

## 論文の内容の要旨

### 論文題目

# **Formation and evolution of hydrous asteroids: constraints from Mn-Cr dating and stable isotopes of meteoritic carbonates**

(含水小惑星の形成と進化：隕石中の炭酸塩の Mn-Cr 年代測定および安定同位体からの制約)

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In the present work, I studied primitive meteorites with secondary alteration products, and investigated formation and evolution of hydrous asteroids where liquid water once existed. Especially, my study focused on the formation age of carbonates, the accretion time and thermal history of hydrous asteroids, and the material evolution during asteroidal alteration.

Carbonaceous chondrites such as CMs and CIs show the evidence for pervasive aqueous alteration, and contain various secondary alteration products which formed during the alteration. Carbonates are one of such alteration products. Because the carbonates contain manganese as a trace element,  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  radiometric ages can be determined for them using secondary ion mass spectrometry (SIMS). However, an accurate measurement of carbonate ages by SIMS is difficult because it is impossible to determine Mn/Cr ratios unless a suitable and matrix-matched carbonate standard material is prepared. Previous studies used silicate minerals as alternative standards, because a suitable carbonate standard is not available in natural terrestrial environments. This use would lead to systematic errors on the  $^{55}\text{Mn}/^{52}\text{Cr}$  of meteoritic carbonates and their ages (de Leuw et al., 2009 and references therein). Actually, previous estimates of carbonate ages include extremely old ages up to ~4571 Ma, which predates the first solids in the solar system (calcium-aluminum-rich

inclusions; CAIs). Unless accurate carbonate ages are obtained, it is impossible to discuss formation and evolution of hydrous asteroids.

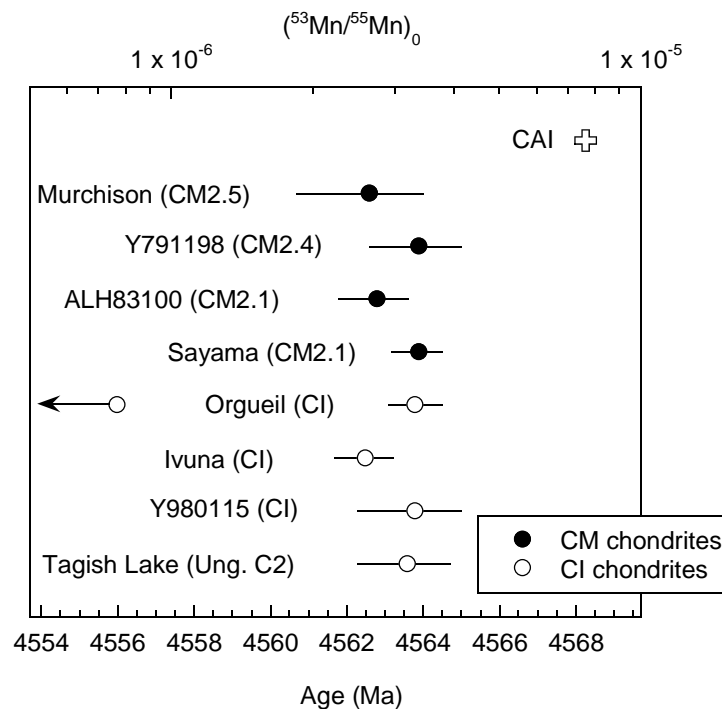
To overcome this problem, I produced a synthetic calcite standard doped with Mn and Cr, and established a SIMS technique for an accurate determination of Mn/Cr for meteoritic carbonates. Using the SIMS technique, I have performed the  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  dating of the carbonates in four CM chondrites (Murchison CM 2.5, Y791198 CM 2.4, ALH83100 CM 2.1 and Sayama CM 2.1) with a NanoSIMS 50. The CM chondrites studied here suffered from aqueous alteration to various degrees, and one would expect that the carbonates in more-altered chondrites (dolomite in ALH83100 and Sayama) are younger than those in less-altered ones (calcite in Murchison and Y791198). However, the carbonate ages of the four CM chondrites are identical within the errors, that is, the initial  $(^{53}\text{Mn}/^{55}\text{Mn})_0$  ratios of the carbonates correspond to absolute ages of 4562.6 (+1.4/-1.9) Ma for Murchison, 4563.9 (+1.1/-1.3) Ma for Y791198, 4562.8 (+0.8/-1.0) Ma for ALH83100 and 4563.9 (+0.6-0.7) Ma for Sayama (errors are  $2\sigma$ ) (Fig. 1). Therefore, I can define the formation age of the CM carbonates and conclude that they precipitated at  $\sim 4563.4$  Ma (4.8 Myr after CAI formation). The Mn-Cr ages of carbonates obtained here are younger than previous estimates. The problem of the very early formation of carbonates as old as CAIs is solved by use of the carbonate standard which is suitable for the Mn-Cr dating by SIMS. On the basis of the formation age of the carbonates, I simulated the thermal history of the CM chondrite parent body by a numerical calculation. According to the calculation, I found that the CM chondrite parent body is likely to have accreted at  $\sim 3.5$  Myr after CAI formation (Fig.2). Based on the present result, I conclude that the CM parent body accreted later than the parent bodies of achondrites and metamorphosed chondrites. This conclusion strongly suggests that the accretion time of asteroids is an important controlling factor of the asteroidal metamorphism and/or melting, and the heat source for the metamorphism is dominated by  $^{26}\text{Al}$  decay.

