Aqueous activity on chondrite parent asteroids

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Outline

- Chondritic meteorites & their classification
- Aqueously-formed minerals & conditions (temperature & water/rock ratio) of chondrite aqueous alteration
- Dating of aqueous alteration
 - ⁵³Mn-⁵³Cr ages of fayalite in CV, CO, & ordinary chondrites
 - ⁵³Mn-⁵³Cr ages of carbonates in CI, CM, & CR chondrites
- Oxygen-isotope compositions of aqueously-formed minerals & estimated D/H values of asteroidal water: Constraints on the origin of asteroidal water



Major chondritic components: Chondrules, matrix, & CAIs



chondrules + Fe,Ni-metal (30–98 vol%)

- Ca,Al-rich inclusions (CAIs) (<1-5 vol%)
- matrix (<2–70 vol%)

In contrast to ISM, chondrites are dominated by crystalline material \rightarrow thermal processing in PPD

Classification of chondritic meteorites (chondrites)

• based on mineralogy, petrography, bulk oxygen-isotope & chemical compositions, chondrites are divided into 15 groups & 3 major classes

		Car	<u>bona</u>	<u>сеои</u>	<u>S</u>			<u>Enstatite</u>	<u>Ordinary</u>	Other
CI	CM	CR	CV	CK	CO	CB	CH	EH EL	H L LL	K R
1	2-3	2-3	3	3-6	3	3	3	3-6	3-6	3 3-6

• letters designating groups refer to a typical meteorite in a group:

- CI Ivuna type
- CM Mighei type
- $C\underline{R} \underline{Renazzo}$ type
- CV Vigarano type
- CK Karoonda type
- CO Ornans type
- CB Bencubbin type

some chondrites are ungrouped (e.g., Tagish Lake)

• petrologic types: 1 2 3 4 5 6 aqueous alteration thermal metamorphism



variations in mineralogy, sizes & abundances of chondritic components 0 among the groups

Bulk chemical compositions



• chondrite groups have distinct bulk chemical compositions

Bulk oxygen-isotope compositions



 $\delta^{17,18}$ O = [(^{17,18}O/¹⁶O)_{sample}/(^{17,18}O/¹⁶O)_{SMOW} - 1] × 1000, Standard Mean Ocean Water chondrite groups occupy distinct regions on three-oxygen isotope diagram chondrite O-isotope compositions very different from Sun, $\delta^{17,18}$ O $\approx -50\%$

Bulk oxygen-isotope compositions



 $\delta^{17,18}O = [(^{17,18}O/^{16}O)_{\text{sample}}/(^{17,18}O/^{16}O)_{\text{SMOW}} - 1] \times 1000, \text{ Standard Mean Ocean Water}$

chondrite groups occupy distinct regions on three-oxygen isotope diagram chondrite O-isotope compositions very different from Sun, $\delta^{17,18}O \approx -60\%$

Aqueously-altered chondrites



Aqueously produced minerals in CI, CM, & CR chondrites

- CM, CI & CR chondrites experienced low-T (< 100°C) aqueous alteration at high water/rock (W/R) ratio (0.2–1)
- phyllosilicates
 - serpentine
 - cronstedtite
- tochilinite
- carbonates
 - calcite
 - dolomite
 - breunnerite
 - aragonite
- sulfides
 - troilite
 - pyrrhotite
 - pentlandite
- magnetitesulfatescohenite

 $Mg_{3}Si_{2}O_{5}(OH)_{4}$ F $e_{2}^{2+}Fe^{3+}(Si,Fe^{3+})_{2}O_{5}(OH)_{4}$ 2[Fe,Mg,Cu,Ni[])S•1.57-1.85[(Mg,Fe,Ni,Al,Ca)(OH)_{2}]

CaCO₃ (trigonal) (Ca,Mg,Fe,Mn)CO₃ Mg(Fe,Mn)(CO₃)₂ CaCO₃ (hexagonal)

FeS Fe_{1-x}S (Fe,Ni)₉S₈ Fe₃O₄ (Mg,Na,Ca,Ni)SO₄•nH₂O (Fe,Ni)₃C

Mineralogy & petrography of Sutter's Mill (CM)



Mineralogy & petrography of Sutter's Mill (CM)



pseudomorphic replacement of chondrules by phyllosilicates & presence of carbonate veins are clear evidence for *in situ* aqueous alteration This document is provided by JA

