



HAL
open science

Recent Advances in our Understanding of Water and Aqueous Activity in Chondrites

Lionel Vacher, Wataru Fujiya

► **To cite this version:**

Lionel Vacher, Wataru Fujiya. Recent Advances in our Understanding of Water and Aqueous Activity in Chondrites. *Elements*, 2022, 18 (3), pp.175-180. 10.2138/gselements.18.3.175 . hal-04028529

HAL Id: hal-04028529

<https://hal.science/hal-04028529v1>

Submitted on 14 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Recent Advances in our Understanding of Water and Aqueous Activity in Chondrites

Lionel G. Vacher¹ and Wataru Fujiya²

ABSTRACT

Water played a critical role in the evolution of rocky material and planetesimals in the early Solar System. Many primitive asteroids (the sources of chondrites) accreted a significant amount of water ice and were affected by aqueous alteration and/or fluid-assisted metamorphism. These secondary parent body processes have strongly modified the primary mineralogy of chondrites in favor of a wide diversity of secondary phases that formed by interaction with water. The mineralogical and isotopic characterization of these secondary phases in chondrites and returned samples from hydrous asteroids Ryugu and Bennu can help us reconstruct the dynamical evolution of water in the early Solar System and understand the timing and mechanisms of aqueous alteration on hydrous asteroids.

KEYWORDS: asteroids; chondrites; aqueous alteration; secondary minerals; isotopes; sample return missions

INTRODUCTION

Chondritic meteorites are rocks from undifferentiated asteroids. They represent an important record of the Solar System's early geological history ~4.6 billion years ago. Chondrites account for >80% of the total meteorite population and consist of three dominant components accreted together to form chondritic parent bodies: chondrules; Ca,Al-rich refractory inclusions (CAIs); and fine-grained matrix (FIG. 1A). The matrix material consists of an assemblage of diverse materials that incorporated a significant proportion of water ice grains, at least ~10–15 wt.% H₂O. After their accretion, chondrites experienced aqueous alteration and/or metamorphism on their parent bodies, resulting in important modifications to their mineralogy and chemical and

¹ Department of Physics

Washington University in St. Louis

St. Louis, MO, USA

E-mail: lionel.vacher@univ-grenoble-alpes.fr

² Faculty of Science

Ibaraki University

2-1-1 Bunkyo, Mito, 310-8512 Ibaraki, Japan

E-mail: wataru.fujiya.sci@vc.ibaraki.ac.jp

isotopic compositions. These “secondary” characteristics form the basis of the classification system for chondrites, in which seven petrologic types are recognized (from 1 to 7), where type 1 is assigned to the most aqueously altered chondrites, and type 7 represents the most thermally metamorphosed chondrites (see Weisberg et al. 2006 for a review).

Among chondrites, carbonaceous chondrites (subset of chondrites, divided into nine groups, namely CI, CM, CR, CY, CO, CV, CK, CB, and CH) of types 1 to 3 have experienced different aqueous alteration histories: (1) low-temperature hydrothermal alteration for petrologic types 1–2 (CI-CM-CR-CY groups); and (2) fluid-assisted metamorphism for petrologic type 3 (CO-CV groups) (FIG. 1B). Most of the hydrated carbonaceous chondrites with petrologic types 1–3 have preserved their secondary mineralogy and, therefore, offer the unique opportunity to study aqueous alteration processes that started ~4–5 million years after the birth of the Solar System. A combination of mineralogical, experimental, modeling, and isotopic studies on these secondary minerals can be achieved to reconstruct the source of water accreted by chondritic asteroids, their accretion time, and the physicochemical conditions of aqueous alteration that affected these hydrated asteroids.

ORIGINS OF WATER IN CHONDRITES

Stable water isotopes (^{16}O , ^{17}O , ^{18}O , H, and D) in chondrites are powerful tools to trace the origin of chondritic water and track the chemical processes that occurred on their asteroidal parent bodies. At present, almost all of the water in chondrites is now retained as hydroxyl (OH) groups or atomic O in various hydrated minerals. Therefore, the hydrogen (D/H) and oxygen ($\delta^{17,18}\text{O}$; see glossary) isotopic composition of chondritic water is usually inferred indirectly from bulk and in situ measurements of secondary minerals that formed from water–rock interaction.

