Conditions for pore water convection within carbonaceous chondrite parent bodies – implications for planetesimal size and heat production

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Abstract

The critical Rayleigh number for convective flow of pore water through a permeable spherical body is derived. The result affords constraints on carbonaceous chondrite planetesimal sizes and rates of heat production. If the chemical compositions of carbonaceous chondrites are taken as evidence against flow of pore water, then the present calculations suggest that the parent bodies were less than ~ 80 km in diameter. The maximum diameter for absence of flow depends in part on the high permeabilities required by estimates of high water/rock ratios in altered carbonaceous chondrites. Pore water would have flowed through parent bodies larger than ~ 120 km in diameter with typical rock-like permeabilities. Convective flow and isochemical alteration are not compatible and our calculations can be used to identify the combinations of parent body size and heat generation consistent with one or the other.
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1. Introduction

Icy bodies in the outermost Solar System (e.g. Trans-Neptunian and Centaur objects) are for the most part dormant today, but there is abundant evidence that ~ 4.5 billion years ago water and other volatiles caused vigorous and sometimes even violent activity within planet precursors [1–6]. These planetary building blocks, or planetesimals, are represented at present by asteroids of the inner Solar System. Residual water ice that may reside deep in the Martian moon Phobos [7] and in 1 Ceres [8], the largest of the asteroids, may be vestiges of the water that was once active in the early Solar System.

Carbonaceous chondrites (hereafter CCs) are vestiges of undifferentiated icy planetesimals. They exhibit clear effects of liquid water–rock interactions. DuFresne and Anders [9] recognized

that an 'internal atmosphere' of water and other volatile species could explain the presence of secondary minerals comprising phyllosilicates, carbonates, sulfates, and oxides in CCs. There has been debate about the source of the water [1] but kinetic arguments suggest that it came from melting ice caused by internal heating (e.g. [10,11]).

The story that CCs might tell about the early Solar System depends largely on our understanding of how water behaved in the parent bodies. At issue is how large and how warm could the bodies have been before buoyancy made pore water flow inevitable. The question is an important one because the ways in which water influenced the isotopic, chemical, and thermal evolution of these planet precursors depends on whether the water was flowing or static [5,12,13].

In this paper we present a new critical Rayleigh number for convection of liquid within the pore space of a permeable spherical body heated from within. Analysis of the stability of a pore fluid in a heat-generating spherical body has not been published previously. Formulations of the critical Rayleigh number for convection based on non-spherical geometries (e.g. slabs) do not account for the low gravity in the center of a spherical body that tends to inhibit convection [12].

Our results show that pore water flow was inevitable for CC parent bodies larger than ~ 120 km in diameter. They suggest further that if chemical similarities between the most altered CCs and the Sun's photosphere are taken as definitive evidence against open-system reactions and fluid flow, then altered CCs must have come from planetesimals that were smaller than ~ 80 km in diameter. Otherwise, the water that caused aqueous alteration of these rocks would have moved and caused dissolution, transport, and precipitation of labile elements. For example, our calculations rule out 1 Ceres as a parent body for altered CCs if these rocks were altered by static water; water occupying pores in a body the size of Ceres would have flowed if heated from within. Conversely, pervasive aqueous alteration occurring throughout a CC parent body would have required vigorous convective flow [12,14]. Our calculations demonstrate that such

bodies, if they existed, must have been larger than ~ 80–120 km in diameter. Convective flow and isochemical alteration are not compatible and our calculations can be used to identify the combinations of size and heat generation consistent with one or the other.

2. Derivation of the critical Rayleigh number for flow through a permeable spherical body

Our calculations are based on a permeable body of rock small enough that self compression can be ignored. We assume that the body produces heat internally at a constant rate described by the parameter A (W kg^{-1}), and that the heat is produced uniformly throughout the body. All of the pore space comprising the volumetric porosity, ϕ, is assumed to be filled with liquid water; our calculations are based on saturated flow. The volumetric flux of water, $\overrightarrow{u}$, is constrained to be 0 at the surface of the body. A zero-flux boundary condition implies a continuous impermeable surface layer that can be envisioned as a veneer of water ice occupying all of the pore volume at the surface.