Then I have expanded the Mn-Cr study to carbonates in CI chondrites (dolomites in the Orgueil, Ivuna and Y980115 CI chondrites and an ungrouped C2 chondrite Tagish Lake). Their absolute ages are estimated to be 4563.8 (+0.7/-0.7) Ma for Orgueil, 4562.5 (+0.7/-0.8) Ma for Ivuna, 4563.8 (+1.2/-1.5) Ma for Y980115 and 4563.5 (+1.1/-1.3) Ma for Tagish Lake (errors are  $2\sigma$ ) (Fig. 1). It should be noted that the dolomite ages of the CI chondrites and Tagish Lake are quite similar to the CM carbonate ages (4.4 to 5.7 Myr after the birth of the solar system). The similar carbonate ages strongly suggest that similar physical and chemical conditions for the dolomite formation (e.g., similar temperatures) were attained at similar times in different hydrous asteroids. According to the calculation of the thermal history, I found that dolomite should have precipitated at  $\sim 3.5$  to 6 Myr after CAI formation as long as one considers  $^{26}\text{Al}$  as the dominant heat source for asteroidal alteration.

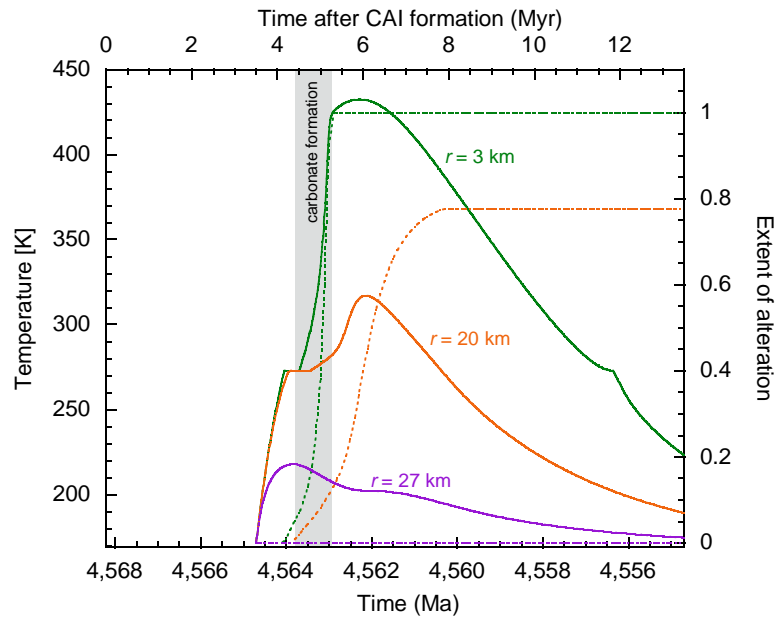
Also, I have measured carbon-isotopic compositions of the Murchison calcite. Carbonates in