At least two main water ice reservoirs with distinct H and O isotopic compositions are commonly inferred for the origin of water in chondrites: (1) locally derived water, directly condensed from the nebular gas; and (2) outer disk water ice, formed in the coldest part of the disk and/or inherited from the parent solar molecular cloud (Alexander et al. 2012) (FIG. 2A). Due to its low-temperature chemistry, interstellar ice is enriched in D by ~2–3 orders of magnitude compared to the solar nebular H_2 . In the early stages of the protoplanetary disk evolution, D-rich pre-solar ice was transported into the warm regions of the inner Solar System and subsequently re-equilibrated with the D-poor nebular H_2 . Thus, it is thought that the D/H isotopic ratio of water ice in planetary bodies increases with increasing heliocentric distance (Jacquet and Robert 2013). Similarly, the wide range of mass-independent O isotopic anomalies ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) observed in most Solar System materials is interpreted as the result of isotopic mixing between

inner Solar System material ($\Delta^{17}\text{O} \approx 0\text{‰}$) with the influx of ^{16}O -poor H_2O ice ($\Delta^{17}\text{O} \gg 0\text{‰}$) formed by a CO self-shielding process (see glossary) in the outer part of the protoplanetary disk or in the parent molecular cloud (see Yurimoto et al. 2008 for a review).

Hydrogen Isotopes

Deciphering the origin of chondritic water using H isotopes is challenging because hydrated chondrite matrices consist essentially of a complex mixture of hydrated minerals and organic matter (the two main H-carrier phases), which are intimately mixed at the sub-micrometer scale. To solve this problem, Alexander et al. (2012) proposed that the D/H composition of chondritic water can be approximated from whole-rock D/H and C/H measurements by subtracting the organic-derived D/H from their bulk H isotopic compositions. They showed that the D/H ratios of C-free phyllosilicate are D-poor ($\text{D}/\text{H} = 70 \text{ to } 100 \times 10^{-6}$) relative to D-rich comets (up to 530×10^{-6}). This result implies that chondrite parent bodies accreted a dominant D-poor local water ice without a significant influx of D-rich outer disk water ice in the inner Solar System (FIG. 2B). However, given that some members of carbonaceous, ordinary (OC), and Rumuruti (R) chondrites (two other subsets of chondrites) also record slightly or very D-rich water in their hydrated minerals relative to carbonaceous chondrites (D/H up to $\sim 1800 \times 10^{-6}$), it was also proposed that the D-rich signature of outer disk or interstellar water ice has been preserved in some chondrite parent bodies (e.g., Piani et al. 2015).

Current debates consider whether the presence of D-rich signatures for chondritic water represents the influx of outer disk or interstellar water into the asteroid accretion region or the role of isotopic fractionation on asteroidal parent bodies. For instance, Alexander et al. (2010) suggested that the H isotopic composition of water in chondrites could have been modified on the asteroidal parent body and become isotopically heavier due to (1) metal oxidation and subsequent loss of isotopically light H_2 and/or (2) the isotopic exchange of H between D-poor liquid water and D-rich organic components. Process (1) would have preferentially enriched in D the most metamorphosed chondrites. In process (2), only chondrites that experienced sufficiently high temperatures ($>200 \text{ }^\circ\text{C}$) and/or a long duration of aqueous alteration could have been affected by this process (Piani et al. 2021).

Oxygen Isotopes

The variation in O isotopic compositions of secondary minerals is much smaller than that for H isotopes (FIG. 2C). For instance, the $\Delta^{17}\text{O}$ values of carbonate, magnetite, phyllosilicate, and fayalite (Fe-rich olivine) in carbonaceous and ordinary chondrites only show modest mass-independent O isotopic variations, ranging from $\sim -5\text{‰}$ to $+7\text{‰}$ (see Yurimoto et al. 2008 for

review). However, it should be noted that the O isotopic compositions of secondary minerals are essentially controlled by isotopic exchange between ^{16}O -poor initial water with ^{16}O -rich anhydrous minerals prior to their formation. Thus, these $\Delta^{17}\text{O}$ values likely represent lower limits on the initial water composition accreted by chondrite parent bodies. Although high- $\Delta^{17}\text{O}$ values are predicted by fluid flow models in carbonaceous chondrites (up to $\sim +16\text{‰}$, Young et al. 1999), the initial O isotopic compositions of chondritic water do not seem to show significant ^{16}O depletion (up to $\sim +7\text{‰}$ in OC chondrites, Yurimoto et al., 2008), in contrast to what is observed for H isotopes.

