5 Gyr (Figures 3 and 4), reflecting its changing composition and fluid-filled porosity, as a result of the imposed free fluid removal rules and the changing equilibrium phase assemblage. Five out of the 40 models resulted in average mantle densities at 4.5 Gyr consistent with Ceres’s current modeled mantle density. Of those, three agreed with the ~2430 kg m−3 average density modeled by Ermakov et al. (2017), and the remaining two agreed with the Mao & McKinnon (2018) average modeled density of ~2700–2800 kg m−3.

Density largely increases with decreasing porosity, which is mainly a function of the imposed \( \Phi_{\text{max}} \) (Section 2.2) and the amount and composition of fluids produced. We describe the temperature-dependent fluid and mineralogical changes affecting density in Sections 3.2 and 3.3, respectively. An inflection in the evolution of mantle densities and porosities is apparent.
between 2 and 3 Gyr for most bodies, which is at the point in Ceres’s thermal evolution with the steepest pressure–temperature profile from surface to center and where peak temperatures occur (Figure 2). The effect is more pronounced in bodies with low $\Phi_{\text{max}}$ (0% or 10%). In other models, particularly those with high $\Phi_{\text{max}}$ or multilayer models, the mean mantle density peaks 100 Myr after formation. The difference in timing occurs because the dehydration temperature of antigorite (720–740 K) is exceeded at >100 MPa at close to 2 Gyr, which releases large amounts of water; in single-layer models with low $\Phi_{\text{max}}$ (0 or 10 vol%), the volume of fluid produced by mineral breakdown exceeds $\Phi_{\text{max}}$ before 2 Gyr, whereas in multilayer or high-$\Phi_{\text{max}}$ models, the volume of fluids produced by 2 Gyr has not exceeded the storage capacity.

Out of the five models consistent with present-day mantle densities (either ∼2430 or 2700–2800 kg m$^{-3}$), two result from the thermal evolution of CM chondrite (±H$_2$O) composition (75% CM chondrite +25% water, $\Phi_{\text{max,1}}$ = 30, $\Phi_{\text{max,1}}$ = 0, yielding a mantle density of 2770 kg m$^{-3}$; and 100% CM chondrite, $\Phi_{\text{max,1}}$ = 100, $\Phi_{\text{max,2}}$ = 50, $\Phi_{\text{max,3}}$ = 0, yielding a mantle density of 2803 kg m$^{-3}$), and the rest result from CI chondrite (±H$_2$O) compositions with $\Phi_{\text{max}}$ = 30. None of the thermal evolution thermodynamic models containing cometary material resulted in a mantle density consistent with models of the present-day mantle; all cometary models produced bodies with mantle densities lower than 2100 kg m$^{-3}$ or higher than 2900 kg m$^{-3}$.

Of the CI chondrite models consistent with the present-day mantle density, all contained ∼30 vol% fluid-filled porosity, and all were consistent with the lower mantle density estimate of Ermakov et al. (2017). The CI-derived mantles with no porosity yielded mean densities of ∼3211 kg m$^{-3}$, on average. To summarize, from these thermodynamic and thermal evolution models, we glean that (1) Ceres’s mantle must contain fluid-filled porosity in order to meet the density constraints derived from Dawn and either Ermakov et al. (2017) or Mao & McKinnon (2018); (2) thermally evolved CI chondrite bodies are consistent with the lower mantle density estimate (∼2430 kg m$^{-3}$), and thermally evolved CM chondrite bodies are consistent with the higher mantle density estimate (2700–2800 kg m$^{-3}$); and (3) a body evolved from a cometary composition is not consistent with any of the present-day mantle density estimates.

