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Origin and Evolution of Volatile-rich Asteroids

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5.1 Introduction

Volatile-rich asteroids represent the largest population, about 42% (DeMeo and Carry, 2014), of objects found between 2 and 3.5 AU. They encompass asteroids from the C complex that are believed to host the parents of most carbonaceous chondrites based on spectroscopic analogies (Hiroi, 1996; Takir *et al.,* 2015), as well as the large icy asteroids found in the outer main belt. The P- and D-type asteroids also found in that region are believed to contain a significant fraction of ices based on their presumed origin from the Kuiper belt (Levison *et al.*, 2009), although no water signatures (ice, hydroxyl, or hydration features) have been detected for these objects. The lack of observational constraints on the physical and chemical properties of these objects makes it difficult to speculate on their internal evolution and they will not be considered further in this chapter.

Key science questions surround C-type asteroids. Arguably the most important is whether they are the remnants of a single reservoir of material that formed near their current positions in the main belt and in the neighborhood of the nearby dry asteroids, or if instead they come from multiple, perhaps more distal, reservoirs. Located at the interface between the inner and outer solar systems, the main belt has witnessed the various large-scale planet migration events that may well have shaped the architecture of the solar system (e.g. Levison *et al.* 2009; Walsh *et al.*, 2012). A likely contribution of volatile material from the outer solar system could affect the long-term chemical and physical evolution of the large asteroids. By analogy with icy satellites, differentiation involving the melting of liquid water carries important implications for the chemical evolution of these objects and their potential contribution to the production of complex organics. The large representatives (>100 km) are believed to have hosted hydrothermal environments for a few million years, offering a playground for prebiotic chemistry (Abramov and Mojzsis, 2011). This idea has also been suggested for Ceres in which liquid media

 https://doi.org/10.1017/9781316339794.005

could have remained present until recent times (Castillo-Rogez and Lunine, 2013). The evolution of planetesimals accreted early in the solar system was controlled primarily by three factors: (1) accretion time, determining the concentration of the short-lived radionuclide ^{26}Al; (2) size, up to a radius of approximately 50 km beyond which thermal diffusivity and the decay rate of ^{26}Al limit the effects of size; and (3) volatile content (mainly H_2O ice fraction). We review these factors and the physical processes believed to have driven the evolution of these objects (Sections 5.2–5.4). Then we suggest a possible evolution pathway for Ceres built on our state of knowledge of chondrite parent bodies (Section 5.5) with the prospect to get relevant observational constraints from the Dawn mission (Section 5.6).

5.2 C-Type Asteroid Inventory

C-type asteroids are found across all regions in the main belt (DeMeo and Carry, 2014) and present a large diversity in terms of surface (spectral) and physical properties. They include some of the largest asteroids, such as (1) Ceres and (10) Hygiea, and the Themis family, in which water ice has been detected (Rivkin and Emery, 2010). They also comprise significant fractions of the asteroids in the 50–150-km range (e.g. DeMeo and Carry, 2014). The latter may be representative of the original population of planetesimals (Cuzzi *et al.*, 2010) while smaller asteroids are interpreted as collisional fragments. The more recent color survey of asteroids between 2 and 5 AU published by De Meo and Carry (2014) utilizes the Sloan Digital Sky Survey database and the WISE database to quantify the mass distribution across the main belt.

Takir and Emery (2012) introduced additional classification by looking at the spectroscopic properties of C-type asteroids in the 2.5–3.5 μm region (Figure 5.1). This region encompasses absorption features related to water, whether water of hydration at 2.7 μm or the free water feature at 3 μm. The former is associated with CM chondrites (Hiroi, 1996) whereas the 3 μm feature is interpreted as evidence for the presence of ice (Takir *et al.*, 2015). Matches between meteorite classes and C-type and other potentially ice-bearing asteroids are often tenuous. (24) Themis has been identified as a probable host of less altered CM chondrites (McAdam *et al.* 2015). However, Ceres' surface does not find any match in the meteorite record. One possible explanation is that meteorites from icy asteroids are too fragile to survive transfer to Earth and that fragments of these bodies are actually mainly in the form of interplanetary dust particles (e.g., Vernazza *et al.* 2015).

The presence of water ice has been directly identified among asteroid families; either directly as in the cases of (24) Themis (Rivkin and Emery, 2010) and (65) Cybele (Licandro *et al.*, 2011), or indirectly with the discovery of active asteroids

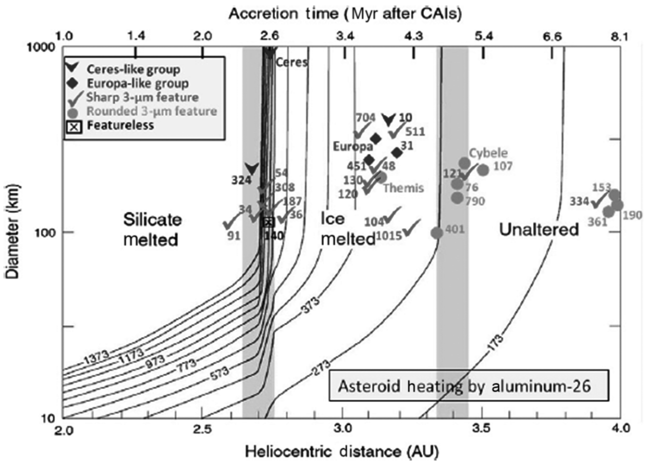

Figure 5.1 Distribution of the four types of 3 μm features in the main belt of asteroids (from Takir and Emery, 2012). Icy asteroids (rounded 3 μm feature) are preferentially found in the outer main belt and beyond, while those asteroids displaying a sharp 3 μm feature are preferentially found closer to the Sun. The dataset is superimposed over a calculation of the maximum temperature theoretically achieved in asteroids as a function of size and distance, after Grimm and McSween, (1993).