Outer disk water ice is predicted to be extremely heavy, but there have only been a few reports of very heavy O isotopic signatures in chondrites. The heaviest O isotopic signature of water ($\Delta^{17}\text{O} \approx$ up to $+85\text{‰}$) was found in cosmic symplectite (COS, an assemblage of ^{16}O -poor magnetite and pentlandite) in the primitive carbonaceous chondrites Acfer 094 (Sakamoto et al. 2007). Although CO self-shielding models predict very extensive ^{16}O -depletion in the outer water ice ($\Delta^{17}\text{O}$ up to $\sim +300\text{‰}$), the O isotopic composition of the ^{16}O -poor reservoir is still poorly known and needs to be better constrained. Consequently, the lack of significant ^{16}O depletion in chondritic water suggests that chondrite parent bodies preferentially accreted a locally derived water ice with near-terrestrial $\Delta^{17}\text{O}$ values. An alternative explanation could be that mass-independent O isotopic anomalies of chondritic water ice may have been erased before their incorporation into the chondritic parent bodies due to reprocessing in the protoplanetary disk (Fujiya 2018).

CONDITIONS OF AQUEOUS ALTERATION IN CHONDRITES

Stable Isotope Geothermometry

Even though much progress has been made in understanding the alteration conditions of chondrites (see Brearley 2006 for review), the physicochemical conditions under which aqueous alteration took place remain only partially understood. Among secondary minerals, carbonate, magnetite, and fayalite minerals are of primary importance because their O isotopic composition can be used as a paleothermometer to constrain the temperatures of aqueous alteration (FIG. 3A, C). Their temperatures of formation can be estimated using either (1) the mass-dependent O isotopic fractionation between a secondary mineral and water, which requires knowing the initial O isotopic composition of the parent fluid, or (2) the mass-dependent O isotopic fractionation between two coexisting phases that precipitated from the same parent fluid in isotopic equilibrium.

In types 1–2 carbonaceous chondrites, most studies have focused on carbonate minerals and the data are in good agreement with low-temperature alteration ($\lesssim 250\text{ °C}$). For example, the

relatively high $\delta^{18}\text{O}$ fractionation determined in situ for calcite–magnetite assemblages in CR chondrites indicates alteration temperatures in the range of $\sim 60\text{--}90\text{ }^\circ\text{C}$ (Jilly-Rehak et al. 2018). Similarly, the small $\delta^{18}\text{O}$ fractionation for bulk calcite, phyllosilicate, and magnetite minerals in CI chondrites suggests slightly higher alteration temperatures, in the range of $\sim 50\text{--}150\text{ }^\circ\text{C}$ (Clayton and Mayeda 1999). In CM chondrites, bulk O isotopic measurements of carbonate and serpentine from several CM chondrites suggest that these two minerals are not in isotopic equilibrium (i.e., did not precipitate from the same fluid), but recorded, instead, a change in composition of the fluid with increasing alteration (Benedix et al. 2003). In fact, carbonate precipitation in CM chondrites was probably complex and episodic, resulting in the formation of two main populations of carbonate: (1) an early ^{16}O -poor generation formed before serpentine; and (2) a later ^{16}O -rich generation formed after serpentine. Considered separately, the first generation appears to form at lower temperature ($\sim 0\text{--}70\text{ }^\circ\text{C}$) than the second generation ($\sim 100\text{--}250\text{ }^\circ\text{C}$), suggesting that the O isotopic compositions of CM carbonates likely recorded an increase of the alteration temperature with time (see Suttle et al. 2021 for review).

In type 3 chondrites, determining the alteration temperatures of CO and CV chondrites are more complex because these chondrites experienced only limited aqueous alteration. However, the low mass-dependent O isotopic equilibrium reported for fayalite–magnetite in the CO and CV chondrites suggests a significantly higher alteration temperature than that of types 1–2 chondrites, from $\sim 150\text{ }^\circ\text{C}$ for CV chondrites to $500\text{ }^\circ\text{C}$ for CO chondrites (Marrocchi et al. 2018).