The acceleration of gravity within the body is $\overrightarrow{g} = \gamma \, \overrightarrow{r}$ where:

$$\gamma = \frac{4}{3}\pi \rho_{\text{bulk}} G \tag{1}$$

and $\overrightarrow{r}$ is the radius vector. In Eq. 1, G is Newton's gravitational constant and ρ_{bulk} is the bulk density of the body, or $(1-\phi)\rho_{\text{r}}+\phi\rho_{\text{f}}$, where ρ_{r} and ρ_{f} are the densities of rock and water, respectively. The temperature gradient due to conduction is given as:

$$\overrightarrow{\nabla} T_0 = -\beta \, \overrightarrow{r} \tag{2}$$

where:

$$\beta = \frac{A}{3(\kappa_{\text{bulk}} C_{\text{p,bulk}})} \tag{3}$$

and the bulk thermal diffusivity κ_{bulk} and bulk isobaric heat capacity $C_{\text{p,bulk}}$ are assumed to be constant (i.e. β is constant).

The gravitational stability of the pore water

depends upon the viscosity of water μ and the interconnectivity of the pores, or permeability k. We express these characteristics of the system using a single constant:

$$K = \frac{\mu}{\rho_f k}. \tag{4}$$

With constant K one can write a linear momentum balance equation that describes the gravitational stability of the pore fluid at each radial position in terms of volumetric fluid flux, dynamic pressure gradient $\overrightarrow{\nabla} P$, and a temperature perturbation relative to conduction Θ (defined as $T - T_o$):

$$\frac{\partial \overrightarrow{u}}{\partial t} = -\frac{1}{\rho_f}\overrightarrow{\nabla} P + \alpha \gamma \overrightarrow{r} \Theta - K\overrightarrow{u}. \tag{5}$$

The thermal expansivity of water, α, is treated as a constant. Thermal perturbations relative to conduction arise when water flows:

$$\frac{\partial \Theta}{\partial t} = \beta \overrightarrow{r} \cdot \overrightarrow{u} + \kappa \nabla^2 \Theta. \tag{6}$$

Heat flow is purely conductive in the absence of flow in our calculations.

The equation of continuity for the fluid phase is obtained by employing the Boussinesq approximation:

$$0 = \overrightarrow{\nabla} \cdot \overrightarrow{u} \tag{7}$$

Eqs. 5–7 describe the convective flux of pore filling water. They can be rewritten in dimensionless form by scaling the position coordinate with the maximum radius of the body r_0 such that $\overrightarrow{r}' = \overrightarrow{r}/r_0$ and defining non-dimensional time, volume flux, pressure, and temperature perturbations as $t' = t\kappa/r_0^2$, $\overrightarrow{u}' = \overrightarrow{u} r_0/\kappa$, $P' = P r_0^2/(\rho_f \kappa^2)$, and $\Theta' = \Theta K/(\kappa\beta)$, respectively. The scaled equations are:

$$\frac{\partial \overrightarrow{u}'}{\partial t'} = -\overrightarrow{\nabla}' P' + R\Theta' \overrightarrow{r}' - Q\overrightarrow{u}' \tag{8}$$

$$\frac{\partial \Theta'}{\partial t'} = Q\overrightarrow{r}' \cdot \overrightarrow{u}' + \nabla'^2 \Theta' \tag{9}$$

$$0 = \overrightarrow{\nabla}' \cdot \overrightarrow{u}'. \tag{10}$$

The dimensionless parameters in Eqs. 8 and 9 are

the Rayleigh number R and the Prandtl number Q given by:

$$R = \frac{\alpha \beta \gamma r_0^4}{K\kappa} \tag{11}$$

$$Q = \frac{K}{\kappa} r_0^2. \tag{12}$$

The gravitational stability of the pore fluid in the permeable spherical body can be evaluated by establishing the critical value for R for which flow occurs subject to the boundary conditions that there is no flow at the surface (i.e. the surface is impermeable) and the surface is isothermal (a simplification representing radiative cooling at the surface). For this purpose the volumetric flux field is expressed in terms of poloidal and toroidal components, v and w, respectively, such that:

$$\overrightarrow{u}' = \overrightarrow{\nabla}' \times \overrightarrow{\nabla}' \times \overrightarrow{r}' v' + \overrightarrow{\nabla}' \times \overrightarrow{r}' w'. \tag{13}$$

Substitution of Eq. 13 into Eq. 8 and application of $\overrightarrow{r}' \cdot \overrightarrow{\nabla}' \times$ to the result yields an equation for the toroidal volumetric flux component:

$$0 = \frac{\partial}{\partial t'}(Lw') + QLw' \tag{14}$$

where:

$$L = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2} \tag{15}$$

and r', θ, and φ are standard spherical coordinates. The solutions to Eq. 14 are of the form $w' \sim \exp(-Qt')$ and thus the toroidal disturbances always decay away such that $w' \to 0$ as $t' \to \infty$. As a result, henceforth we will only be concerned with the poloidal (radial) volumetric fluid flux component v'.

