

**METASOMATISM ON EARLY CERES: A GLOBAL ROCK ALTERATION AND FLUID TRANSFER.**

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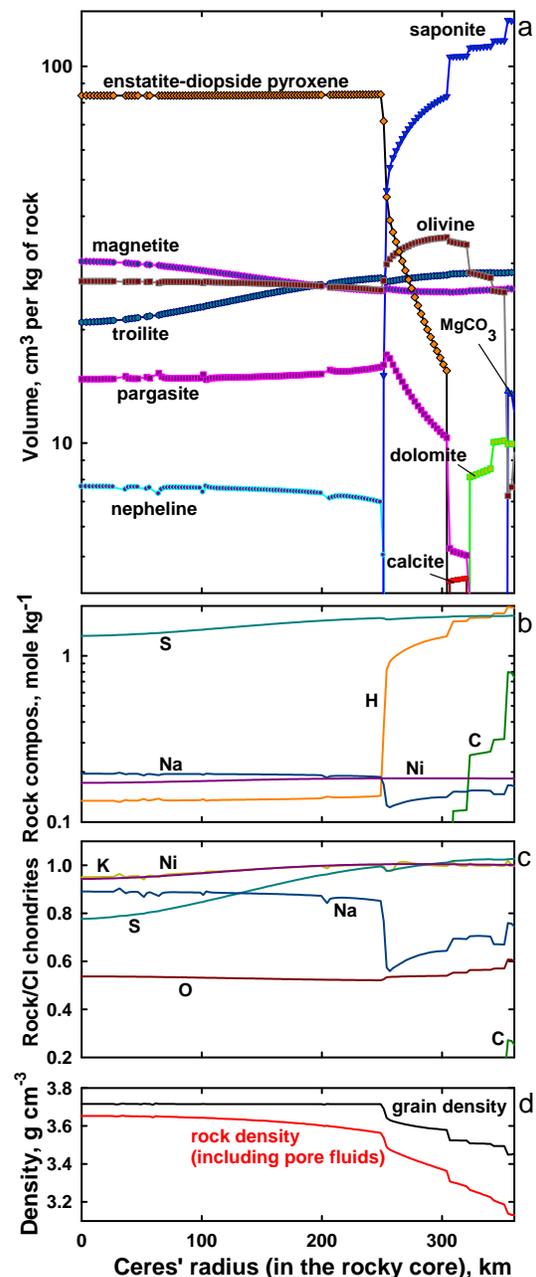
**Introduction:** Metasomatism is a high-temperature open system alteration of subsurface rocks by fluids released in metamorphic or igneous processes. It implies non-isochemical alteration due to the transfer of chemical species with fluids. Although chondrites do not reveal large-scale metasomatic processes on their parent asteroids [1], fluid motions are expected during global thermal processes on large water-rich bodies [2]. The large size (~950 km in diameter) of the dwarf planet (1) Ceres suggests at least some thermal processing of the water-bearing interior leading to water-rock separation [3-5]. Thermal evolution models show that Ceres could have warmed, partially dehydrated, and water-rock differentiated even if accreted rocks did not contain any <sup>26</sup>Al [4, 5]. Here, we model a global-scale metasomatism in the interior of a Ceres-sized body accreted from hydrated, oxidized, and <sup>26</sup>Al-free materials of CI carbonaceous chondrites.

**Methods:** We evaluated the phase composition in warmed Ceres' interior, the upward transfer of fluids formed through dehydration of minerals, and the accumulation of water mantle. The used temperature (*T*) profile [5] in the interior reflected Ceres' warming by long-lived radionuclides when *T* in the center reached ~700 °C. We assumed rock fracturing and release of the fluid if fluid pressure (*P*) exceeded lithostatic *P* by a value of rock's tensile strength [6]. At each depth, used pressures exceeded lithostatic *P* by the value of the rock's tensile strength (~10<sup>2</sup> bars).

The phase composition was calculated in spherical rock layers (~5 km thick) starting at the body's center. Initial rocks had the grain density of 2.42 g cm<sup>-3</sup> [7]. For each layer, the calculated grain and fluid densities together with an adopted porosity were used to compute the rock's density and the compressed layer's new thickness. The fluid that did not fill the pore space was transferred to the overlying layer and was allowed to react with the fresh rock. For each rock layer, we computed an apparent radius of altered rocky core and a thickness of forming water envelope that could condense above the core. A gas escape to space was not considered. The computation stopped when a radius of the differentiated body achieved 470 km, the average pre-Dawn radius of Ceres [8].

The phase composition was evaluated through calculations of chemical equilibria in the O-H-C-Cl-S-Mg-Ca-Si-Al-Na-K-Cr-Mn-Fe-Co-Ni-P water-rock-gas system with GEOCHEQ codes [9] which have been applied for aqueous alteration in chondrites [e.g. 10].

**Figure 1.** The secondary mineralogy (a), the selective rock composition (b), the selective rock composition relative to CI chondrites (c), and density (d) of Ceres' core formed through dehydration and metasomatism of initial CI carbonaceous materials.



The models for the organic-inorganic equilibration and organic speciation were tentative. The formation of

methane was either allowed or suppressed. Water-soluble organic compounds were represented by one C-atom species which may equilibrate at lower temperatures: formate, methanol, and formaldehyde. Condensed organic species were represented by pyrene ( $C_{16}H_{10}$ ), and the formation of graphite was suppressed.

**Results:** The calculations led to compositional and density profiles together with masses and volumes of all constituents (rocks, minerals, pore fluids, and water mantle) and the whole body. The models demonstrate the formation of a dehydrated rocky core surrounded by more hydrated and carbonated rocks. The forming ocean accumulates chemical species leached from rocks and released through redox alteration of minerals and organic compounds.