Mineralogy and Stability Fields of Secondary Phases

The restricted stability fields of hydrous minerals, such as serpentine and clays in types 1–2 chondrites, are particularly sensitive indicators of aqueous alteration and can place limits on the physicochemical conditions during aqueous alteration. In less-altered CM chondrites (petrologic subtype CM2.9–2.7 in the Rubin et al. 2007 classification), the most abundant alteration products are tochilinite–cronstedtite intergrowth (TCIs) (FIG. 3B), whereas chrysotile–greenalite serpentine solid solution dominates in more altered occurrences (subtypes CM2.2–2.1) (Velbel et al. 2015). Thermodynamic simulations and hydrothermal experiments indicate that TCIs formed under reducing conditions (low $f\text{O}_2$ fugacity), at moderate temperatures ($\sim 50\text{--}150\text{ }^\circ\text{C}$) and neutral to alkaline pH (pH $\approx 7\text{--}12$) (e.g., Pignatelli et al. 2016). As alteration progressed, the fluid composition evolved to become more reducing, as indicated by the presence of Fe^{2+} in the greenalite solid-solution end-member in CM2.2 and 2.1 chondrites (Velbel et al. 2015). The alteration conditions of CI–CR chondrites are less constrained than those of CM chondrites because of their scarcity, but these two groups of chondrites probably shared similar alteration conditions, as suggested by the presence of serpentine interlayered with saponite in their matrices.

Constraints provided by mineralogical observations and thermodynamic modeling indicate that aqueous alteration in CI chondrites occurs at high water/rock ratio relative to CM chondrites, neutral to alkaline pH (pH \approx 7–12), and moderate temperature (\sim 20–150 °C) (Brearley 2006).

Although type 3 carbonaceous chondrites do not contain a high abundance of hydrous minerals, CV and CO chondrites contain a wide diversity of secondary anhydrous phases, such as Ca-Fe-rich silicates (i.e., hedenbergite associated with andradite; Fig. 3D), magnetite, Fe-Ni sulfide, and Na-Al-Cl-rich feldspathoids. Recent mineralogical studies on Ca-Fe-rich and Na-Al-Cl-rich secondary silicates in CV and CO chondrites argue for a formation in fumarolic-like reduced environment from hot hydrothermal vapor (\sim 200–600 °C) (Ganino and Libourel 2020).

MODELING OF AQUEOUS ALTERATION AND FLUID CIRCULATION IN CHONDRITE PARENT BODIES

Chronology of Aqueous Activity and Thermal Modeling

Combined physical and chemical models of aqueous alteration on carbonaceous parent bodies have been constructed. These models aim to account for the characteristics of aqueously altered carbonaceous chondrites, especially in terms of their mineralogy and isotopic compositions. These physical models have simulated the thermal evolution associated with fluid flow in carbonaceous asteroids, which is required to satisfy the chronological constraints from carbonaceous chondrites. For example, carbonates in carbonaceous chondrites formed \sim 4–5 My after the birth of the Solar System, placing a constraint on the time when aqueous alteration initiated. In most models, thermal conduction is calculated within asteroids of a few tens of km in diameter heated by the decay of radionuclides (e.g., Fujiya et al. 2012). If the ambient temperatures of such small asteroids are assumed to be low (\sim –100 °C), they cool quickly within millions of years by thermal conduction. Thus, radioactive nuclides with half-lives comparable to the cooling timescale were effective heat sources in the early Solar System. Among short-lived radionuclides, ^{26}Al was the major heat source because of its short half-life of \sim 700,000 years, high decay energy of 4 MeV per atom, and abundance in the early Solar System. Thermal models have concluded that the carbonaceous parent bodies of aqueously altered carbonaceous chondrites likely formed 3–4 My after the birth of the Solar System to satisfy the carbonate age constraints and achieve a relatively low peak temperature of 250 °C under which aqueous alteration took place (FIG. 4).

Fluid Flow Models

Some models have incorporated fluid flow in asteroids either as exhalation flow from the interior to the surface driven by vapor pressure or as fluid convection driven by buoyancy (e.g., Palguta et al. 2010). The extent of fluid flow is controlled by the asteroid permeability. Permeability is a measure of the ability of a porous material to transmit fluid, and is not unambiguously determined for “initial” carbonaceous asteroids. The models invoking fluid flow often assume a relatively high permeability (up to 10^{-11} m²), consistent with that of terrestrial sediments. However, the extremely fine grain size observed in primitive carbonaceous chondrites suggests that these asteroids may have had a much lower permeability than previously estimated (down to 10^{-19} m²) (Bland et al. 2009). As a result, the distances of fluid flow in carbonaceous asteroids would have been limited to only hundreds of microns at most. Thus, whether fluid flow in carbonaceous asteroids actually occurred still remains unclear. The limited fluid flow may be consistent with the apparent isochemical nature of CM chondrites, i.e., their chemical compositions are as expected from aqueous alteration in a closed system. Furthermore, carbonates with a wide variety of C isotopic compositions ($\delta^{13}\text{C}_{\text{PDB}} = \sim 20\text{‰} - 80\text{‰}$) are observed within mm-sized thin sections of CM chondrites, suggesting heterogeneous fluid compositions, which reflect varying physicochemical conditions and, thus, limited mobility of the aqueous fluids (see Suttle et al. 2021 for a review). On the other hand, the depletion of thermally mobile trace elements in hydrated and then metamorphosed chondrites provides evidence for open system loss and fluid-assisted escape of these elements.