Application of the operator $\overrightarrow{r}' \cdot \overrightarrow{\nabla}' \times \overrightarrow{\nabla}' \times$ to both Eqs. 8 and 9 following substitution of Eq. 13 yields for the poloidal component of flow:

$$-\frac{\partial}{\partial t'}(L\nabla'^2 v') = RL\Theta' + QL\nabla'^2 v' \tag{16}$$

and:

$$\frac{\partial \Theta'}{\partial t'} = QLv' + \nabla'^2 \Theta' \tag{17}$$

where:

$$\nabla'^2 = \left(\frac{2}{r'}\frac{\partial}{\partial r'} + \frac{\partial^2}{\partial r'^2}\right) - \frac{1}{r'^2}L. \qquad (18)$$

The gravitational stability of the pore fluid is described by Eqs. 16 and 17.

At the onset of convection the initial growth of poloidal flow and temperature perturbations can be approximated as $v' \cong \hat{v}'\exp(\delta t')$ and $\Theta' \cong \Theta'\exp(\delta t)$, respectively. Eqs. 16 and 17 then simplify to:

$$0 = \delta\,\nabla'^2 v' + R\Theta' + Q\nabla'^2 v' \qquad (19)$$

and:

$$0 = \delta\,\Theta' - QLv' - \nabla'^2\Theta' \qquad (20)$$

The onset of flow corresponds to $\delta = 0$. Elimination of Θ' by combining Eqs. 19 and 20 then gives:

$$0 = RLv' - \nabla'^4 v' \qquad (21)$$

or:

$$0 = RLv' - \left[\left(\frac{2}{r'}\frac{\partial}{\partial r'} + \frac{\partial^2}{\partial r'^2}\right) - \frac{L}{r'^2}\right]^2 v'. \qquad (22)$$

Solutions of Eq. 22 for the poloidal volumetric flux component v' can be written as the product of the spherical Bessel function and a spherical harmonic, representing the radial and angular (co-latitudinal and longitudinal) parts of the solution, respectively:

$$v' \sim j_l(qr')Y_l^m(\theta\,\varphi) \qquad (23)$$

where l is the positive integer order of the Bessel function and the degree of the spherical harmonic, m is a positive integer order of the spherical harmonic, and q is given by:

$$q = [Rl(l+1)]^{1/4}. \qquad (24)$$

The boundary condition of no flow at the surface of the spherical body where $r' = 1$ requires that q be a zero of the spherical Bessel function. The smallest zero of j_l corresponds to the minimum critical value of the Rayleigh number corresponding to initiation of flow subject to the no-flow boundary condition. This smallest zero for j_l

corresponds to $q = 5.7635$ and $l = 2$. Therefore the critical value for the Rayleigh number is:

$$R_2 = \frac{5.7635^4}{2(2+1)} = 183.91 \qquad (25)$$

and the condition for buoyancy driven flow of pore fluid in a permeable sphere heated internally is:

$$R = \frac{\alpha\beta\gamma r_0^4}{K\kappa} > 183.91. \qquad (26)$$

The poloidal component for this critical mode of flow can be calculated using the critical value for R, yielding:

$$v'_c \sim j_2([6\times183.91]^{1/4}r')\,Y_2^m(\theta,\varphi),\ m = 0,1,2,.... \qquad (27)$$

3. Conditions for convective flow

Solution of the critical Rayleigh number equation for the radius of the body allows investigation of the combinations of sizes and rates of heat production consistent with convective flow of pore water. The relevant equation is obtained from Eq. 26:

$$r_c = \left(183.91\,\frac{\kappa K}{\alpha\beta\gamma}\right)^{1/4} \qquad (28)$$

where r_c is the minimum radius necessary to sustain convection.

Constants for chondritic rock and water used to evaluate the critical radius are given in Table 1. Because r_c depends on the material constants to the one fourth power, there is no need to be concerned with variations in these properties over the temperature ranges pertinent for CC parent bodies (e.g. T varying from ~ 273 K to perhaps 400 or 500 K, for example).