(see review by Jewitt *et al.*, 2015). A subcategory of these comet-like active asteroids are the main-belt comets (MBCs) that exhibit activity attributed to water sublimation that entrains surface dust from their surfaces and varies as a function of mean longitude. Thirteen main-belt comets have been confirmed to date, all found in the Themis or Hygiea families (e.g. Jewitt *et al.*, 2015); the dynamical relationship between MBCs and these families has been confirmed (e.g. Haghighipour, 2009). Jewitt and Guilbert-Lepoutre (2012) showed that main-belt comets are activated by small impacts that excavate water ice, and the same process could be responsible for the exposure of water ice at Themis. These same authors predicted that decameter-sized objects have an impact frequency of 1 per thousand years. While there has not been any direct detection of water ice at Ceres at this time, the direct detection of water vapor by the Herschel Space Observatory (Kueppers *et al.*, 2014) also argues for the presence of free ice in the subsurface that may be exposed via impacts or landslides.

Takir and Emery (2012) noted that many objects display a roundish 3 μm feature, like Themis, which suggests that ice may be displayed at these objects but cannot be resolved from Earth-bound observatories. The gradient in C-type asteroid surface properties across the main belt highlighted by Takir and Emery (2012) was previously noted by Jones *et al.* (1990) and interpreted by Grimm and McSween (1993) as the expression of a gradient in the extent of evolution and thus available heat in these objects. This assumes an *in situ* origin of the icy main belt asteroid, which has been the leading theory until the introduction of the Grand Tack (Walsh *et al.*, 2011, see below). However, the scarce detection of free ice at other C-type asteroids and in other parts of the main belt should not be construed as evidence for the lack of that material at depth. While exploring the Thousand Asteroid Light Curve Survey, Sonnett *et al.* (2011) found an outgassing background for about 5% of main belt asteroids. This suggests that many objects can actually retain free ice but exposure of that material at any given time is limited in time and space. Indeed, it does not take much surface debris to bury ice in these objects; Schorghofer (2008) showed that ice can be stable under meters of regolith.

5.3 Origin Scenarios and Accretional Environments

Origin and evolution are tightly coupled in that the accretional environment determines the heat budget of asteroids and their volatile makeup, both of which bear major influence on the long-term evolution of these bodies. For example, the volatile composition determines the thermophysical properties and melting temperature and thus the temperature at which a body may experience physical differentiation (see Figures 5.1 and 5.2). The origin determines the forming

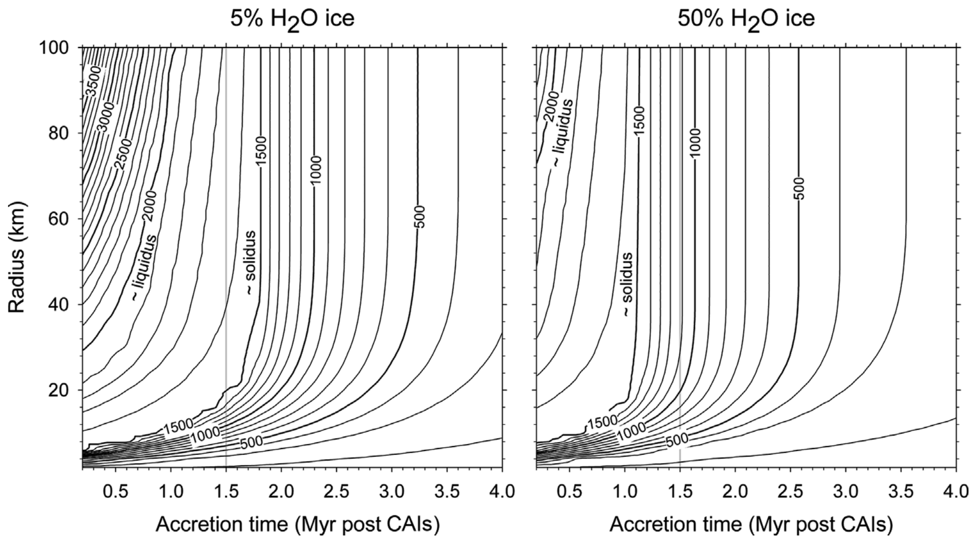

Figure 5.2 Contours of maximal temperature of planetesimals as a function of terminal radius and accretion time relative to CAIs in the early solar system. Left panel shows bodies with 5% by volume water ice at the time of accretion and the right panel shows results for bodies with 50% water by volume.

temperature as well as the amount of short-lived radioisotopes that accreted with a body, and potentially accretional heating.

Different origins have been suggested for volatile-rich asteroids (see Bottke and Morbidelli, Chapter 3, this volume, for a more extensive review). As noted earlier, formation *in situ* was the leading hypothesis for decades (Grimm and McSween, 1993). This scenario raised the question of why the water-ice line, a feature of the early solar system that must have migrated inward with waning accretion rate of the protoplanetary disk, would just happen to be recorded by the existence of predominantly wet and dry asteroids within the relatively narrow asteroid belt itself. Recognition of the potential importance of giant planet migration has broadened our perspective. Walsh *et al.* (2011) introduced the Grand Tack model, for example, in which the asteroid belt forms from Jupiter's migration and is populated by planetesimals derived from within Earth's orbit at 1 AU (thought to be mainly dry) and from the region from 4 to 15 AU (thought to be icy). This scenario offers the major advantage that it explains why C-type asteroids are intimately mixed with S-type asteroids across the main belt (De Meo and Carry, 2014), and why metallic asteroids (M-types) are found in the outer main belt (e.g. (16) Psyche at 3 AU). (4) Vesta and Ceres, two bodies in the same vicinity but with contrasted compositions, also suggest large-scale migration (Bottke *et al.*, 2006), although *in situ* growth at different times cannot be excluded. Vesta is believed to be one of the driest objects in the solar system.