An alternative asteroid model describes the structure of the carbonaceous parent bodies as giant convecting mud balls (Bland and Travis 2017). In this model, it is assumed that solid materials making up the parent bodies were not lithified when liquid water circulated through the asteroid. Consequently, solid materials in the parent bodies could have behaved as a mobile mud moving together with aqueous fluids, rather than a rigid, spatially fixed rock. One important implication from this model is that the chemical compositions of aqueously altered carbonaceous chondrites will necessarily be kept because the system is thoroughly mixed. The individual mud particles are predicted to have undergone aqueous alteration under varying physicochemical conditions, such as temperatures and redox states during convection, and to have subsequently been brought together to form the aqueously altered carbonaceous chondrites. Thus, this model potentially explains the heterogeneous O and C isotopic compositions of carbonates observed in single CM chondrite specimens. Finally, this model predicts the size-sorting of particles during mud convection. This means that large particles (>100 μm) could have sunk to the core of the parent bodies, and that the mantle would have been dominated by fine particles. CI chondrites are the most aqueously altered chondrites and do not contain chondrules, which are mm- to sub-mm-sized silicate spherules of olivine and pyroxene once melted in the solar nebula. Therefore, CI

chondrites may represent the mantle of their mud-ball parent body from which chondrules sank to the parent body's center. It is argued that the mineralogy and geochemistry of dwarf planet Ceres are consistent with CM/CI-like chondrites. However, Ceres has experienced more advanced alteration, likely due to convection, which increased the effective water/rock ratios (McSween et al. 2018).

POSSIBLE TESTS ON AQUEOUS ALTERATION MODELS BY SAMPLE RETURN MISSIONS

Sample Return

Recently, two space missions aiming to bring extraterrestrial samples back to Earth, so-called sample return missions, have successfully collected surface materials from volatile-rich, primitive carbonaceous asteroids. The Hayabusa2 spacecraft of the Japan Aerospace Exploration Agency (JAXA) reached the near-Earth CB-type (see glossary) carbonaceous asteroid (162173) Ryugu in June 2018 (Watanabe et al. 2019). This spacecraft carried out touch-down operations twice in February and July 2019 and acquired ~5.4 g of material from the surface of Ryugu. The second touch-down site on Ryugu was located ~20 m from the artificial crater (~2.7 m depth) created by the Small Carry-on Impactor (SCI) in April 2019. Thus, it is likely that not only surface materials but also subsurface materials were acquired. The Hayabusa2 spacecraft delivered its collected samples to Earth in December 2020. NASA's OSIRIS-REx spacecraft also reached another near-Earth B-type (a subcategory of C-type) carbonaceous asteroid (101955) Bennu in December 2018 (Lauretta et al. 2019). The spacecraft collected a plentiful amount of surface materials, expected to be >60 g. The OSIRIS-REx spacecraft began its two-year journey back to Earth in May 2021 and will return with its samples to Earth in September 2023.

Aqueous Alteration on the Ryugu and Bennu Parent Bodies

Asteroids Ryugu and Bennu both have a spinning top-shape (i.e., a pronounced equatorial ridge) (FIG. 5A), low density of ~1.2 g/cm³ consistent with a rubble-pile structure with a high porosity, and a low geometric albedo of approximately 4.4%–4.5%. The rubble-pile structure and high porosity suggest that these asteroids are re-accreted fragments generated by catastrophic disruption of their original, larger parent bodies. The Near-Infrared Spectrometer (NIRS3) boarded on the Hayabusa2 spacecraft has detected a weak and narrow absorption feature at ~2.7 μm in the surface materials across the entire surface of Ryugu (FIG. 5B), corresponding to OH-bearing minerals (phyllosilicates) that resemble those observed in CI chondrites experimentally heated to 500 °C (Kitazato et al. 2019) (FIG. 5C). Similarly, the SCI experiment of Hayabusa2 also