A range of heat production values β and permeabilities k must be considered. We make use of the decay of ^{26}Al as a heat source [15] in what follows, but our calculations are general and can accommodate any other mechanism for internal heating. The heat production term β for the body is expressed in terms of the heat production of Al decay in the rock using:

$$\beta = \frac{\left(6.3\times10^{-3}\frac{^{26}\mathrm{Al}}{^{27}\mathrm{Al}}\right) W/(\mathrm{kg\ rock})(1-\phi)}{3(\kappa_{\mathrm{bulk}}C_{\mathrm{p,bulk}})}. \quad (29)$$

The numerator of the right-hand-side of Eq. 29 is the heat production from decay of $^{26}\mathrm{Al}$ based on 4.003×10^{6} eV per $\beta+$ decay, corresponding to a heat production of 0.0119533 W/(mol $^{26}\mathrm{Al}$) as prescribed by the $^{26}\mathrm{Al}$ decay constant of 0.976 Ma^{-1}, and a chondritic Al concentration of 13.05×10^{-3} kg Al per kg rock [5].

It is possible that the source of heat for such bodies was something other than $^{26}\mathrm{Al}$. Other potential sources of heat include magnetic induction and impacts. Critical evaluation of the different proposed mechanisms for heating CC parent bodies is beyond the scope of this contribution (see review by Rubin [16]) except to note that

extensive aqueous alteration of CC rocks appears to require some internal source of heat. The analysis presented here requires only that the source of internal heat was uniformly distributed and capable of melting water ice throughout much of the parent body. For this reason our results may not be applicable to impact heating [16].

The maximum permeability k for lithified asteroidal rock is on the order of 10^{-13} m^2 [12] while the maximum permeability for unlithified material, e.g. lunar regolith, is $\sim10^{-11}$ m^2 [12]. We used this range of k values in our calculations of K. Although the critical radius is rather insensitive to the porosity, allowing us to present results for a single ϕ, it is crucially dependent on permeability since k can vary by several orders of magnitude.

Fig. 1 shows the range of critical radii for a

Table 1
Symbols, definitions, and values for constants

Symbol	Name and definition	Value
r	Rock subscript	
f	Fluid subscript	
V	Volume	
P	Pressure	
T	Temperature	
α	Isobaric thermal expansivity of water: $1/V(\partial V/\partial T)_P$	2.1×10^{-4} K^{-1}
β	'Thermal' constant: $A/(3(\kappa_{\mathrm{bulk}}C_{\mathrm{p,bulk}}))$	
γ	'Gravity' constant: $4/3\pi\rho_{\mathrm{bulk}}G$	
T_0	Temperature due to conduction	
Θ	Temperature perturbation: $T-T_0$	
κ_{f}	Fluid thermal diffusivity	2×10^{-7} m^2 s^{-1}
κ_{r}	Rock thermal diffusivity	1×10^{-6} m^2 s^{-1}
κ_{bulk}	Bulk thermal diffusivity: $(1-\phi)\kappa_{\mathrm{r}}+\phi\kappa_{\mathrm{f}}$	
K	Viscosity/permeability constant: $\mu/\rho_{\mathrm{f}}k$	
ϕ	Rock porosity: $V_{\mathrm{f}}/(V_{\mathrm{f}}+V_{\mathrm{r}})$	
μ	Fluid viscosity	8.54×10^{-4} Pa s
ρ_{f}	Fluid density	995 kg m^{-3}
ρ_{r}	Rock density	2800 kg m^{-3}
ρ_{bulk}	Bulk density: $(1-\phi)\rho_{\mathrm{r}}+\phi\rho_{\mathrm{f}}$	
$C_{\mathrm{p,r}}$	Rock isobaric heat capacity	1000 J K^{-1} kg^{-1}
$C_{\mathrm{p,f}}$	Fluid isobaric heat capacity	4200 J K^{-1} kg^{-1}
$C_{\mathrm{p,bulk}}$	Bulk isobaric heat capacity: $(1-\phi)C_{\mathrm{p,r}}+\phi C_{\mathrm{p,f}}$	
k	Permeability	
A	Heat production: W kg^{-1}	
$\vec{r}$	Position coordinate	
$\vec{u}$	Darcy (volumetric) flux: m^3 fluid m^{-2} s^{-1}	
G	Newton's gravitational constant	6.7×10^{-11} Nm^2 kg^{-2}
$\vec{g}$	Gravitational acceleration: $-\gamma\vec{r}$	