carbonaceous chondrites are generally known to have high  $\delta^{13}\text{C}$  values, however, the origin of the heavy carbon remains controversial (Grady et al., 1988). The major reservoirs of carbon in carbonaceous chondrites are carbonates and organic matter, and hence, investigation of C-isotopic evolution during asteroidal alteration could provide a better understanding of the interaction between water and organics.

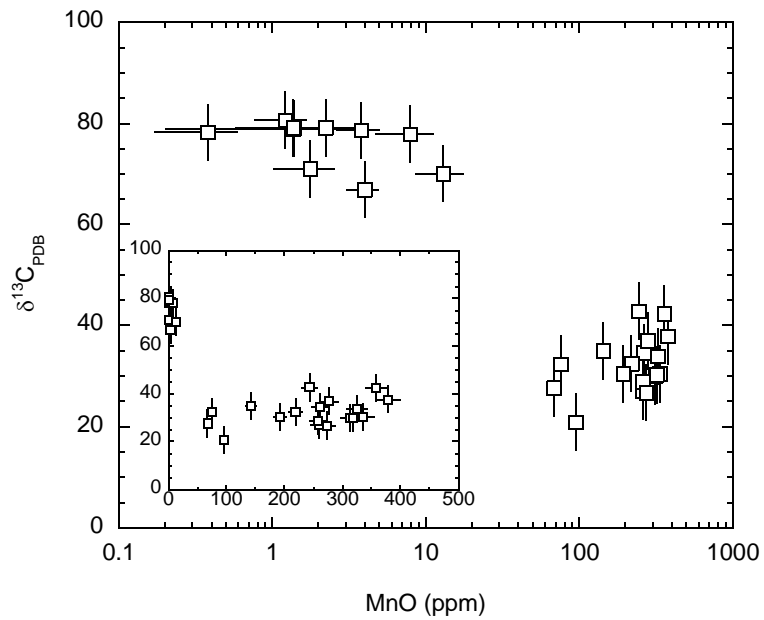
In the present work, I have performed in-situ analyses of cathode-luminescence intensities, C-isotopic compositions and minor-element concentrations. I developed a SIMS method to measure C-isotopic compositions with a fine ( $\sim 5 \mu\text{m}$ ) spatial resolution, and found inter- and intra-grain heterogeneities of  $\delta^{13}\text{C}_{\text{PDB}}$  ranging from  $\sim 20$  to  $80\%$  in the Murchison calcite. Moreover, the  $\delta^{13}\text{C}$  values of the calcites show a bimodal distribution corresponding to their morphology and minor-element concentration (Fig. 3). The  $\delta^{13}\text{C}$  value of  $\sim 80\%$  is among the highest for CM carbonates, and such a significant isotopic heterogeneity has never been recognized. This variation in  $\delta^{13}\text{C}$  can be considered as evidence for C-isotopic evolution in the early stage of aqueous alteration. According to the cathode-luminescence characteristics and minor-element concentrations, the calcites with high  $\delta^{13}\text{C}$  precipitated prior to those with low  $\delta^{13}\text{C}$ , and the alteration fluid was initially rich in  $^{13}\text{C}$ . As a possible source for the primarily heavy carbon, I suggest very  $^{13}\text{C}$ -rich components found in meteoritic organic matter. A preferential destruction of such  $^{13}\text{C}$ -rich components could have provided the primarily heavy carbon.



**Fig. 1.** Mn-Cr ages of carbonates in CI and CM chondrites.



**Fig. 2.** Thermal history of the CM chondrite parent body.



**Fig. 3.** Carbon-isotopic compositions and Mn concentrations of the Murchison calcite.