Levison *et al.* (2009) demonstrated that the P- and D-type asteroids are planetesimals that migrated from the proto-Kuiper belt. That study nicely reproduced the observed inclinations and eccentricities. McKinnon (2008) went one step further by suggesting that Ceres itself could have migrated from the proto-Kuiper belt. However, slowing down an object of Ceres' size is more difficult to demonstrate, and McKinnon (2012) noted that capture in the main belt is of low probability. Recent discovery of ammoniated silicates by the Dawn mission (De Sanctis *et al.*, 2015) sheds new light on that debate, although it is not possible at this stage to conclude whether Ceres accreted these volatiles in the outer solar system or following their migration to the main belt (Mousis and Alibert, 2005).

5.3.1 Accretion Timeframe

Carbonaceous chondrites indicate that their parent bodies have been the objects of extensive hydrothermal activity that requires a significant heat source. With definitive proof of the existence of the extinct short-lived nuclide ^{26}Al in the solar system (Lee *et al.*, 1977) came the realization that the major heat source for smaller bodies must have been from the decay of ^{26}Al (Herndon and Herndon, 1977). Internal evolution models generally assume an accreted abundance of ^{26}Al tied to the time of formation of the calcium–aluminum inclusions (CAIs). Johansen *et al.* (2015) suggest a time of formation of the water asteroids of 2–4 Myr after CAIs, based on the relative timescales of chondrules and CAIs. These timescales depend critically on the assumption that ^{26}Al was distributed uniformly throughout the solar system. The level of heterogeneity of ^{26}Al concentrations is, however, debated in the cosmochemical literature (e.g. Krot *et al.*, 2012; Makide *et al.*, 2012). It has been suggested that ^{26}Al was injected into the solar system from an external, proximal supernova source (e.g. Ouellette *et al.*, 2007), allowing for heterogeneity due to incomplete mixing. More recently, it was pointed out that the solar system's complement of ^{26}Al is normal for massive star-forming regions in general (Jura *et al.*, 2013; Young, 2014), suggesting a homogeneous distribution inherited from the parental molecular cloud. Nevertheless, the precise "canonical" abundance of ^{26}Al at time zero in the solar system has been revisited over the years (e.g. Young *et al.*, 2005, Kerekgyarto *et al.*, 2015).

5.3.2 Original Composition

Distance to the Sun determines the nature of the volatiles compounds condensed into planetesimals. CI materials exhibit certain volatiles generally expected to have condensed in the outer solar system, in particular nitrogen (e.g. Dodson-Robinson *et al.*, 2009) and carbon compounds. Desorption of ammonia was also observed during heating of CR meteorite organics (Pizzarello *et al.*, 2011) and the first results released by the Dawn mission concluded on the presence of ammoniated phyllosilicates (De Sanctis *et al.*, 2015).

Dyl *et al.* (2010) pointed out that the cronstedtite that is commonly found in CM chondrites, but not in terrestrial environments, implies aqueous alteration in the presence of carbon compounds. These authors suggested the accretion of CO_2 as a sink of hydrogen for the formation of CH_4 in order to warrant cronstedtite stability (see details in Section 5.4). However, cosmochemical models do not agree on the origin of these materials, which makes it difficult to test migration models. Dodson-Robinson *et al.* (2009) modeled the snowlines for a variety of volatiles and showed that carbon-rich compounds do not accrete within 4 AU. On the other hand Nuth *et al.* (2014) suggested the production of CO_2 closer to the Sun as a product of the Fischer-Tropf reaction. As an alternative approach, Mousis and Alibert (2005) suggested that outer main-belt volatiles could have been supplied by small (hundreds of meters in size) planetesimals migrating in the early solar nebula. Another recent approach proposed that some of the volatiles present in the outer main belt could come from the giant-planetesimal reservoirs that destabilized when those planets reached their current size (Grazier *et al.*, 2014). These various models seem to agree that at least a fraction of the volatile-rich asteroids could have acquired a few percent of carbon species early in their history even if they formed *in situ*.

5.3.3 Accretion Timescale

While the accretional timeframe is tied to a chronology based on multiple chronometers, the accretion timescale is not well understood. The formation timescale is important because it determines whether large asteroids accreted from smaller, pristine asteroids, or if they accreted from planetesimals that were already evolved as a consequence of short-lived radioisotope decay heat, and, for example, lost the hydrogen produced during serpentinization. The most recent models suggest that accretion timescale could have been as short as a few thousand years for 100-km objects (Johansen *et al.*, 2014), validating models that assume nearly instantaneous accretion relative to the timescale of ^{26}Al heating. Rapid accretion implies that the material accreted into an object like Ceres was not affected by ^{26}Al prior to accretion. Accretional heating of bodies formed in a belt of planetesimals is actually very small because the relative speed of merging objects is a few kilometers per second. Hence, accretional heating is generally not considered a process of significance in asteroids. Similarly, conversion of gravitational potential energy to heat is trivially small for bodies of the order of 100 km. So if small icy asteroids accreted fast then they likely preserved their bulk of volatiles. If large volatile-rich asteroids formed at once without an intermediate stage of incremental accretion from 100-km planetesimals, then there is a greater chance that they could have preserved the bulk of their original volatiles.