Values for fluid properties are taken at a temperature of ~300 K. Constants are either median values from a variety of sources or taken directly from the CRC handbook of chemistry and physics.

spherical planetesimal with a total volumetric porosity of 0.20. The lower bound on the heat production rate shown in Fig. 1 coincides with the minimum capable of melting water ice in the bodies [14]. The maximum is based on the assumption that Al in chondritic concentrations had the 'canonical' initial ^{26}Al/^{27}Al for the Solar System as determined by analyses of calcium–aluminum-rich inclusions in CCs. Because upper limits on the sizes of planetesimals correspond to minimum heat production rates, extending the plot to higher rates of heat production would not affect the implications of the calculation as summarized in Fig. 1.

4. Discussion

4.1. Modes of water–rock interaction

There are three end-member modes of water–rock interaction in a planetesimal composed of water and rock and heated from within. The three classes of interaction are summarized in Fig. 2. The first mode is water–rock interaction in the absence of fluid motion. Exchange between mo-
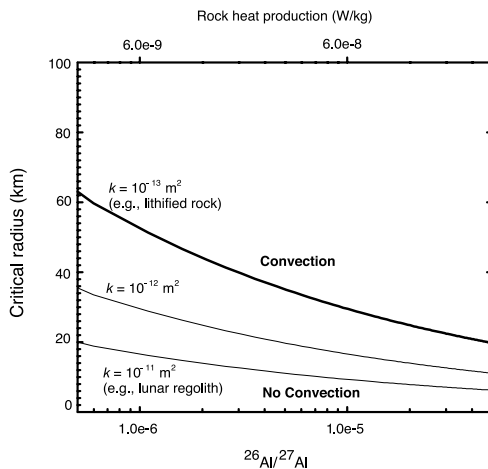

Fig. 1. Plot of minimum radii (r_c) and rates of heat production (in terms of ^{26}Al/^{27}Al, bottom, and W kg^{-1} rock, top) consistent with the onset of convection for a porosity of 0.20. Contours are for different permeabilities k spanning the probable range of values. The upper contour for $k = 1.0 \times 10^{-13}$ m^2 is appropriate for lithified rock while the lower-most contour for $k = 1.0 \times 10^{-11}$ m^2 is appropriate for loosely aggregated rock materials resembling lunar regolith.

tionless liquid water and rock has been invoked to explain oxygen isotope ratios in altered CCs [13,17,18]. The static models for water–rock oxygen exchange require volumetric porosities of 0.38–0.55. These are minimum estimates based on the assumption that every molecule of water present in the pores reacted with the rock. The porosity applies to the scale of individual mineral grains because oxygen exchange occurred at this scale. Such large volumes of water exceed the 0.05–0.29 porosities typical of CC rocks [19,20] and suggest that the CC precursor material was loosely consolidated during alteration and oxygen exchange. In other words, the material could not have been lithified rock. Clayton and Mayeda [13] referred to the porosities required by the static model as comparable to that for 'water-saturated sand'.

The implication of closed-system water–rock reaction is that CI meteorites (the most altered CC rocks) must represent *comet-like* material [21] lithified *subsequent* to alteration. If the CC material was in the form of unbound regolith during alteration, as suggested by the high porosities, then the permeability would have been on the order of 10^{-11} m^2 [12]. Our calculations show that liquid water occupying pores with a permeability of $\sim 10^{-11}$ m^2 could only have remained motionless if the parent bodies were less than ~ 40 km in diameter (20 km radius in Fig. 1). However, our basic state of incompressible rock with pores filled with water is unlikely to be satisfied by mixtures of water and regolith with porosities approaching 0.5. Confining our results to permeabilities applicable to lithified, incompressible rock, it can be stated that the maximum diameter of a *consolidated* body consistent with motionless water in the pore space is ~ 80 km (radius of 40 km in Fig. 1). This figure is based on the assumption that the permeability was high, to accommodate the large porosity, but still lower than that for unconsolidated regolith (approximately 10^{-12} m^2 in Fig. 1). A more precise determination of the appropriate permeability to use in evaluating the likelihood for flow cannot be made because of the lack of an explicit function relating permeability to porosity for CC material in the early Solar System.