Aqueously produced minerals in ordinary chondrites

- ordinary chondrites experienced aqueous alteration at ~100–200°C & low W/R ratio (<0.2) & were subsequently metamorphosed at higher temperature
- saponite
- magnetite
- fayalite
- Fe,Ni-carbides
- pentlandite
- Ni-rich metal
- nepheline

 $\frac{\text{Ca}_{0.25}(\text{Mg},\text{Fe})_3(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}}{\text{Fe}_3\text{O}_4}$ $\frac{\text{Fe}_2\text{SiO}_4}{(\text{Fe},\text{Ni})_3\text{C}, (\text{Fe},\text{Ni})_{23}\text{C}_6}$ $(\text{Fe},\text{Ni})_9\text{S}_8$ $\text{FeNi}, \text{FeNi}_3$ NaAlSiO_4



Aqueously produced minerals in ordinary chondrites



in situ growth of fayalite & magnetite

Aqueously produced minerals in CV & CO chondrites

• CV & CO chondrites experienced aqueous alteration ~100–200°C & low W/R ratio (<0.2) & were subsequently metamorphosed at higher temperature

Fe₂SiO₄

 Fe_3O_4

- fayalite
- magnetite
- phyllosilicates
- pentlandite
- hedenbergite
- andradite
- Fe,Ni-carbides
- Ni-rich metal
- nepheline
- anorthite
- corundum
- forsterite
- grossular
- kushiroite
- monticellite
- kirschsteinite
- Na-melilite
- sodalite
- wadalite
 - wollastonite

- $(Fe,Ni)_{9}S_{8}$ CaFeSi₂O₆ $Ca_3Fe_2Si_3O_{12}$ $(Fe,Ni)_{3}C$, $(Fe,Ni)_{23}C_{6}$ FeNi, FeNi₃ NaAlSiO₄ CaAl₂Si₂O₈ Al_2O_3 Mg_2SiO_4 $Ca_3Al_2Si_3O_{12}$ CaAl₂SiO₆ CaMgSiO₄ CaFeSiO₄ $(CaNa)_{2}(Al,Mg)[(AlSi)_{2}O_{7}]$ $Na_8Al_6Si_6O_{24}Cl_{12}$ $Ca_6(Al,Si,Mg)_7O_{16}Cl_3$ CaSiO₃
- Kaba (CV3)



Aqueously produced minerals in CV & CO chondrites



fayalite associated with magnetite, hedenbergite, kirschsteinite, & Fe,Nisulfides in hydrated matrices; no corrosion by phyllosilicates

Aqueously produced minerals in CV & CO chondrites



fayalite-hedenbergite-magnetite veins, indicative for *in situ* growth

Isotope measurements of aqueously-altered meteorites by SIMS

Dating of aqueous alteration using Mn-Cr isotope system

53
Mn $\rightarrow ^{53}$ Cr, $t_{1/2} \sim 3.7$ Myr

• ⁵³Mn was present & uniformly distributed in the early Solar System

• can be used for chronology of the early Solar System processes, including aqueous alteration

⁵³Mn-⁵³Cr is a relative chronometer

 $\Delta t_{\text{slope-1}-\text{slope-2}} = 1/\lambda \times \ln[({}^{53}\text{Mn}/{}^{55}\text{Mn})_{\text{slope-1}}/({}^{53}\text{Mn}/{}^{55}\text{Mn})_{\text{slope-2}}], \text{ where } \lambda \text{ is a decay constant of } {}^{53}\text{Mn} (= \ln(2)/t_{1/2})$

⁵³Mn-⁵³Cr chronology can be anchored to absolute U-Pb chronology, e.g., D'Orbigny angrite with $({}^{53}Mn/{}^{55}Mn)_0 = (3.24 \pm 0.04) \times 10^{-6}$ & U-corrected Pb-Pb age of 4563.4±0.3 Ma (*Glavin et al. 2008; Brennecka et al. 2012*) & compared with U-corrected Pb-Pb ages of CV CAIs 4567.30±0.16 Ma (*Connelly et al. 2012*)

Dating aqueous alteration: ⁵³Mn-⁵³Cr ages of carbonates & fayalite

- Relative Sensitivity Factor (RSF) = $({}^{55}Mn^{+}/{}^{53}Cr^{+})_{SIMS} / ({}^{55}Mn/{}^{53}Cr)_{EPMA}$; it depends on a number of factors (*Hoppe et al. 2007; Sugiura et al. 2010; McKibbin et al. 2013; Doyle et al. 2013*)
 - mineral composition
 - analytical conditions
- proper standards for Mn-Cr isotope measurements of carbonates & fayalite are required
- San Carlos olivine (Fa₁₀) was used a standard for Fa_{95-100} & carbonates
 - Mn- & Cr-bearing calcite (Sugiura et al. 2010)
 - Mn- & Cr-bearing fayalite (Doyle et al. 2013)