5.4 Processes Driving the Evolution of Volatile-rich Bodies

The physical and chemical evolution of volatile-rich asteroids is primarily driven by early melting of their volatile component as a consequence of ^{26}Al decay heat and the capacity of these objects to retain volatiles. These dependences are illustrated in Figure 5.2.

This figure shows contours for the maximum temperature achieved in the core of rocky bodies of carbonaceous chondrite composition as a function of accretion time and size. Two examples are shown, one for 5% water by volume and the other for 50% water ice by volume. Details of the models upon which these contours are based are described by Zhou *et al.* (2013). The important conclusions from these models is that bodies of sufficient size that accreted within approximately 1.0 to 1.6 Myr after time zero for the solar system (as defined by the initial ^{26}Al/^{27}Al in CAIs) will have melted and likely experienced metal core formation. Bodies that accreted within ~ 4 Myr of time zero will have experienced

H_2O melting, accelerating the potential for ice–rock differentiation. Bodies smaller than ~10 km in radius, if they ever existed (Morbidelli *et al.*, 2009, cf. Weisdenschilling, 2011; Schlichting *et al.*, 2012), and which accreted > ~ 2.5 Myr post-CAI, would have never experienced melting of water ice.

The degree of rock–metal or ice–rock differentiation is a clue to the time of accretion for any asteroidal parent body. In the rest of this section we focus on objects large enough for water to have melted shortly following accretion.

5.4.1 Aqueous Alteration

The alteration of rock upon interaction with warm water develops in several stages. It starts with the formation of tochilinite (~$(Mg,Fe,Ni,Al,Ca)(OH)_2 \cdot (Fe,Mg,Cr,Ni)S$) and iron-rich phyllosilicates, especially cronstedtite ($Fe_2{}^{2+}Fe^{3+}(SiFe^{3+})O_5(OH_4)$, a form of serpentine) (e.g. McSween, 1979). McSween noted that Fe/Si ratios in matrices decrease progressively with increasing alteration due to the formation of new phyllosilicate phases with higher Mg/Fe ratios and opaque minerals. The latter are compounds of iron and other metals in the form of magnetite and sulfides.

A net oxidation reaction that describes the early phases of aqueous alteration is

$$\begin{aligned} 5Fe^0 + Fe_2SiO_4[\text{oliv}] + 9H_2O[\text{liq}] \rightarrow\ & Fe_2^2Fe_2^{3+}SiO_5(OH)_4[\text{cronst}] \\ & + Fe^{2+}Fe_2^{3+}O_4[\text{mgt}] + 7H_2 \end{aligned}$$

in which Fe metal and the iron component in olivine (oliv) produce cronstedtite (cronst) and magnetite (mgt). The volumetric water/rock ratio for this idealized reaction is slightly greater than 2. Cronstedtite is rare in terrestrial environments but is the dominant component of the CM chondrite matrix (Browning *et al.*, 1996). The early production of cronstedtite is due to the poor stability of iron-rich silicates in general. Hence, cronstedtite is a marker of the environmental conditions dominating parent-body interiors. Dyl *et al.* (2010) pointed out that the stability of cronstedtite could be explained by the abundance of CO_2 – or other reactive organic compounds – that reacts with H_2 to form methane. This scenario is consistent with isotopic analyses by Guo and Eiler (2007) who also inferred the existence of abundant methane in the environment in which the CM mineralogical assemblages formed.

Mg-phyllosilicates are last to form in the matrix of aqueously altered carbonaceous chondrites due to early sequestration of oxidized iron as described above. Later products include Mg-rich serpentines $Mg_3Si_2O_5(OH)_4$, saponite $(Ca, Na)_{0.3}(Mg,Fe^{2+})_3$-$(Si, Al)^4O_{10}(OH)_2 \cdot 4H_2O$ and vermiculate $(Mg, Fe^{2+}, Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$.

Aqueous alteration reactions described above are accompanied by a significant production of H_2. However, in small asteroids (< 100 km) the partial pressure of

H_2 formed during serpentinization rapidly builds up beyond the internal pressure and excess hydrogen tends to escape (McKinnon and Zolensky, 2003, Wilson *et al.*, 1999). Evolution of the redox conditions of the hydrothermal environment is recorded in the mineralogy of carbonaceous chondrites, see for example Briani *et al.* (2013). This change in partial pressure of H_2 has been interpreted as outgassing in open systems. Further outgassing of volatiles may occur, for example, if cometary volatiles were originally present and exposed via tectonic or convective processes. Geophysical models of meteorite parent bodies generally assume that an outer layer of material remains static. In practice, the large volume changes incurred by serpentinization (up to 15%) are likely to open cracks in the surface of the object and create conduits for volatile loss. The nature and fraction of loss is determined by the object internal pressure and gas solubility.

5.4.2 Salt Production

The alteration of the original feldspars and pyroxenes also involves the leaching of alkaline and alkaline earth metals to the ocean (Zolotov, 2012). Water is released in a supercritical state and with a very low density (~0.32 g cm^{-3}). Being extremely buoyant, supercritical water is likely to escape and vaporize, leaving an evaporite.

We have a direct data point with Earth's ocean, where epsomite is formed from the reaction of forsterite with iron sulfide, but we lack insights into the extent of that process in other bodies. A few measurements at icy satellites suggest the presence of brackish oceans in these objects. For example, Khurana *et al.* (1998) inferred from the Galileo magnetometer data a salt density of Europa's ocean similar to Earth's oceans; chlorides were detected in Enceladus' plumes (Postberg *et al.*, 2009); Hand and Carlson (2015) also interpreted colored material at the surface of Europa as evidence for chlorides directly supplied from a deep ocean. Furthermore, clasts of pristine halite and sylvite found in two ordinary chondrites (Monahans and Zag) have been associated with a large water- and carbon-rich parent body, tentatively suggested to be Ceres (Fries *et al.*, 2014).

