TIMING AND METAMORPHIC TEMPERATURE YIELD DIFFERENT BRINE COMPOSITIONS AT DWARF PLANET CERES.
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Introduction: Several strong lines of evidence point towards dwarf planet Ceres being or having been a habitable world for *life as we know it*. Most notably, NASA's Dawn spacecraft revealed mineral salts and organics expressed at the surface, which are inferred to be the result of deep-seated briny fluids migrating from the mantle to the surface in the recent past [e.g. 1]. Here we describe the results of thermodynamic models used to decipher the precise origin, composition, and subsurface pervasiveness of the brines, which may help resolve whether Ceres was, and continues to be, a habitable world.

Methods, constraints, and assumptions: Dawn's gravity data constrains the present-day mantle density (ρ_{mantle}) to ~2700 kg/m^3 [2] or ~2430 kg/m^3 [3], which is consistent with a partially hydrated rocky interior containing fluid-filled porosity (φ_{mantle}) up to ~30 vol. %. We performed thermodynamic models using programs Perple_X [4] and Rcrust [5] to determine the changing mineralogy and fluids in Ceres' mantle from shortly after accretion until the present day, anchoring the pressure and temperature conditions in the thermodynamic models to the thermal evolution model by [6]; the nominal case is shown in Figure 1.

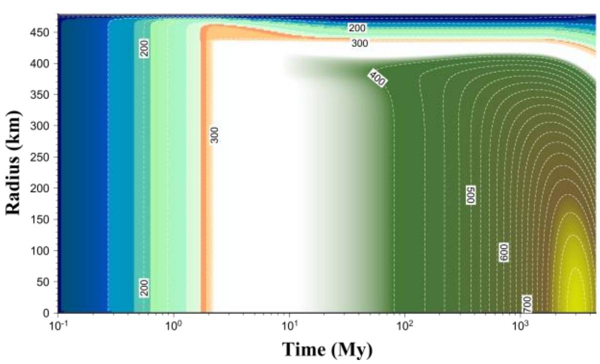

Figure 1. Thermal evolution model of Ceres from [6] used to anchor the pressure and temperature conditions of the thermodynamic model, from the surface to the center of Ceres. Temperature units shown in the figure are Kelvin.

We used appropriate solution models and thermodynamic data implemented in Perple_X, including data for the speciation of solutes in aqueous fluids [7]. We assumed a variety of possible initial compositions for Ceres after accretion, based on whether the building blocks of Ceres were primarily CM-chondrite-like, CI-chondrite-like, cometary, a mixture of cometary and CI-chondrite materials, and various amounts of additional water (0, 10, 25 wt. %) beyond that already trapped in the minerals and organics present in chondrites and comets. Finally, we also allowed the release and extraction of any fluids in excess of predetermined volumes to reside in the mantle (0, 10, 30 vol. %, or multiple layers of decreasing porosity from surface to core). A total of 40 thermodynamic – thermal evolution models were performed.

Results and discussion: Only eight of the combinations of variables tested in the evolution models resulted in mantle densities consistent with the Dawn spacecraft's observations. Five of these cases resulted from a thermally evolved body of CI chondrite composition (±H_2O) containing φ_{mantle} = 17–30 vol. %, yielding $\rho_{mantle} \approx$ 2430 kg/m^3. Two other consistent cases developed from the thermal evolution of CI chondrite compositions without additional water, yielding $\rho_{mantle} \approx$ 2740 kg/m^3, and $\varphi_{mantle} \approx$ 21 vol. %.

Only one body evolved from a CM chondrite composition yielded a mantle density consistent with Dawn data (CM chondrite + 25 wt. % H_2O, with $\varphi_{mantle} \approx$ 17 vol. %, and $\rho_{mantle} \approx$ 2712 kg/m^3).

None of the thermodynamic – thermal evolution models using cometary building blocks resulted in ρ_{mantle} consistent with Dawn data: they resulted instead in ρ_{mantle} < 2100 kg/m^3 or ρ_{mantle} > 2900 kg/m^3.

Mineralogy, fluid volumes generated, and timing. During the thermal evolution of the candidate primordial Ceres bodies, the changing density of the mantle is a result of the changing mineralogy, which was tracked by the thermodynamic programs.

Figure 2 illustrates a typical evolution of the phase assemblage as a function of the thermal evolution, shown here only along the 100 MPa isobar for simplicity, for a case where Ceres is initially composed of 90 wt. % CI chondrite material plus 10 wt. % H_2O, and the maximum fluid-bearing capacity of the mantle is fixed at 30 vol. % (fluids in excess are extracted to the surface). At this pressure within the interior of Ceres, free fluids are in excess of the fluid-bearing capacity of the mantle, and are extracted from the interior <100 Myr after accretion. The phases at this depth, at 100 Myr, in order of descending abundance, are: antigorite, magnesite, free fluids (i.e. unbound from minerals), pyrite, talc, clinopyroxene, dolomite, chlorite, stilpnomelane, and minor mounts of graphite. At 100 Myr, a total of ~11 wt. % of fluid has been extracted to the surface from this depth.