Mn-Cr relative sensitivity factors (RSF) in ferromagnesian olivine

• San Carlos olivine is not a proper standard for ⁵³Mn-⁵³Cr systematics of fayalite

⁵³Mn-⁵³Cr dating of fayalite formation: RSF effect

• $7.9^{+0.6}_{-0.5}$ Myr after CV CAIs

• $5.1^{+0.5}_{-0.4}$ Myr after CV CAIs

• San Carlos olivine is not a proper standard for Mn-Cr isotope measurements of fayalite $\rightarrow {}^{53}$ Mn- 53 Cr ages of fayalite published prior to 2013 are incorrect (*Hutcheon et al. 1998; Krot et al. 2000; Hua et al. 2005; Jogo et al. 2009 etc.*)

⁵³Mn-⁵³Cr dating of fayalite formation in CO & CO-like chondrites

$5.1^{+0.5}_{-0.4}$ Myr after CV CAIs

• $5.5^{+1.5}_{-1.2}$ Myr after CV CAIs

⁵³Mn-⁵³Cr dating of fayalite formation in CV & ordinary chondrites

 $4.2^{+0.8}_{-0.7}$ Myr after CV CAIs

• $2.4^{+1.8}_{-1.3}$ Myr after CV CAIs

Synthetic Mn- & Cr-bearing calcite (N. Sugiura, U. Tokyo)

Synthetic Mn- & Cr-bearing calcite (N. Sugiura, U. Tokyo)

Synthetic Mn- & Cr-bearing calcite (N. Sugiura, U. Tokyo)

Mn-Cr relative sensitivity factors in SC olivine vs. synthetic calcite

Courtesy of C. Jilly

- ⁵³Mn-⁵³Cr dating of carbonates by SIMS requires proper standards
- ⁵³Mn-⁵³Cr ages of carbonates published prior to 2012 are incorrect
- ⁵³Mn-⁵³Cr ages of dolomite [*Fujiya et al. (2012, 2013)*] were measured using calcite standard & should be considered as preliminary

⁵³Mn-⁵³Cr dating of dolomite in CO chondrites

• $3.5_{-0.8}^{+0.7}$ Myr after CV CAIs

⁵³Mn-⁵³Cr ages of fayalite & carbonates in UOCs & CCs

Part IV. Oxygen-isotope compositions of aqueously-formed minerals & estimated D/H ratios of asteroidal water: Constraints on the origin of asteroidal water

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O-isotope compositions of fayalite & magnetite in MAC 88107

Krot et al. (2013)

• fa & mgt along slope-0.5 line

• $\Delta^{17}O \sim -1.6 \pm 0.9\%$, where $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$

• chondrule *ol*

- type I: Δ^{17} O ~ -6.9 $\pm 1.8\%$
- type II: $\Delta^{17}O = -3.2 \pm 0.8\%$

• *fa* & *mgt* are in oxygen isotopic disequilibrium with chondrule *ol*

O-isotope compositions of fayalite & magnetite in CO chondrites

- *fa* & *mgt* along slope-0.5 line
 - $\Delta^{17}O \sim -0.3 \pm 0.4\%$
- chondrule *ol*
 - type I: $\Delta^{17}O \sim -5\%$
 - type II: $\Delta^{17}O \sim -2\%$
- fa & mgt are in oxygen isotopic disequilibrium with chondrule of

O-isotope compositions of fayalite & magnetite in UOCs

Kita et al. (2010); Krot et al. (2012); Doyle et al. (2013)

- *fa* & *mgt* along slope-0.5 line
 - $\Delta^{17}O \sim +4.5\%_{0}$
- chondrule silicates
 - *ol*: Δ^{17} O ~ +0.6±0.5‰
 - *mes*: Δ^{17} O +1 to +4.5‰
- *fa* & *mgt* in oxygen isotopic disequilibrium with chondrule *ol*
- chondrule *mes* experienced O-isotope exchange with a fluid

Oxygen-isotope compositions of aqueous solutions

Clayton & Mayeda (1999); Krot et al. (2013); Doyle et al. (2013)

• in UOC, CV & CO:

- Δ^{17} O of *fa* & *mgt* differ from chondrule silicates & bulk chondrites
- plot along slope-0.5 line