### 3.2. Composition of Fluids Produced by Metamorphic Reactions

As unequilibrated materials, carbonaceous chondrites and comets contain phases that are not in thermodynamic equilibrium with each other. Thus, the Gibbs energy minimization routine applied to the tested bulk compositions (Table 1) predicts phase assemblages that do not entirely reflect the mineralogy observed in carbonaceous chondrites. The abundance of fluids, controlled by the retention rules we imposed, also result in different mineralogies in the models; this effect can only be inferred or calculated from chondrite hand samples, because fluids and ice are absent from chondrites collected on Earth. Here we relate the compositions and abundances of fluids evolved from the mantle of Ceres for those bodies that result in mantle densities of ∼2430 or 2700–2800 kg m$^{-3}$.
Pressure showed little influence on fluid composition. The main control over fluid composition appeared to be temperature (given by the thermal evolution; Figure 3), which in turn controls the mineralogy (Section 3.3). Here we focus on the CI chondrite model 10% H2O, 30% Φmax and the CM chondrite model 25% H2O, 30% Φmax to illustrate the changes in fluid composition over time for different starting bulk compositions (Figure 5), but we note that broadly similar compositions result from the other models, consistent with Ceres’s observed mantle density. Finally, we note that the self-ionization constant of water is temperature-dependent, so we report the real fluid pH and the pH adjusted to 298 K and 1 bar (i.e., so that neutral pH = 7; Figure 6).

3.2.1. Composition of the Earliest Fluids (<100 Gyr)

Thermodynamic equilibration at the uniformly low temperatures at up to 100 Myr after formation (Figure 3) predicts the stability of massive amounts of fluid in the mantles of all models, even for initial compositions without additional water. These initial fluids are Na+ and HS−-rich (Figure 5). The adjusted mantle fluid pH for the CI and CM chondrite bodies was nearly identical (adjusted pH ≈ 8) and constant throughout the depth of the mantle (Figure 6). The most significant difference between CI and CM chondrite-derived early fluids is the higher concentration of K+ in CM chondrite-derived fluids, which is surprising considering that [K] is 30% less abundant in the latter than in CI chondrites (but see Section 3.3.1).

As for carbon-bearing species, these early fluids are charged in CO32−, and hydrocarbons exist only in very minor concentrations (<10−7 mol kg−1 for both formate and methane).

3.2.2. Fluids at the Temperature Maximum (2–3 Gyr)

Temperature does not change uniformly along the radius of Ceres in time; by the time the deeper mantle reaches its highest temperature, 2–3 Gyr after formation, the temperature in the outer parts of the mantle is ∼500 K lower (Figures 3 and 6). This results in a markedly different fluid composition evolved from the top of the mantle versus the lower mantle (Figure 5). Notably, fluids in the lower mantle are in the supercritical region, where we are unable to compute the solute concentrations accurately with our present thermodynamic approach. Based on the compositional trend with increasing temperature, we infer that fluids become more solute-rich. With increasing temperature, CO32− fluids are replaced by CO2-rich fluids, as magnesite (MgCO3) destabilizes (Section 3.3). At depth, fluids become more solute-rich, as Na+, HS−, K+, and OH− increase by over 1 order of magnitude compared to fluids ∼100 Myr after formation. At >550 K, the concentration of the molecular solutes SiO2, H2, H2S, NaOH, CO, and CH4 increases (Figure 5). Accordingly, the fluid pH is also markedly different from fluids at the top of the mantle (adjusted pH ≈ 8.1) versus fluids derived from the deeper mantle (adjusted pH ≈ 6.7; Figure 6).
3.2.3. Fluid Compositions Close to Present Day (4.5 Gyr)

Temperatures follow a retrograde path from the temperature maximum, resulting in a significantly cooler thermal gradient in the mantle 4.5 Gyr after Ceres’s formation compared to the temperature maximum. In the upper portions of the mantle, any resulting fluids are dilute, comparable to fluids 100 Myr after formation, with \([\text{CO}_2^{2-}] \gg [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-]\). However, in the lower mantle, fluid compositions more closely resemble those produced \(\sim 3\) Gyr after formation, as temperatures approach the supercritical region, and \([\text{CO}_2(\text{aq})] > [\text{HCO}_3^-] > [\text{CO}_2^{2-}]\) (Figure 5). The concentration of hydrocarbons and carbonates (namely \(\text{CH}_4\) and \(\text{NaHCO}_3\)) is only appreciable in the deeper mantle. The pH variations between the upper and lower mantle regions reach their most extreme values, with an adjusted pH at 40 MPa \(\sim 9\) and 100 MPa \(\sim 6.6\) (Figure 6).