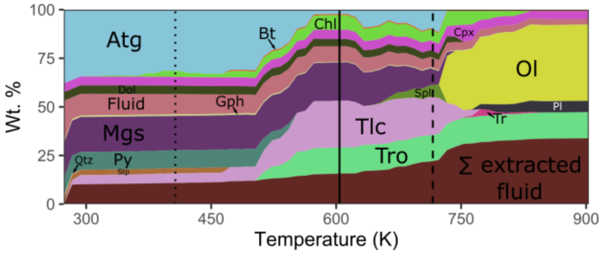

Figure 2. Phase assemblage abundance along the 100 MPa isobar within Ceres, with increasing temperature. Vertical dotted line denotes the temperature at 100 Myr after formation, vertical dashed line denotes the temperature at 3 Gyr after formation, vertical solid line denotes the temperature at 4.5 Gyr. Phase abbreviations are: Atg = antigorite, Bt = biotite, Chl = chlorite, Cpx = clinopyroxene, Dol = dolomite, Fluid = free fluids, Gph = graphite, Mgs = magnesite, Ol = olivine, Pl = plagioclase, Py = pyrite, Spl = spinel, Qtz = quartz, Stlp = stilpnomelane, Tr = tremolite, Tro = troilite, ∑ extracted fluid = sum of fluid mass extracted since accretion.

Temperatures within Ceres peak at around 3 Gyr after formation (Fig. 1). At 100 MPa and 3 Gyr, the phases in order of descending abundance consist of: talc, troilite, magnesite, antigorite, chlorite, free fluids, clinopyroxene, spinel, dolomite, and minor biotite and graphite. At this depth, temperatures within Ceres do not reach the stability field of olivine (Fig. 2). By 3 Gyr, an additional ~10 wt. % fluid has been extracted from the interior as a result of the destabilization of volatile-bearing minerals (namely antigorite, magnesite, talc, pyrite), for a cumulative ~21 wt. % fluid extracted to the surface from this depth, since the formation of Ceres.

Temperatures in the interior of Ceres decrease from about 3 Gyr until the present day (Fig. 1), and the equilibrium phase assemblage changes as a result (Fig. 2), with the net effect of replacing antigorite with talc. In order of descending abundance, the equilibrium phase assemblage consists of: talc, magnesite, troilite, free fluids, chlorite, clinopyroxene, dolomite, antigorite, and minor biotite and graphite. The mean ρ_{mantle} = 2432 kg/m^3, consistent with Dawn data.

Brine compositions. Following the same representative model, we describe the composition of the fluids generated and extracted from the interior over time. The earliest (i.e. low temperature) fluids released at 100 MPa from the 90 wt. % CI chondrite plus 10 wt. % H_2O Ceres are very dilute, as expected from the additional water. However, as fluids are irreversibly removed and temperatures in the mantle increase during the thermal evolution of Ceres, fluids become progressively more enriched in Na^+, HS^-, dissolved CO_2, K^+ and OH^-. Fluids released from this depth within Ceres are reducing and very basic (pH = 11 – 14).

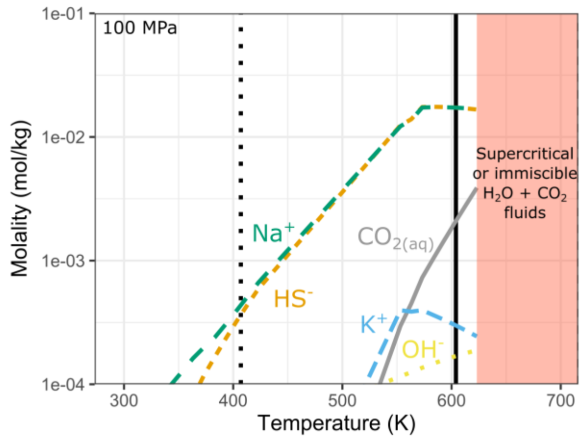

Figure 3. Solute concentration in the aqueous fluids released at 100 MPa within Ceres. Early, low temperature fluids are dilute, whereas later fluids produced with increasing temperature become more Na^+, HS^- and CO_2-rich. Vertical dotted line denotes the temperature 100 Myr after formation, and vertical solid line denotes temperature in the present day. For clarity, solutes <10^{-4} mol/kg are not shown here.

Conclusions: We have presented a series of models for the generation of different brine compositions within Ceres, that strive for geochemical and geophysical consistency with current spacecraft constraints. Metamorphic phase changes caused by the thermal evolution of Ceres are likely to produce fluids that may be released to the surface, as volatile-rich minerals exsolved volatiles with varying temperature in time. For example, Figures 2–3 show that pyrite transforms to troilite, consuming acidity and releasing dissolved sulfide into the aqueous phase:

$$FeS_2 \rightarrow FeS + S^{2-} \xrightarrow{+H^+} FeS + HS^-$$

Similarly, carbonates destabilize and release CO_3^{2-}, HCO_3^- and $CO_{2(aq)}$, and Na-rich clinopyroxene releases Na^+ as it transforms into Na-free clinopyroxene with increasing temperature (Figs. 2–3), which is consistent with $NaCO_3$ minerals observed by Dawn [1].

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