More generally, 78 products of hydration have been reported in carbonaceous chondrites (Brearley, 2006), and these include sulfides, sulfates, hydroxides, and phosphates, suggestive of concentration of rock-forming elements by fluids. Post-processing in terrestrial environments can alter the nature of minerals retrieved in carbonaceous chondrites, requiring caution when ascribing significance to labile mineral products. Gounelle and Zolensky (2001) pointed out that sulfates are the product of oxidation in storage and the original composition was dominated by sulfides, more typical of a reduced environment. Indeed, McKinnon and Zolensky (2003) noted that sulfides are expected in asteroids greater than 50 km when the pressure is large enough to promote a partial pressure of hydrogen conducive to a reducing environment.

5.4.3 Hydrothermal Circulation

A key feature of aqueous alteration of carbonaceous chondrites is the apparent requirement for relatively large water/rock ratios. Large water/rock ratios associated with carbonaceous chondrite alteration are inferred from both oxygen isotope studies and thermodynamic calculations. Studies of oxygen isotope exchange during aqueous alteration of these rocks require volumetric water/rock ratios of ~ 0.6 to > 1 (Clayton and Mayeda, 1984; Leshin *et al.*, 1997; Clayton and Mayeda, 1999). In a closed system these water/rock ratios correspond to water- or ice-filled porosities of 38% to > 55%. These large porosities contrast with the much smaller porosities of 5 to 29% exhibited by these rocks today (Britt and Consolmagno, 1997; Flynn *et al.*, 1999). Thermodynamic simulations of closed-system carbonaceous chondrite alteration also suggest large water/rock ratios with values ranging from 0.6 to ~ 50 (Zolensky *et al.*, 1989; Rosenberg *et al.*, 2001; Dyl *et al.*, 2010). These fluid volumes correspond to porosities of 40% to more than 90% and are again minimum estimates that far exceed rock porosities. However, it is important to recognize that water/rock ratios are a measure of mineralogical or isotopic reaction progress only. They should not be taken as literal measures of the amount of water present in the meteorite parent bodies (i.e. C-type asteroid precursors). The water/rock ratios defined by aqueous alteration products in chondrites are minimum estimates based on the assumption that each and every molecule of pore-filling water reacted with the rock. In terrestrial settings, water/rock ratios that exceed pore volumes are interpreted as indicators of fluid flow (Gregory and Criss, 1986).

The prospects for liquid water flow in an asteroidal setting have been addressed from chemical and as well as physical perspectives. It is possible that the first stages of water/rock differentiation are recorded in the aqueous alteration of carbonaceous chondrites. Young *et al.* (1999) and Young (2001) pointed out that the first-order isotopic and mineralogical features of aqueously altered carbonaceous chondrites are well explained if liquid (or vaporous) water flowed within their asteroidal parent bodies. In particular, these authors predicted a sequence of alteration along flow paths that resembles the variety of altered rocks exhibited by carbonaceous chondrites. The mode of flow depends on the rate of heat production and size of the bodies. Young *et al.* (2003) derived the critical Rayleigh number for convection within small water-bearing bodies. These authors found that convective flow was likely on even relatively small bodies with radii of a few tens of kilometers with modest permeabilities. Palguta *et al.* (2010)

reexamined the mineralogical and isotopic characteristics of carbonaceous chondrites in the context of convective flow and again found that the features of aqueous alteration observed in carbonaceous chondrites are explainable in the context of flow. This migration of water inferred from the isotopic and mineralogical products of water–rock reactions in meteorites may be vestiges of the parent-body differentiation process. However, the likelihood for flow of water on carbonaceous chondrite parent bodies has been questioned on the basis that the most altered rocks are the most pristine chemically. For example, the highly altered CI chondrites, of all carbonaceous chondrite groups, most faithfully resemble the Sun in their elemental concentrations (Kallemeyn and Wasson, 1981). Bland *et al.* (2009) concluded that the nearly isochemical nature of the aqueous alteration precluded fluid flow and that the absence of flow was due to very low permeabilities suggested by small grain sizes in the matrix of these rocks. This led to the suggestion by Bland *et al.* (2013) that the parent bodies of the aqueously altered carbonaceous chondrite behaved as giant mud balls, with fluid and loosely consolidated solids moving together.

The debate over the likelihood of flow in carbonaceous chondrite parent bodies continues (see Fu *et al.*, Chapter 6, this volume). Measured permeabilities as low as ~10^{-15} to 10^{-14} m^2 have been measured in some chondrite materials (Sugiura *et al.*, 1984; Corrigan *et al.*, 1997), allowing for convective flow in bodies the size of the largest C-type asteroids. What is more, convection is not the only driving force for flow. In microgravity settings, surface tension and gas pressures can facilitate motion of liquid water (Young, 2001), leading to the possibility for single-pass flow rather than convection (Figure 5.3). Isochemical alteration evidently precludes the highest water/rock ratio of order 500 observed in some serpentinized rocks, but is not necessarily indicative of lack of flow. Isochemical aqueous alteration is observed in terrestrial, aqueously altered mafic and ultramafic rocks where fluid/rock ratios are modest but nonetheless exceed porosities (e.g. water/rock $>$ 1 but likely less than ~ 50) (Li and Lee, 2006; Ehlmann *et al.*, 2012).