•
$$\Delta^{17}O_{fa \& mgt} = \Delta^{17}O_{fluid}$$

 \rightarrow fluid shows no evidence for exchange with ¹⁶O-enriched anhydrous silicates

Oxygen-isotope compositions of aqueous solutions & water ices

Clayton & Mayeda (1999), Rowe et al. (1994), Benedix et al. (2003) Leshin et al. (1997, 2011) increasing degree of aqueous alteration

 Δ^{17} O of *fa* & *mgt* in ordinary, CO & CV, & of *mgt* & *carb* in CI & CM chondrotes can be used as a <u>proxy</u>* for Δ^{17} O values of water ices that accreted into their parent bodies

* Δ^{17} O of water prior to formation of *mgt*, *fa*, & *carb* is not known

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Sources of water ices on chondrite asteroids

• in the CO self-shielding models (Yurimoto & Kuramoto, 2004; Lyons & Young, 2005), water ices in the outer disk is highly ¹⁷O & ¹⁸O-enriched relative to gas & solids in inner disk

- iron oxides in Acfer 094 (ungrouped): $\Delta^{17}O \sim +90\%$ (Sakamoto et al., 2007)
- grains in IOM from Y-793495 (CR): $\Delta^{17}O \sim +500\%$ (Hashizume et al., 2007)

• water ices on OC & CC asteroids were not anomalously ¹⁷O- & ¹⁸O-enriched, suggesting a local origin

Sources of water ices on chondrite asteroids

Hashizume et al. (2011)

• local, inner Solar System origin of asteroidal water ices is consistent with the inferred D/H ratios of chondritic water (*Alexander et al. 2012*), which are very different from D/H ratios in Oort Cloud Comets measured

Role of Jupiter in isolating inner disk from the outer Solar System

low influx of water from the outer Solar System
 ≥2.5 Myr after CAI formation could be due to an early growth of Jupiter that opened a gap in the disk & prevented significant radial transport of dust from outside its orbit

pre-transitional disk with a gap

Conclusions (I)

- CI, CM, CR, CV, CO, & UOCs experienced various degrees of aqueous alteration
- ⁵³Mn-⁵³Cr dating of carbonates in CI, CM, & CR chondrites, & fayalite in CV, CO, & UOCs indicate aqueous activity occurred ~3–5 Myr after CV CAIs
- old ages of aqueous alteration & their narrow range are consistent with heating of chondrite asteroids by ²⁶Al, & inconsistent with a significant role of impact heating

Conclusions (II)

• near the terrestrial O-isotope compositions of fayalite, magnetite, & carbonates in UOCs & CCs imply that asteroidal water had preferentially a local, inner Solar System origin, consistent with the inferred D/H ratio of chondritic water (*Alexander et al. 2012*)

• ordinary chondrites accreted isotopically heavier water than CCs & may have had a higher proportion of the outer Solar System water

• low influx of water from the outer SS during accretion of CC asteroids could be due to an early growth of Jupiter that opened a gap in the disk & prevented significant radial transport of dust from outside its orbit

Extra slides

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A low mass for Mars from Jupiter's early gas-driven migration

Kevin J. Walsh^{1,2}, Alessandro Morbidelli¹, Sean N. Raymond^{3,4}, David P. O'Brien⁵ & Avi M. Mandell⁶

Nature (2011)

Sources of water on asteroids: Insights from H & N isotopes

Fig. 1. (**A**) The bulk compositions of the carbonaceous chondrites analyzed here. The lines are fits to the CR and CM data. Open red squares are CMs that were not included in the CM fit. (**B**) An expanded scale to show

that the CR and CM lines pass through the compositions of the most primitive chondritic insoluble organic matter (IOM) (11, 14). The bulk composition of the OC Semarkona is also included.

- CM & CR chondrites experienced different degrees of aqueous alteration
- bulk H-isotopic compositions of a chondrite = hydrated silicates + organics
- δD vs. C/H → isotopic composition of water; $\delta D = (D/H_{sample}/D/H_{SMOW} 1) \times 1000$
- CM & CR trends converge on the region where the most primitive insoluble organic matter (IOM) plots \rightarrow share a common primitive organic component

- if comets were not the sources of Earth's water, asteroids become the most likely candidates, along with some nebular gas
- most of H & N (as well as other volatiles) accreted in CI-like material along with ~10% contribution to both elements from material with a solar isotopically solar compositions

The Provenances of Asteroids, and Their Contributions to the Volatile Inventories of the Terrestrial Planets

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Science, 337, 721 (2012)