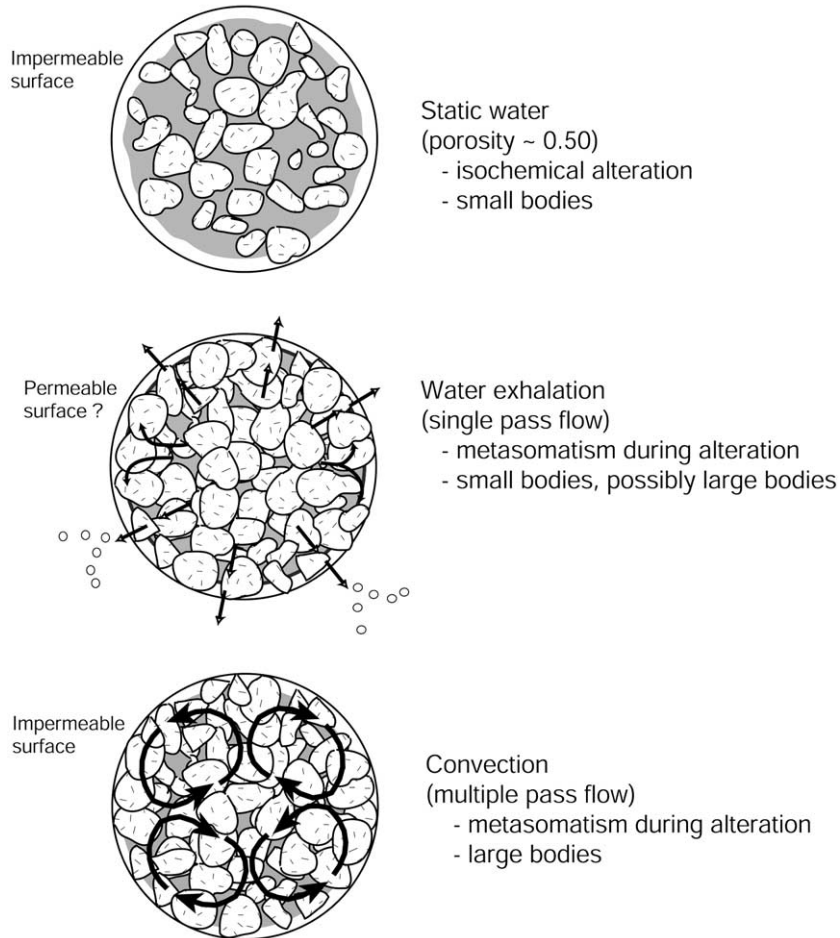# Modes of water-rock interaction in planetesimals

Fig. 2. Schematic illustration of the three end-member modes of water–rock interaction within a planetesimal composed of rock and water. In each illustration white represents frozen water (primarily near the outer surfaces), gray represents liquid water, and black is void space. Rock is represented by the hash pattern. For illustration purposes the diagram shows porosity at a macroscopic (km) scale while the calculations are based on a microscopic (grain-scale) porosity. Arrows show the patterns of pore water flow.

The CC oxygen isotope data have also been interpreted in the context of a model in which water moves outward in a single pass through the body [5,14]. This 'water exhalation' model comprises the second mode of water–rock interaction. It is analogous to the migration of liquid water from higher to lower temperatures in frozen and partially frozen soils [22]. A front of liquid water moves through the body as ice melts pro-gressively from the center outward. Water flows in this case as a result of pressure gradients imposed by in situ melting of ice at locations determined by the outward propagation of the 273 K isotherm through the body [14]. Migrating fronts of liquid water like those in the exhalation model have been observed in frozen soils in the laboratory [23]. The water comprising the moving front either exhales from the body into space through a

permeable surface or refreezes in vacant pore space near the cold surface of the body where it will eventually sublime [8].

Fig. 1 provides no constraints on the sizes and rates of heat production for bodies experiencing flow by the water exhalation process because in this case the flow does not rely on buoyancy. Constraints on water exhalation in terms of heating rates and size have been described elsewhere [14], but the process involves flow of both liquid and gas (unsaturated two phase flow) and is therefore difficult to describe with a simple parameterization. Nevertheless, a simple calculation can be used to gain some insight into the efficacy of water exhalation. By comparing the temperature-dependent equilibrium vapor pressure of water with hydrostatic pressure in a microgravity environment one can show that a column of water 40 km high would be supported by water vapor pressure alone at 400 K. The column height supported by vapor pressure drops to about 5 km at a lower T of 280 K. This simple calculation suggests that exhalative flow may occur in bodies too small to sustain convective flow. Exhalation may be less efficient for objects with diameters greater than approximately 80 km, although thermocapillary forces and non-conductive heat transfer, both of which contribute to the potential for flow in microgravity environments [24], are not accounted for in this calculation. The essential point is that exhalation could have driven pore water migration in bodies too small for convection. In other words, absence of convection does not guarantee absence of flow.