3.3. Mineralogy

### 3.3.1. Mantle Mineralogy in Bodies Derived from Carbonaceous Chondrites

As shown in Section 3.2, fluid compositions derived from the thermal metamorphosis of the mantle were not especially different for CI and CM chondrite bodies; the main driver of compositional differences is the temperature. While temperature also alters the mineral assemblage, the effects of different starting bulk compositions for Ceres are more apparent. Figure 7 shows the changing mineralogy at 100 MPa for different starting compositions.

At 100 Myr after formation, the mineralogy of CI chondrite-derived bodies and CM chondrite-derived bodies are fairly similar, with >30 wt% antigorite and \(\sim 10\) wt% fluid. However, the remaining phase assemblage for CI chondrite-derived bodies consists of magnesite > pyrite > talc \(\approx\) clinopyroxene \(\approx\) dolomite > chlorite > stilpnomelane, whereas for CM chondrite-derived bodies, it consists of spinel (mainly magnetite) > greenalite > dolomite > chlorite > pyrite > clinopyroxene \(\approx\) graphite (Figure 7). Stilpnomelane \(K_{0.5}\) (\(\text{Mg,Fe}_2\text{Al}_2\text{Si}_5\text{O}_{12}\)) \(H_{2.5}\) is a K-bearing mineral sink, which explains why the fluids derived from CM chondrite bodies have a higher [K] (Section 3.2). As mantle temperatures increase, antigorite progressively loses water as it is replaced by talc, and pyrite transforms to troilite, consuming acidity and releasing \(\text{HS}^-\) and \(\text{H}_2\text{S}\) in solution (Section 3.2):

\[
\text{FeS}_2 \rightarrow \text{FeS} + \text{S}^2^- + \text{H}_2\text{S} + \text{HS}^- \\
\text{pyrite} \rightarrow \text{talc} + \text{chlorite} \rightarrow \text{talc} \rightarrow \text{quartz} + \text{clinoenstatite}
\]

Interestingly, antigorite returns to replace talc + magnesite + aqueous fluid between 600 and 725 K, causing the fluid to become \(\text{CO}_2\)-rich (Section 3.2), although antigorite is entirely replaced at higher temperatures, yielding a final pulse of fluid between 725 and 735 K:

\[
3 \text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Mg}_2\text{Si}_4\text{O}_6 + \text{H}_2\text{O} + 2\text{H}_2\text{O}
\]

\[
\text{antigorite} + \text{forsterite} + \text{clinoenstatite}
\]

At 3 Gyr after formation, the mineral assemblage in the mantle is formed of talc > troilite > antigorite > magnesite \(\approx\) magnetite \(\approx\) clinoenstatite \(\approx\) chlorite \(\approx\) dolomite for CI chondrite-derived bodies and antigorite > magnetite > clinopyroxene \(\approx\) troilite \(\approx\) fluid > talc > tremolite \(\approx\) chlorite > dolomite for CM chondrite-derived bodies (Figure 7).

Finally, temperatures in the interior of Ceres decrease from about 3 Gyr until the present day. At 4.5 Gyr, the phase assemblage at 100 MPa consists of talc \(\approx\) magnesite > troilite > fluid \(\approx\) chlorite > clinopyroxene > dolomite > antigorite for CI chondrite-derived bodies and antigorite > magnetite > talc > fluid > troilite > dolomite > chlorite + clinopyroxene > forsterite > antigorite > clinoenstatite > magnetite for CM chondrite-derived bodies (Figure 7). These distinct phase assemblages yield different mantle densities at 4.5 Gyr after formation (~2431 kg m\(^{-3}\) for the CI chondrite-derived body versus ~2770 kg m\(^{-3}\) for the CM chondrite-derived body), but both are consistent with values derived from Dawn observations (Sections 1 and 3.1).