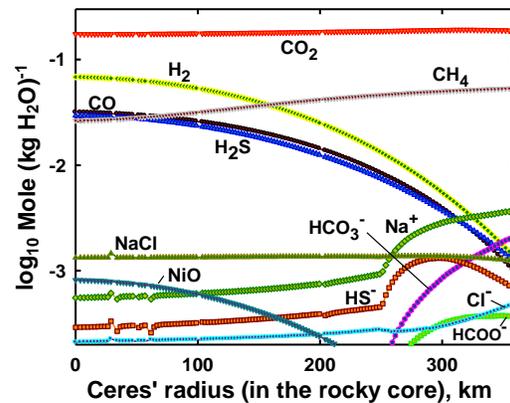
**Altered rocks.** The inner part of the rocky core mainly consists of Mg-Ca rich pyroxene, olivine, magnetite, and troilite (Figure 1a). The major OH-bearing phase is pargasite. Minor minerals are nepheline, Ni sulfide, phlogopite, whitlockite, rhodonite, and Ni-Co rich metal. The outer part of the core mainly consists of saponite, olivine, magnetite, and troilite. Ca and Mg carbonates form closer to the core-mantle boundary.

Compared to initial CI-type solids, all altered rocks are depleted of O, H, C, Cl, and Na, which were removed with alteration fluids (Figures 1b and 1c). In the current model, all chlorine is leached from the rock. All carbon is extracted from the inner high- $T$ - $P$  core, which is implied through decomposition of organic compounds (in reality, a fraction of C could be graphitized). S, K, and Ni are partially leached from the inner core. Other considered elements are not mobile owing to low solubility of corresponding secondary minerals.

**Fluid composition.** Aqueous fluids are rich in dissolved gases ( $CO_2$ ,  $H_2$ ,  $CH_4$ , CO, and  $H_2S$ ) as well as in sodium and chlorine species ( $NaCl$ ,  $Na^+$ , and  $Cl^-$ ) (Figure 2). In the inner core, high- $T$ - $P$  fluids contain abundant neutral solutes ( $H_2$ , CO,  $H_2S$ , NaCl, and NiO). Closer to the core-mantle boundary, fluids contain more methane and ion species ( $Na^+$ ,  $HCO_3^-$ ,  $Cl^-$ , and  $HCOO^-$ ). If formation of methane is inhibited,  $CO_2$ , CO, and  $H_2$  are the most abundant solutes. A gas phase separates in the forming ocean.  $Na^+$ ,  $Cl^-$ , and bicarbonate/carbonate ions are major impurities in a degassed and cooled ocean.

**Formed internal structure.** The calculated internal structure consists of the rocky core with a radius of  $360 \pm 15$  km and the water mantle with a thickness of  $\sim 110 \pm 15$  km. The dehydrated inner part of the core has a density of  $3.6 \pm 0.05$  g  $cm^{-3}$  (Figure 1d). In the hydrated upper core, the rock density decreases with the radius from  $\sim 3.5$  to  $3.1$  g  $cm^{-3}$ . The mantle's mass fraction is  $\sim 26$  %. Assuming the density of the water mantle to be  $0.92$  g  $cm^{-3}$ , the computed body's density of  $\sim 2.0$  g  $cm^{-3}$  is only slightly less than the pre-Dawn data for

**Figure 2.** Speciation of aqueous fluids formed through dehydration in the rocky core. The data correspond to results presented in Figure 1.



Ceres ( $\sim 2.1$  to  $\sim 2.2$  g  $cm^{-3}$ ). The evaluated density implies some removal of water mantle materials through escape and collisions, and an addition of a rocky cap.

**Discussion:** A dehydration of Ceres' interior could have been accompanied by redox transformations of organic compounds, reduction of sulfates, leaching of some elements from the rocks, rock's fracturing by overpressured gas-rich Na-C-Cl aqueous fluids, and the corresponding heat transfer by upwelling solutions. A deposition of Fe sulfides from cooling fluids is expected at the rock-early ocean interface. Partial degassing and escape of gases ( $H_2$ ,  $CH_4$ , CO,  $CO_2$ , and  $H_2S$ ), and a downward freezing of the ocean could have led to accumulation of Na chloride and Na carbonate salts at the core-icy mantle interface. Some  $CH_4$ ,  $CO_2$  and  $H_2S$  could be trapped in clathrates. A possible early leaching of Cl's sulfates during warming of the body does not exclude their presence in a primordial ocean and subsequent accumulation at the core-mantle boundary. None of these chemical species can be seen in Ceres' regolith. Analogous processes could have occurred on other large carbonaceous bodies.

**References:** [1] Bland P. A. et al. (2009) *Meteoritics & Planet. Sci.*, 287, 559–568. [2] Young E. D. et al. (2003) *Icarus*, 213, 249–259. [3] McCord T. B. and Sotin C. (2005) *J. Geophys. Res.*, 110, E05009. [4] Castillo-Rogez J. C. and McCord T. B. (2010) *Icarus*, 205, 443–459. [5] Castillo-Rogez J. C. (2011) *Icarus*, 215, 599–602. [6] Wilson L. et al. (1999) *Meteoritics & Planet. Sci.*, 34, 541–557. [7] Consolmagno G. J. et al. (2008) *Chemie der Erde*, 68, 1–29. [8] Drummond J. D. et al. (2014) *Icarus*, 236, 28–37. [9] Mironenko M. V. et al. (2008) GEOCHEQ\_M: Program complex ... In: *Vestnik Otdelenia Nauk o Zemle RAN*, 1(26). [10] Zolotov M. Yu. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 1775–1796.