The third mode of water–rock interaction is convection bounded by an impermeable surface. Fig. 1 shows that convective flow of pore water is expected if CC parent bodies were larger than about 120 km in diameter (based on minimum estimates for rock permeability). Liquid pore water would not have been static in CC parent bodies larger than $\sim$120 km in diameter.

4.2. Implications

Two of the three end-member water–rock interaction modes involve movement of pore water. Whether water was moving or not has profound implications for the way in which isotopic and chemical compositions of CC rocks are interpreted. For example, convecting fluids would have drastically altered the thermal evolution of icy bodies, in some cases resulting in differences in peak temperatures of 200° relative to bodies with static fluids [12], and moving fluids could have resulted in heterogeneous CC parent bodies in which aqueous alteration was localized [5]. Whole-sale alteration of the parent body, on the other hand, would have required not just fluid flow but vigorous convection [12,25].

Perhaps the final arbiter for whether or not water flowed within CC parent bodies will be the interpretation of their chemical compositions. In terrestrial settings, flow of water through permeable rock, even at relatively low temperatures associated with groundwater, results in substantial changes in rock chemistry over meter to kilometer length scales and geologically brief time intervals [26–30]. It is reasonable to assume that protracted flow of water within planetesimals would have caused similar changes in chemical composition as different minerals dissolved and precipitated.

The chemical compositions of CCs are not generally interpreted as being affected by reactions with water. Rather, they can be understood in terms of the relative volatilities of the elements in the early solar nebula [31]. The highly altered CI chondrites have relative elemental abundances of rock-forming elements similar to those of the Sun's photosphere. The less altered CO and CV chondrites are depleted in alkali metals, zinc, and other moderately volatile elements relative to CIs and the photosphere. Plots of normalized elemental abundances vs. 50% condensation temperatures for the elements comprising CC rocks show correlations that are taken as evidence for volatility control. The inference is that differences in elemental abundances between CC rocks were caused by different degrees of partial condensation and partial evaporation of precursor mineral material in the early solar nebula.

However, it turns out that those elements that are most refractory are also least soluble in hydrothermal systems (e.g. Al) while those elements that are most volatile are also the most soluble (e.g. K) in hydrothermal systems. This often over-

looked correspondence between volatility and solubility makes it difficult to distinguish a priori between the chemical effects of evaporation–condensation in the early solar nebula and aqueous alteration that occurred later. Calcium is a rare exception because it is refractory but also soluble in waters reacted with terrestrial rocks containing feldspar. But calcium is likely to be much less soluble in waters reacted with chondrites in which clinopyroxene, rather than feldspar, is a primary host for Ca.

Whatever the reason, the chemical compositions of CC rocks are well correlated with degree of alteration. As an example, Fig. 3 shows that there is a correlation between Mn/Al, representing the concentration of a relatively labile element normalized to a refractory and insoluble element, and degree of alteration among CM chondrites. The correlations within individual CC groups, including the CVs [32], CMs (Fig. 3), and CRs (not shown), persist between groups; there are systematic chemical trends from least altered (e.g. CV) to most altered (CI) CC rocks (Fig. 4).

Correlations between elements comprising different CC rocks are also correlated in analogous fashion in reactive aqueous fluids. This is true even for elements that are thought of as being chemically different. The two moderately volatile elements Fe and K, with similar 50% condensation temperatures of 1337 K and 1000 K at 10^{-4}

Fig. 4. Top: K/Al (mass) vs. Fe/Al (mass) for individual CV, CM, and CI chondrites showing that the intragroup trends exhibited by these rocks (e.g. Fig. 3) are consistent with the intergroup trends. CVs include Vigarano (reduced group, least altered), Allende, Bali, and Mokoia (oxidized group, most altered). CIs comprise Alais and Orgueil. The CMs are the same as in Fig. 3. Data represent means for each meteorite [36]. Bottom: plot of dissolved K vs. dissolved Fe for water reacted with deep sea sediments [29].