### 3.3.2. Mantle Mineralogy in Bodies Derived from Comets

While there are differences in the mantle mineralogy derived from CI chondrites versus CM chondrites, ultimately, the differences between them are small compared to the mantle mineralogy derived from the evolution of cometary material (Figure 7). While none of the bodies derived from comets result in mantle densities consistent with Dawn’s observations, we focus on the one that yielded the closest mean density (100% 67P/C-G, \(\Phi_{\text{max}} = 0\), yielding a mantle density of ~2935 kg m\(^{-3}\); Section 3.1). From the start, the mantle loses >60% of its mass as fluid. The remaining phase assemblage consists of quartz > clinoenstatite > talc > greenalite > graphite \(\approx\) pyrite > stilpnomelane \(\approx\) chlorite at 100 Myr after formation. The assemblage evolves to quartz > clinoenstatite > talc \(\approx\) troilite > graphite > plagioclase \(\approx\) magnetite \(\approx\) ferroanorthophyllite at 3 Gyr.
with only an extra ∼1 wt% free fluid being produced. Finally, as temperatures cool until the present day, the mantle mineralogy evolves to quartz > clinopyroxene > talc ≈ troilite > graphite > stilpnomelane ≈ magnetite at 4.5 Gyr.

4. Implications and Discussion

4.1. Metamorphic Brines as the Low-density Phase Present in the Mantle

As shown in Figures 3 and 8, the residual rock density of a few CI chondrite-derived bodies and one CM chondrite-derived body can meet the average mantle density inferred from the Dawn data, provided that the mantle layer contains a significant porosity fraction occupied by low-density material. Metamorphism of chondritic materials releases brines that fill the role of the low-density material. Other low-density phases, such as graphite, only occurred in insufficient amounts to account for the low bulk mantle density, even in the cometary cases. Porosity occupied by brines would thus constitute ∼13–30 vol% of the mantle. Bodies derived from cometary material did not lead to densities consistent with Dawn observations.

Based on observations from the Dawn mission, brines are likely present at least in two places below Ceres’s crust: Hanami Planum (Raymond et al. 2020) and Ahuna Mons (Ruesch et al. 2019). Aqueous CO₂ and other gases produced by metamorphism (Figure 5) could drive buoyancy and upwelling (Quick et al. 2019).

As shown by Castillo-Rogez (2011), an ice-poor interior but with abundant porosity and phases of low thermal conductivity (e.g., organic matter, salts, and phyllosilicates) compacts and dehydrates over a scale of about 1 Gyr. As shown for Europa in Melwani Daswani et al. (2021) and here (Section 3.2), devolatilization events can lead to the production of a layer rich in water, salts, and minor concentrations of hydrocarbons overlaying metamorphosed residual rock with a density of 2420–2740 kg m⁻³. This outcome is independent of the time of formation with respect to CAIs. Hence, a model of Ceres dominated by carbonaceous material and a high fraction of organics but no ice is not stable over the long term. Even if the volatile-rich shell produced from metamorphic fluids was entirely removed by impacts, as suggested by Zolotov (2020), the average density of the remaining material would be that of partly dehydrated rock (2930–3210 kg m⁻³; Figures 3 and 4), i.e., too high with respect to Ceres’s bulk density (2162 kg m⁻³). Hence, this study indicates that an ice-poor interior framework cannot account for the geophysical observations returned by Dawn once thermal evolution is accounted for.