5.4.4 Physical Differentiation

The mechanisms for carbonaceous chondrite asteroidal bodies to differentiate a core, mantle, and volatile-rich shell are difficult to evaluate directly because convection and particle settling in low-gravity environments have not been studied experimentally. If aqueous fluids did flow, this provides a mechanism for transporting water ice from the interior to the pemanently frozen exterior. Flow in an unsaturated interconnected pore space would naturally lead to rock–ice differentiation. As discussed above, for the largest bodies, this seems likely, consistent with our understanding of the large icy satellites. Contingent upon the gravity field,

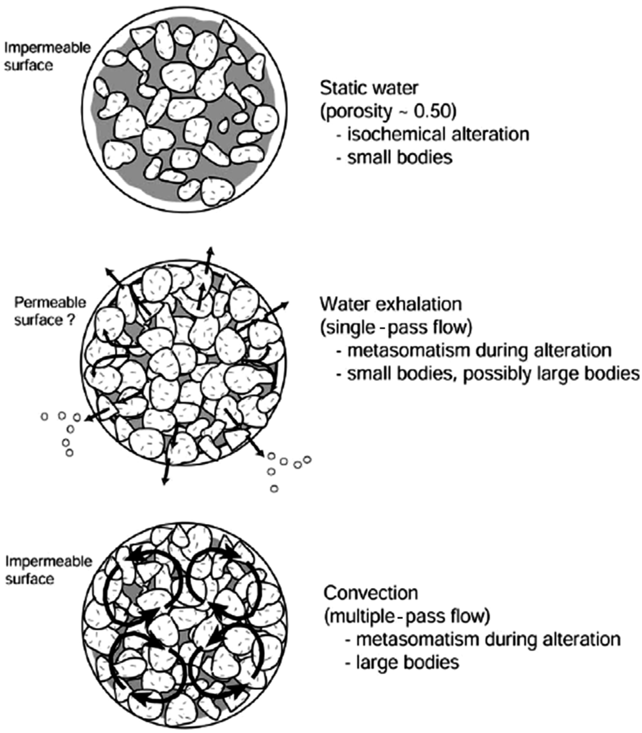

Figure 5.3 Illustration of the different types of heat-transfer regime in small carbonaceous chondrite parent bodies as a function of size, going from about 10 km (top) to > 50 km (bottom). The exact dependence on size is a function of the heat budget, i.e. the time of formation after CAIs (from Young *et al.*, 2003).

compounds mobile at low temperature may be segregated from the core and stored at the interface with the volatile-rich shell, for example in the form of hydrated salts (e.g. Zolotov and Shock, 2001; Kargel *et al.*. 2000). Salts and organics mixed with the rock are also expected to be mobile at low temperature and migrate upward (Castillo-Rogez, 2011). The extent of differentiation of ice from the rock would have determined the amount of ice exposed and/or lost by sublimation upon subsequent impacts. If ice and rock remain intimately mixed, then free ice may not be visible in some bodies today.

Further physical differentiation is possible as a consequence of thermal metamorphism. In volatile-rich asteroids the main expression of thermal metamorphism is the dehydration of phyllosilicates, organics, and other hydrated materials. The extent of metamorphism provides clues to the thermal history of their parent bodies. Various degrees of metamorphism have been observed in CV, CO, and CR meteorites in particular, and CM meteorites to a lesser extent (see Keil (2000) for a review). These meteorites exhibit mineralogies typical of the greenschist facies. For example, chlorite in COs and amphiboles in CVs. Dyl *et al.* (2014) showed that the maximum temperature achieved in CV meteorites was greater than 675 K and up to 825 K in the CV3 Allende meteorite whereas phyllosilicate dehydration starts at temperatures greater than 580 K. It is expected that by the time of dehydration the parent body is depleted in free ice that was mostly consumed in serpentinization reactions or outgassed. Such high temperatures place constraints on the size and accretion time of these parent asteroids. For example, maximum temperatures of ~800 K require accretion no later than approximately 2 Myr post CAI for wet bodies or 2.5 Myr for dryer bodies (Figure 5.2). However, latent heat of dehydration (233 kJ kg^{-1}) makes of that process a heat sink while the high-temperature water released upon dehydration is a very efficient heat vector. As a result, dehydration is a self-regulated process. Water flow is accompanied by redistribution of water loaded in salts and other compounds, a process commonly referred to as metasomatism. Carbonaceous chondrites display multiple signatures of that type of process (see Brearley and Krot (2013) for a review).

Dyl *et al.* (2013) consider that the higher-temperature chondrites could come from large bodies like the Themis family parent body or Ceres. This is unlikely for two reasons. As noted above, abundance of water is likely to regulate thermal increase via latent heat and hydrothermal circulation (e.g. Figure 5.2); also the parent bodies of metamorphosed chondrites are likely to contain little water at the time of dehydration. Instead, Castillo-Rogez and Schmidt (2010) showed for the Themis family parent body (~210-km radius) that temperatures do not increase beyond 350 K, in the most favorable case. Similarly, Neveu *et al.* (2015) showed that temperatures in Ceres' core could remain below 700 K as a consequence of several episodes of hydrothermal circulation following the opening of cooling cracks.

5.5 Differentiation of Large Volatile-rich Asteroids

The original heat budget and size of C-type planetesimals drove the extent of ice melting and ultimately ice/rock differentiation. Castillo-Rogez and Schmidt, (2010) suggested that the thermal evolution of the Themis family parent body likely lead to significant differentiation as well as heterogeneity in the lithologies (i.e. degree of aqueous alteration), similar to the conclusions obtained from the meteorite record (Young *et al.*, 1999; Palguta *et al.*, 2010). This hypothesis is also supported by spectroscopic observations. De León *et al.* (2012) found that members of the Themis family exhibit spectral characteristics linking them to CV3 to CM2 carbonaceous chondrite types, spanning the range from nearly anhydrous rocks to rocks composed of > 60 % hydrous phyllosilicates. These data, and the detection of water ice (Rivkin and Emery, 2010), suggest that the Themis family is the result of disruption of a differentiated and mineralogically heterogeneous parent body.