bar [33], respectively, illustrate the point (Fig. 4). Because Fe is siderophile and K is lithophile it is normally assumed that these elements are correlated in CCs because they are similar in volatility, the only apparent link between them being their volatility. But Fig. 4 shows that these elements are also correlated in hydrothermal waters. At higher temperatures (> 300 K) both Fe and K are readily leached from sediments (and rocks) while at lower temperatures (near 273 K) both elements cease to be labile. As a consequence, reactions between moving water and rock at higher temperatures will deplete rocks in both Fe and K (flow is necessary to carry away the labile elements) while reactions between rock and flowing water at lower
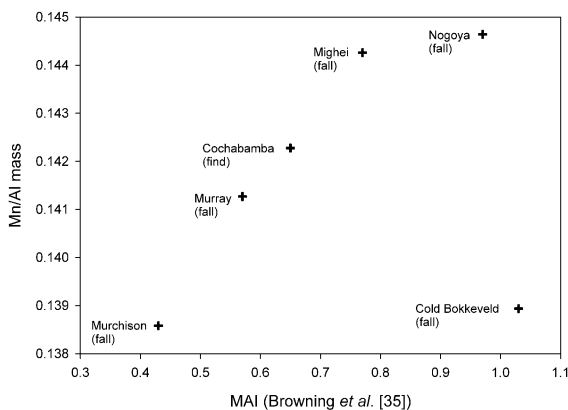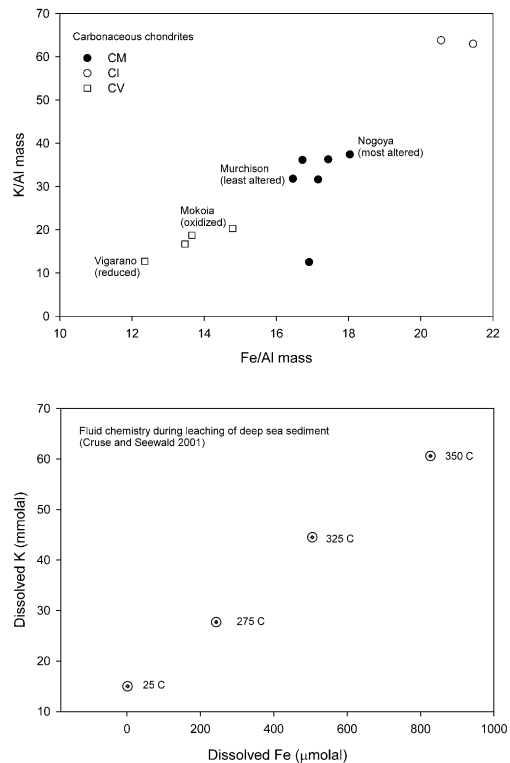

Fig. 3. Plot of Mn/Al (mass) vs. the mineralogical alteration index, or MAI, proposed by Browning et al. [35] for CM chondrites. Data represent averages for each meteorite and were taken from Kallemeyn and Wasson [36].

temperatures will not. The end result will be a correlation between concentrations of Fe and K in rocks reacted with water at different temperatures and over different time spans. Despite common practice [34], correlations between elements with comparable volatilities but different chemical affinities cannot alone be used as evidence against the possibility that the chemical compositions of CCs were affected by aqueous alteration.

If the trends in Figs. 3 and 4 are indicative of metasomatism (elements moving in response to mineral solubility in a flow system) then aqueous alteration of CC rocks was not isochemical and flow of reactive water through pores could have occurred during alteration. In this case the restriction on the maximum size of altered CC parent bodies imposed by our calculations can be relaxed. Alternatively, if the trends in Figs. 3 and 4 are not the result of open-system alteration, then aqueously altered CC parent bodies must have been small (< 80 km) and the correlations between chemistry and aqueous alteration represent a phenomenon in the early solar nebula that is yet to be identified.

5. Conclusions

Pore water within CC parent bodies larger than ~120 km in diameter would have flowed in response to gravitational instability. Absence of flow requires that the parent bodies of the most altered CCs were smaller than approximately 80 km in diameter. Flow of water in the absence of convection could have occurred in bodies with diameters < ~80 km but the details of this phenomenon, if it occurred, are not yet well understood.

If the chemical compositions of CCs are taken as evidence against flow of pore water, then the aqueously altered CCs evolved in small parent bodies.

Acknowledgements

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