4.2. Heat Pulse Associated with Water Flow: A Possible Geological Signature

In the thermal model taken as reference in this study, silicate dehydration starts at about 1 Gyr after formation.
The fluids are buoyant and reach the interface between the rocky mantle and crust. Several evolutionary scenarios for that large amount of liquid can be envisioned and are left for future study. First, the continuous release of $4 \times 7 \times 10^{19}$ kg of water between 0.1 and 3 Gyr ($\sim 1.4 \times 2.4 \times 10^{19}$ kg yr$^{-1}$) after formation contributes to replenishing and maintaining Ceres’s relict ocean. Discrete phase transitions also contribute large punctuated pulses of water (e.g., antigorite and magnesite to olivine and fluid at $>100$ MPa and $\sim 725$ K contributes $1 \times 10^{19} \rightarrow 2 \times 10^{19}$ kg of H$_2$O + CO$_2$ fluids in the CI and CM chondrite mantles $\sim 3$ Gyr after formation; Sections 3.2 and 3.3). While the temperature of Ceres’s “first” ocean was inferred to be relatively mild ($<100$°C; Castillo-Rogez et al. 2018 based on Neveu et al. 2017), metamorphic fluids are several hundred degrees, depending on the depth of their formation (Figure 8). Their interaction with the relict ocean can lead to new chemical reactions in Ceres. The associated heat anomaly could potentially trigger convective upwelling in the crust and destabilize clathrates, if present. Transportation to the surface depends on pathways in the crust. Geological observations indicate that Ceres’s crust is highly fractured (Scully et al. 2017; Zeilhofer & Barlow 2021), with evidence for fault connections with the deep brine reservoir (Raymond et al. 2020). While the details need to be worked out, we expect that the heat pulse associated with the release of hot fluids would leave some signature on the surface. A possible consequence is viscous relaxation of the crust on a global scale. Marchi et al. (2016) reported a dearth of large craters between 200 and 300 km radius on Ceres compared to predictions from crater chronology models. A heat pulse released after 1 Gyr could potentially erase large craters, the bulk of which should have formed earlier in Ceres’s history (Marchi et al. 2016). On the other hand, that heating event should happen before the formation of basins inferred in Ceres’s geology (Marchi et al. 2016). Another potential geological expression of hot fluid released from the mantle could be in one or several of the cryovolcanic features identified by Sori et al. (2018). Detailed comparison of the thermal evolution and geological timelines is left for future work. The thermal evolution timeline can be shifted somewhat by changing the time of formation of Ceres with respect to CAIs. Figure 9 shows the onset time for the dehydration of antigorite and the volume fraction of the dehydrated mantle as a function of the time of formation with respect to CAIs and rock thermophysical properties. The onset of antigorite destabilization may be delayed to 3 Gyr after formation if the rock thermal conductivity is $>2$ W m$^{-1}$ K$^{-1}$ and the fraction of potassium leached from the rock, for example, as a result of ammonium-cation exchange, is $>40\%$. However, in these conditions, the affected volume is less than 10 vol%. On the other hand, early dehydration is achieved in conditions that also lead to advanced dehydration, for example, when the time of formation with respect to CAIs is $<4$ Myr.

Finally, fluid compositions generated from CI and CM chondrite-like mantles differed mainly by CM chondrite-derived mantle fluids having somewhat higher K$^+$ concentrations at low temperatures (i.e., early in Ceres’s history; Figure 5). For the mantles consistent with the allowable densities, the mean concentration of potassium remaining in the
CM and CI chondrite-derived mantles is 0.034 and 0.049 wt%, respectively. This corresponds to ~97% of the original concentration of K in both cases. Given the lower concentration of potassium in CM chondrites versus CI chondrites (Table 1), this may imply an early delivery of a long-lived source of radioactive heat to the ocean and a relative depletions of potassium in the mantle if Ceres’ss bulk composition more closely resembles CM chondrites versus CI chondrites, leading to a slightly colder mantle evolution.

4.3. Fate of Organics

The thermodynamic database we have employed contains a wide suite of organic species (see the Appendix); however, the only hydrocarbons that were produced in the metamorphic fluids were minor amounts of CH$_4$, and formate (CHOH$^-$; Figure 5). The comet-derived bodies produced up to ~20 wt% graphite; large amounts of methane, ethane, and propane; and minor amounts of ethylene, acetic acid, ethanol, hexane, and propanol, which is consistent with results from experimental work heating materials analogous to precometary material (Nakano et al. 2020), but the resulting mantle density in the comet-derived models did not match Ceres’s interior. The remaining concentration of carbon after metamorphism in the mantles of the CM and CI chondrite-derived bodies is 1,253–1,781 and 1,851–2,795 wt%, respectively, or a remaining [C] of 74 wt% for CM chondrite mantles and 79% for CI chondrite mantles with respect to the accreted carbon. For the comet-derived mantle resulting in a density close to the allowable density, the remaining [C] is ~3.584 wt%, or only ~13 wt% of the initial carbon.