A similar structure may exist for Ceres: an example of petrological evolution model for Ceres, following the approach described in Castillo-Rogez and McCord (2010), is presented in Figure 5.4. This model assumes that Ceres accreted rapidly from planetesimals following Johansen *et al.* (2015). Besides the hydrothermal processes described in this chapter, other processes are expected to occur in a 940-km ice-rich body, based on our understanding derived from icy satellite observations. First and foremost, large asteroids may have differentiated an icy shell subject to endogenic processes like solid-state convection (Kargel, 1991; McCord and Sotin, 2005). Based on the Europa literature (e.g. Kargel *et al.*, 2000;

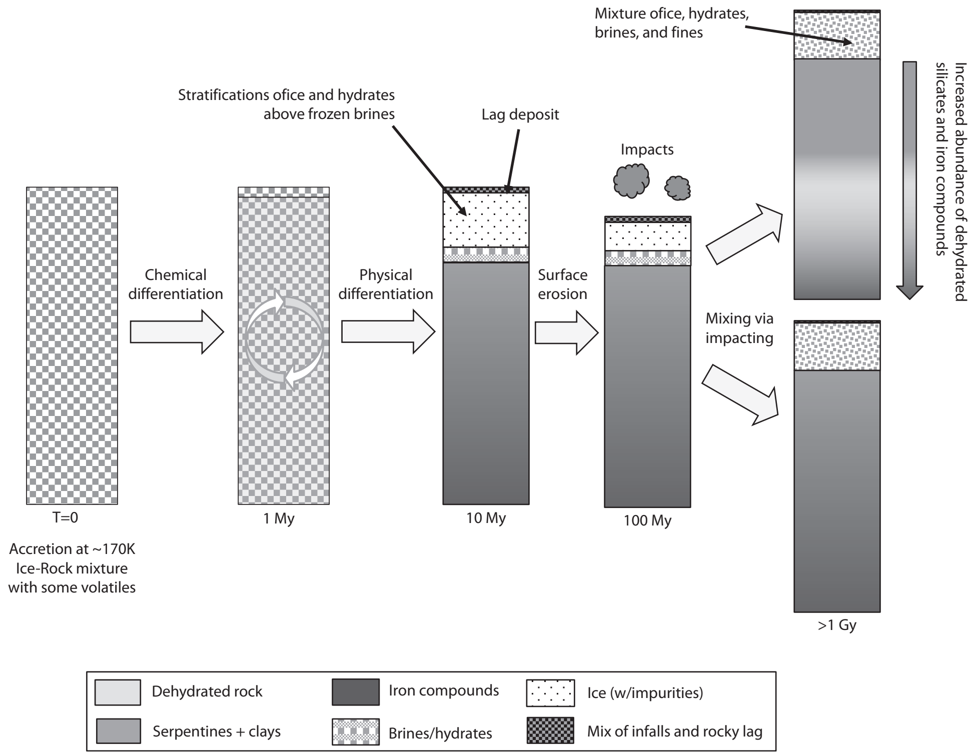

Figure 5.4 Possible physical and chemical evolution models for Ceres assuming a rapid (100 kyr) accretion about 3 Myr after CAIs. Based on thermal modeling, assuming a loss of 20% or 50% of ^{40}K from the rock to the shell, which moderates the extent of thermal metamorphism in the core. The approach follows Castillo-Rogez and McCord (2010) updated with a low thermal conductivity salt layer at the interface between core and shell. A black and white version of this figure will appear in some formats. For the colour version, please refer to the plate section.

Zolotov and Shock, 2001) we infer that Ceres' shell should contain a large variety of salts (hydrated and anhydrous) whose stratification sequence is determined by the composition of the early ocean, temperature, and pressure. However, it is likely that Ceres' original shell has been disturbed by intense impacting, as illustrated by the early images released by the Dawn mission. Kargel (1991) also suggested a salt-rich framework for large volatile-rich asteroids including the possibility for brine-driven cryovolcanism.

Salt compounds can have profound effects on the thermal evolution of asteroidal bodies and precursors. Castillo-Rogez (2011) showed that the mobility of salts and organics at low temperature is likely to result in the migration of these compounds from a chondritic core. Low-thermal-conductivity salts stored at the interface between rock and ice shell present a barrier to heat flowing from the rocky core. Leaching to form salts could have caused a redistribution of radioactive heat sources, especially ^{40}K (e.g. Engel and Lunine, 1994). CI chondrites present the highest abundance of potassium across all types of carbonaceous chondrites, which may be interpreted as a signature of advanced alteration. The rock being deprived of a key heat source, thermal metamorphism of the phyllosilicates is expected to be limited in extent. Leaching of potassium may be more advanced in the presence of ammonium that easily substitutes with potassium in the phyllosilicate structure. While potassium is very mobile and soluble, uranium and thorium species, two other long-term heat sources, saturate at very low concentrations (Shock *et al.*, 1997) and precipitate in the form of ores (similar to the ores found on Earth) mixed rock.

Another process that may occur in a Ceres-sized body is the fractionation of metals from the rock under moderate temperature due to the fact that iron-rich silicates are unstable under hydrothermal environments (see Section 5.4); experimental simulations in conditions relevant to carbonaceous chondrite parent bodies (Jones and Brearley, 2006) and larger ice-rich bodies (Scott *et al.*, 2002) indicate that iron-rich silicates rapidly destabilize and may combine with sulfur (e.g. pyrrhotite FeS) or get oxidized (magnetite, Fe_3O_4). These dense minerals may sink and concentrate in the rocky mantle, although the weak gravity gradient may not be sufficient to promote a clean differentiation of the iron-rich minerals from the silicates as suggested by Scott *et al.* (2002) for Ganymede.