revealed a slightly stronger –OH absorption of the excavated materials found nearby the artificial impact. It is likely that both the surface and subsurface materials of Ryugu contain hydrous minerals, but underwent heating in the range of ~300–700 °C (temperatures where phyllosilicates dehydrate), and that surface processes, such as space weathering and radiative heating, have induced subtle spectral changes of the uppermost surface. Overall, these observations suggest that (1) hydrous minerals are ubiquitous on Ryugu’s subsurface, (2) Ryugu materials are likely thermally metamorphosed, and (3) the primary thermal metamorphism occurred on the original, larger parent body of Ryugu.

An apparent absorption feature at ~2.7 μm, similar to that observed for CM and CI chondrites, can be found for all of the spectra of Bennu acquired by the OSIRIS-REx Visible and InfraRed Spectrometer (OVIRS). It is known that the exact position of the ~2.7-μm band minimum varies with mineral and chemical composition. The band center of Bennu occurs at 2.74 μm, consistent with petrologic subtype CM2.1–2.2 and corresponding to the most aqueously altered CM chondrites. The detection of spectral absorption at 0.55 μm, corresponding to magnetite, also supports the affinity of Bennu with heavily altered CM or CI chondrites. These observations suggest that Bennu materials have a phyllosilicate-dominated composition. The deeper 2.7-μm band of Bennu than that of Ryugu indicates that Bennu is less heated than Ryugu and that their materials differ from each other (Hamilton et al. 2019).

The returned samples from Ryugu and Bennu will first tell us whether their spectra actually correspond to carbonaceous chondrites in our collection, and whether they are asteroidal materials we have not yet obtained as meteorites. The variability of the sample’s mineralogy and chemistry will provide crucial information about the structure of their original, larger parent bodies. The timescales of heating by ²⁶Al are much shorter than the timescales of cooling determined by the thermal conductivity. Therefore, we can expect that the peak temperatures experienced by large asteroids do not drastically vary from the center to the subsurface regions of the asteroids. Thus, if we find diverse mineralogy and chemistry among individual specimens in the returned samples, then the original asteroids may have been relatively small. Moreover, we may find evidence for fluid flow in the returned samples, such as carbonate veins filling fractures. It should be noted that centimeters-thick, roughly meter-long bright carbonate veins were found from remote sensing observations on Bennu (Kaplan et al. 2020). The analyses of the returned samples will unveil the evolution of the carbonaceous asteroids, and help to understand the fate of the water that these asteroids accreted in the early history of our Solar System.

GLOSSARY

Delta notation – The delta notation (δ) represents a per mil (‰: 10^{-3}) deviation of the isotopic ratio of a given sample from a terrestrial standard value. The isotopic ratios of an elements are often expressed by the delta notation because their natural variation is commonly small, on the order of 1% or less.

CO self-shielding – Carbon monoxide (CO) molecules at the surface of the parent molecular cloud or protoplanetary disk are dissociated by UV irradiation. The intensity of UV with the wavelengths of dissociation lines for abundant $C^{16}O$ rapidly attenuates at the surface, which is referred to as self-shielding. This process can produce a selective enrichment in ^{16}O for CO gas in the deeper region, because less abundant $C^{17}O$ and $C^{18}O$ can still be dissociated by UV there.

Asteroid taxonomy – Classification of asteroids according to their reflectance spectra, i.e., the change in reflectance with wavelength. C-complex asteroids, including Ryugu and Bennu, tend to have weak UV features and relatively flat to bluish spectra at longer wavelengths. The average visible albedo of C-complex objects is ~6 %, and ~60% of observed C-complex objects have 3- μ m bands, indicating hydrated silicates on their surfaces.

ACKNOWLEDGMENTS

The authors wish to thank Guest Editors Yves Marrocchi and Pierre Beck, and Principal Editor Richard J. Harrison for the invitation to contribute to this thematic issue. We are very grateful to Martin D. Suttle, Michael A. Velbel, and Ryan C. Ogliore for constructive comments and suggestions. Lionel Vacher acknowledges funding by the McDonnell Center for Space Sciences at Washington University in St. Louis (USA).