Determining the source(s) of hydrogen, carbon, and nitrogen accreted by Earth is important for understanding the origins of water and life and for constraining dynamical processes that operated during planet formation. Chondritic meteorites are asteroidal fragments that retain records of the first few million years of solar system history. The deuterium/hydrogen (D/H) values of water in carbonaceous chondrites are distinct from those in comets and Saturn's moon Enceladus, implying that they formed in a different region of the solar system, contrary to predictions of recent dynamical models. The D/H values of water in carbonaceous chondrites also argue against an influx of water ice from the outer solar system, which has been invoked to explain the nonsolar oxygen isotopic composition of the inner solar system. The bulk hydrogen and nitrogen isotopic compositions of CI chondrites suggest that they were the principal source of Earth's volatiles.

Origin of fayalite-bearing assemblages

Zolotov et al. (2006)

• fayalite & magnetite formed *in situ*, during fluid-rock interaction at water/rock ratio ~0.1–0.2 & temperatures ~100–300°C

• differences in Δ^{17} O of fayalite+magnetite in UOCs & CCs

UOC: +4.5±1.1‰

CV & CO: -0.4±0.9‰

CO-like: -1.6±0.9‰

may reflect spatial or temporal variations in O-isotope compositions of water ices that accreted into their parent asteroids

Accretion time of the CI parent body

CIs accreted 3–4 Myr after CV CAIs: based on peak temperature experienced by CIs & ⁵³Mn-⁵³Cr ages & formation temperature of carbonates

•

Accretion ages of CV & CO asteroids

- COs & CVs define metamorphic sequences of petrologic types 3.0–3.7 & 3.1–3.6 with peak metamorphic temperature of ~600°C (*Huss et al. 2006; Bonal et al. 2006, 2007*)
- ²⁶Al major heating source of asteroids
- $({}^{26}\text{Al}/{}^{27}\text{Al})_0$ in the disk after epoch of CAI formation could have been uniform at ~5×10⁻⁵ (e.g., Schrader et al. 2013)
- $\rightarrow\,$ peak metamorphic temperatures can be used to constrain accretion ages of CV & CO parent asteroids

Accretion ages of CV & CO asteroids & formation of fayalite

numerical modeling of thermal history of CV & CO like asteroids with radius of 50 km, water/rock ratio 0.2, & peak metamorphic temperature ~600°C

- CV & CO asteroids must have accreted within ≤ 2.6 Myr after CV CAIs, consistent with 26 Al- 26 Mg ages of CO chondrules (2.8±0.8 Myr after CAIs, *Kita & Ushikubo 2012*)
- CV & CO fayalite could have precipitated < 5 Myr after CAIs in the outer portions of these asteroids
- \rightarrow CO & CV asteroids accreted with water ices shortly after chondrule formation
- CI & CM parent bodies accreted 3–4 Myr after CAIs (Fujiya et al. 2012, 2013)

Chondritic water as a potential record of influx of ice from the outer into the inner Solar System

Oxygen-isotope composition of water ices in CCs

Previous estimates of the initial Δ^{17} O values of water ices in carbonaceous chondrites

- CMs & CRs: +0.9% ÷ +3% (Clayton & Mayeda 1999)
- CIs: +1.7‰ (Leshin et al. 1997)
- CMs: > -0.7‰ (Benedix et al. 2003)
- up to $+\overline{20\%}$ (Young et al. 1999; Young 2001)

Sources of water on asteroids: Insights from H, N & O isotopes

• variable amounts of the outer solar system water re-equilibrated at high temperature during chondrule formation with nebular H_2 acquiring ~solar H-isotopic compositions

• expected inverse correlation between chondrule abundances in chondrites & their initial water D/H values

chd abundances: $OC \approx RC > CV \approx CO \approx CR > CM > Tagish Lake > CI$ initial water D/H: $RC > OC > CR > CV \approx CO \approx CM \approx Tagish Lake \approx CI$

Sources of water on asteroids: Insights from H, N & O isotopes

• isotopically solar-like water re-equilibrated with nebular H_2 sunward of the snow line & subsequently migrated out to the chondrite-formation region beyond the snow line, e.g., via the cold finger effect

• water in OCs & RCs would then be essentially pure outer solar system ice

• water in OCs & RCs should be more ¹⁶O-depleted than in CCs (need to check) "Thus, at present there is inconsistency between the ice influx model & our results, unless, perhaps, the major ice influx occurred long before chondrite formation & the ice that chondrites accreted formed locally (with smaller isotopic anomalies) because transport in the disk had become less efficient"

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