We already have constraints on the degree of differentiation of Ceres from the observation of its global shape obtained with the Hubble Space Telescope (Thomas *et al.*, 2005) and adaptive optics (e.g. Drummond *et al.*, 2014). The shape constitutes direct information on the density profile of a body under the assumption of hydrostatic equilibrium. Despite discrepancies between the absolute dimensions derived by these two studies, they agree that Ceres is only partially differentiated, most likely with a core dominated by hydrated silicates. Rambaux *et al.* (2015)

further suggested that the Drummond *et al.* (2014) observations point to a high-density outer shell that may be evidence for a large fraction of salts and enrichment in clay material (see also Neveu and Desch, 2015).

5.6 Addressing Differentiation at Ceres with the Dawn Mission

At the time this chapter is written the Dawn spacecraft is in orbit around Ceres and starting its extensive mapping of Ceres' morphology, and its elemental and mineralogical composition. A summary of Dawn's science objectives at Ceres and strategies to combine observations anticipated from the four instruments are described in McCord *et al.* (2011). These instruments are: visible and infrared spectrometer for mineralogy, gamma-ray and neutron spectrometer for elemental composition, high-resolution multispectral camera, and radio science subsystem. Combined element counts and mineralogy can provide insight into the early aqueous environment of Ceres. Markers of aqueous activity include alkali and alkaline earth metals (Zolotov and Shock, 2001). The detection of magnesite ($MgCO_3$) and ammoniated phyllosilicates (De Sanctis *et al.*, 2015) are strong indications of past activity and suggest that Dawn will find other products of hydrogeochemistry, such as salt compounds. Detecting markers of origin is a rather more challenging task. It depends on the processes involved in forming Ceres' surface and whether those processes preserved the deep interior composition with fidelity or filtered the species exposed at the surface.

5.7 Summary

This chapter covered the processes driving the evolution of volatile-rich asteroids and the diversity of evolutionary pathways possible for these objects (see Figure 5.5). Observations suggest that the main belt hosts two populations of C-type bodies, one exhibiting a sharp hydration feature that is similar to that in CM chondrites, and one that is believed to correspond to free water ice. Physical and chemical models build on knowledge gained from the study of meteorites, as well as observational constraints. Further input comes from models of the environments in which these objects are believed to have originated. Water plays a key role in governing the thermal and chemical evolution of C-type bodies. Up to a radius of approximately 50 km, asteroid size as well as accretion time determine the thermal structure of the body. Prospects for hydrothermal activity depend on permeability, accretion time, and size. Progressive aqueous alteration of carbonaceous chondrite meteorites may be indicative of the process of water/rock differentiation. However, in these small objects, some of the water and other volatiles

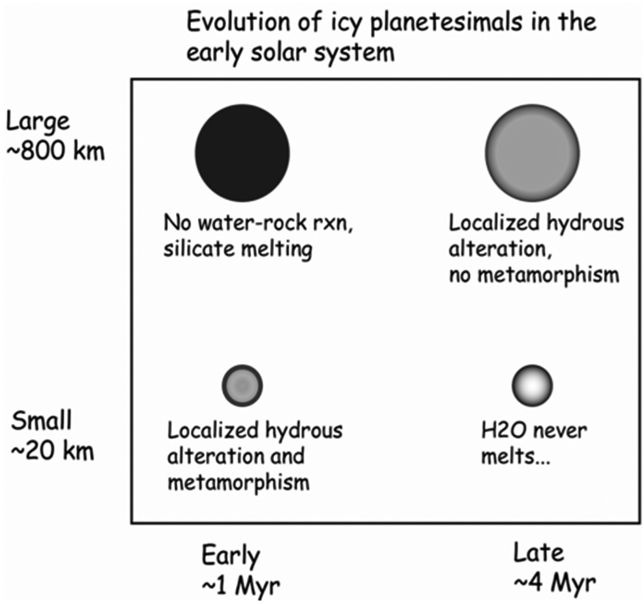

Figure 5.5 Summary of possible internal evolution outcomes for volatile-rich asteroids from aqueous alteration as a function of size and accretion for water–rock reactions. A black and white version of this figure will appear in some formats. For the colour version, please refer to the plate section.

can be lost, as suggested by the redox signature recorded in the mineralogy; and water can be concealed, still mixed with rock.

Icy asteroids discovered so far are large bodies, which is likely an observational bias, but also reflects the greater potential of these objects to retain water ice via efficient hydrothermal convection. Also, these objects are expected to differentiate an ice shell (Castillo-Rogez and Schmidt, 2010) that is easily exposed via small impacts. Convection efficiency also drives the water to rock ratio and thus the chemical evolution of the interior.

The Dawn mission has performed detailed chemical, geological, and geophysical observations of Ceres that will undoubtedly advance our understanding of C-type bodies. Comparisons with observations of large icy satellites offer complementary insights into the processes driving the evolution of large, volatile-rich asteroids. More generally, bridging between icy-satellite science and asteroid science can help leverage best practices from each field.

Acknowledgments

The authors are thankful to Bill McKinnon and an anonymous reviewer for their thorough and valuable comments. This study was carried out at the Jet Propulsion

Laboratory, California Institute of Technology, under contract to NASA. Government sponsorship acknowledged. J. Castillo-Rogez is thankful to Hal Levison for insightful discussions on Ceres' origin. E. Young acknowledges support from the NASA Emerging Worlds program.

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