5. Conclusions

Metamorphic fluids generated by the loss of volatiles from mantle minerals during thermal evolution may create a second-generation ocean in Ceres and potentially provide an additional process for explaining the presence of liquid below Ceres’s crust at present. Low volumes of fluids produced in the mantle would continuously replenish the ocean over time, but punctuated fluid pulses are expected at important dehydrating phase transitions (e.g., antigorite → olivine + water). Follow-up modeling is needed to understand the migration pathways from the mantle to the base of the crust and the present-day fate of these fluids. Depending on the timescale of migration, we anticipate that (hot) migrating fluids from the deep interior could react with (cooler) overlying rock. However, the total volume of fluids transferred from the interior to the base of the crust are unlikely to change significantly from the work presented here because temperatures in the deep interior are higher than at shallower depths; therefore, fluid migration most likely progressed from the bottom up. Resequestration of volatiles by top-down rehydration of the deeper rocks after their partial dehydration is likely inefficient because pore compaction after fluids migrated from the deep interior likely precluded fluid percolation; in addition, volatile diffusion through anhydrous minerals is slow on gigayear timescales (e.g., Demouchy & Bolfan-Casanova 2016). On the other hand, solid volume expansion caused by reserpentinization of the interior could enable fracture formation and further percolation (Vance et al. 2007; Neveu et al. 2015; Vance & Melwani Daswani 2020).

The composition of the metamorphic fluids is a strong function of their temperature, rather than whether they are derived from CI or CM chondrite-like compositions. The resulting fluids are Na$^+$- and HS$^-$-rich and become more CO$_2$-rich with rising temperature as carbonates destabilize in the mantle. By comparison, metamorphic fluids that may have produced Europa’s ocean are predicted to have contained comparable concentrations of Na$^+$ but $\geq 10\times$ more CO$_2$ early
in its history, leading to a mildly acidic ocean (pH = 4.5–6), where sulfur would be present as sulfate (SO\text{4}^{2-}) instead of sulfide (Melwani Daswani et al. 2021). A more relevant comparison may be Enceladus’s predicted ocean composition. We predict a present-day mantle mineralogy mainly composed of antigorite, talc, pyrrhotite, troilite, magnesite, chlorite, clinopyroxene, magnetite, and 13–30 vol% of fluid-filled porosity. The resulting mantle density appears consistent with inferred densities from Dawn observations. Thermal evolution of cometary compositions does not appear to result in such densities, although cometary metamorphic fluids are hydrocarbon-rich, in contrast to chondrite-derived fluids.

These results are relevant to other mid-sized, ice-rich bodies whose rocky mantles may be large enough to host temperatures...
greater than 700 K but too small for silicate melting to occur, e.g., other dwarf planets, potentially Uranus’s satellites.

Future efforts should be made to study the interaction of metamorphic fluids delivered to an existing ocean, including chemical reactions promoting or impeding habitable conditions and the implied heat transfer. The migration of substantial fluid volumes from the interior could cool the interior more rapidly but deliver heat and potassium that could extend the ocean’s lifetime. The relaxed topography may represent geological evidence of fluid delivery into the crust and subcrustal ocean over time. The recent exposure of natrite found at Occator crater suggests a large fraction of HCO$_3^-$ in the brine reservoir below Hanami Planum and temperatures $\geq$ 265 K (Castillo-Rogez et al. 2019), which could also point to a supply of bicarbonate-rich fluids.

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Appendix
Thermodynamic Modeling Details

Gibbs free energy minimization code Perple_X version 6.8.7 (Connolly 2005, 2009, 2017) was used, together with a lagged speciation algorithm (Galvez et al. 2015; Connolly & Galvez 2018) and the Perple_X implementation of the Deep Earth Water (DEW; Pan et al. 2013; Sverjensky et al. 2014) model “DEW17HP622ver_elements,” to quantify fluids and their compositions, including the following aqueous organics and hydrocarbons: toluene, propanol, propanoic acid, propanoate, propane, sodium acetate, methanol, methane, lactic acid, lactate, hexane, H-succinate, glycolic acid, glycolate, glutaric acid, glutarate, formic acid, formate, iron acetate, ethylene, ethanol, ethane, benzene, acetic acid, and acetate.

We also use a generic hybrid molecular fluid equation of state model including CO$_2$-CH$_4$-H$_2$-CO$_2$-H$_2$O-H$_2$S-SO$_2$-N$_2$-NH$_3$ fluid with linear subdivisions (“COH-Fluid”). Activity-composition models and solution model thermodynamic data for mineral phases were mainly selected from the “igneous set” implemented in Perple_X, adapted mainly from Holland et al. (2018), shown in Table 3 and also used in the phase equilibrium software THERMOCALC (Powell & Holland 1988). The igneous set of equations of state (the other two families are the “metapelite set” and the “metabasite set”) is calibrated up to 6 GPa and is the most appropriate for the pressure and temperature range and wide compositional space explored here (García-Arias 2020). For carbonates, we use the solution models Do(HP) and M(HP) derived from Holland et al. (1998), including the calcite (CaCO$_3$), aragonite (CaCO$_3$), magnesite (MgCO$_3$), dolomite (CaMg(CO$_3$)$_2$), ankerite (CaFe(CO$_3$)$_2$), and siderite (FeCO$_3$) end-members. Some mineral and melt end-members (e.g., fo8L, qiL) were excluded because of their incompatibility with the solution models used or suspect stability. The h2oL melt end-member was also excluded because it overstabilizes silicate melt at low temperature. Perple_X has been used extensively to constrain the decarbonation and dehydration of mantle rocks and subducting crust on Earth, and validation of thermodynamic models and code are available in the literature. The most relevant calibration and validation of the dehydration and decarbonation reactions are found in Bjerga (2014), Bjerga et al. (2015), Bretscher et al. (2018), and Connolly (2005). Gorce et al. (2019) verified that thermodynamic models of decarbonation and dehydration with Perple_X approximate field volatile flux measurements; like in the models presented in this work, carbon release is facilitated by low- to moderate-temperature deserpentinization or high-temperature destabilization of carbonates. Recent tests with Perple_X for serpentine stability and the devolatilization of talc-carbonate rocks relevant to those presented in this work can be found in Nozaka et al. (2017) and Menzel et al. (2020).

The Rcrust program (version 2019-12-04; Mayne et al. 2016) was used to calculate the isobaric prograde heating paths from 273.15 to 903.15 K in 10 K increments ($\Delta T$). No fluids were extracted at the 273.15 K isotherm to equilibrate the composition at all pressures; fluid extraction is first allowed to occur at the first temperature increment (283.15 K). At each depth (10 MPa increments from the surface to the center) in the silicate interior, where pressure is assumed to remain constant, prograde reactions with increasing temperature are net fluid-producing; therefore, fluids permeating from underlying layers are assumed to not have significant interactions with overlying layers, as fluids are already in excess. The spacing of the temperature and pressure increments was chosen to obtain accurate results while keeping model run times and output file sizes reasonable (<3 hr and ~200 MB, respectively). Given the wide pressure–temperature (PT) space explored here, the model PT spacing is reasonable in order to constrain volatile mass fluxes, instead of the precise PT location of potentially thousands of phase reactions and relations. Here Rcrust was used to retain and extract fluids during metamorphism. A $\Phi_{\text{max}}$ equal to zero does not signify that all volatiles are extracted but rather that all free fluids are extracted.
**Table 3**

Solution Models Used in the Perple_X Thermodynamic Phase Equilibrium Calculations with the DEW17HP62ver Elements Thermodynamic Data

| Solution Model | Type | Source |
|----------------|------|--------|
| Agt(PN) | Antigorite | Padrón-Navarta et al. (2013) |
| Bi(HGP) | Biotite | Holland et al. (2018) |
| Chl(HP) | Chlorite | Holland et al. (1998) |
| COH-Fluid | fluid with linear subdivisions | Connolly & Galvez (2018) |
| Cpx(HGP) | Clinopyroxene | Holland et al. (2018) |
| Do(HP) | Dolomite-ankerite | Holland & Powell (1998) |
| GrHGP | Garnet | Holland et al. (2018) |
| M(HGP) | Magnesite-siderite- rhodochrosite | Holland & Powell (1998) |
| Melt(HGP) | GENERIC silicate melt | Holland et al. (2018) |
| Mica(CF) | Fe-Mg-K Na mica | Chatterjee & Froese (1975); Holland & Powell (1998) |
| O(HGP) | Olivine | Holland et al. (2018) |
| Omph(HGP) | Omphacite | Green et al. (2007) |
| Opx(HGP) | Orthopyroxene | Holland et al. (2018) |
| Pl(JH) | Plagioclase | (Jennings et al. 2016) |
| Pu | Pumppylite | DEW17HP62ver_elements |
| Sp(HGP) | Spinel | Holland et al. (2018) |
| Stilp | Stilpnomelane | DEW17HP62ver_elements |
| T | Talc | DEW17HP62ver_elements |

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