REFERENCES

- Alexander CMO'D and 5 coauthors (2010) Deuterium enrichments in chondritic macromolecular material—implications for the origin and evolution of organics, water and asteroids. *Geochimica et Cosmochimica Acta* 74: 4417-4437, doi: [10.1016/j.gca.2010.05.005](https://doi.org/10.1016/j.gca.2010.05.005)
- Alexander CMO'D and 5 coauthors (2012) The provenances of asteroids, and their contributions to the volatile inventories of the terrestrial planets. *Science* 337: 721-723, doi: [10.1126/science.1223474](https://doi.org/10.1126/science.1223474)
- Benedix GK, Leshin LA, Farquhar J, Jackson T, Thiemens MH (2003) Carbonates in CM2 chondrites: constraints on alteration conditions from oxygen isotopic compositions and petrographic observations. *Geochimica et Cosmochimica Acta* 67:1577-1588, doi: [10.1016/S0016-7037\(02\)01078-5](https://doi.org/10.1016/S0016-7037(02)01078-5)
- Bland PA and 11 coauthors (2009) Why aqueous alteration in asteroids was isochemical: high porosity ≠ high permeability. *Earth and Planetary Science Letters* 287: 559-568, doi: [10.1016/j.epsl.2009.09.004](https://doi.org/10.1016/j.epsl.2009.09.004)
- Bland PA, Travis BJ (2017) Giant convecting mud balls of the early solar system. *Science Advances* 3:e1602514, doi: [10.1126/sciadv.1602514](https://doi.org/10.1126/sciadv.1602514)
- Brearley AJ (2006) The action of water. In: Lauretta DS, McSween HY (eds) *Meteorites and the Early Solar System II*. University of Arizona Press, Tucson, pp 587-624
- Clayton RN, Mayeda TK (1999) Oxygen isotope studies of carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 63: 2089-2104, doi: [10.1016/S0016-7037\(99\)00090-3](https://doi.org/10.1016/S0016-7037(99)00090-3)
- Fujiya W, Sugiura N, Hotta H, Ichimura K, Sano Y (2012) Evidence for the late formation of hydrous asteroids from young meteoritic carbonates. *Nature Communications* 3: 627, doi: [10.1038/ncomms1635](https://doi.org/10.1038/ncomms1635)
- Fujiya W (2018) Oxygen isotopic ratios of primordial water in carbonaceous chondrites. *Earth and Planetary Science Letters* 481: 264-272, doi: [10.1016/j.epsl.2017.10.046](https://doi.org/10.1016/j.epsl.2017.10.046)
- Ganino C, Libourel G (2020) Fumarolic-like activity on carbonaceous chondrite parent body. *Science Advances* 6: eabb1166, doi: [10.1126/sciadv.abb1166](https://doi.org/10.1126/sciadv.abb1166)
- Hamilton VE and 33 coauthors (2019) Evidence for widespread hydrated minerals on asteroid (101955) Bennu. *Nature Astronomy* 3: 332-340, doi: [10.1038/s41550-019-0722-2](https://doi.org/10.1038/s41550-019-0722-2)
- Jacquet E, Robert F (2013) Water transport in protoplanetary disks and the hydrogen isotopic composition of chondrites. *Icarus* 223: 722-732, doi: [10.1016/j.icarus.2013.01.022](https://doi.org/10.1016/j.icarus.2013.01.022)
- Jilly-Rehak CE, Huss GR, Nagashima K, Schrader DL (2018) Low-temperature aqueous alteration on the CR chondrite parent body: implications from in situ oxygen-isotope analyses. *Geochimica et Cosmochimica Acta* 222: 230-252, doi: [10.1016/j.gca.2017.10.007](https://doi.org/10.1016/j.gca.2017.10.007)
- Kaplan HH and 29 coauthors (2020) Bright carbonate veins on asteroid (101955) Bennu: implications for aqueous alteration history. *Science* 370: eabc3557, doi: [10.1126/science.abc3557](https://doi.org/10.1126/science.abc3557)
- Kitazato K and 66 coauthors (2019) The surface compositions of asteroid 162173 Ryugu from Hayabusa2 near-infrared spectroscopy. *Science* 364: 272-275, doi: [10.1126/science.aav7432](https://doi.org/10.1126/science.aav7432)
- Lauretta DS and 29 coauthors (2019) The unexpected surface of asteroid (101955) Bennu. *Nature* 568: 55-60, doi: [10.1038/s41586-019-1033-6](https://doi.org/10.1038/s41586-019-1033-6)

- Marrocchi Y, Bekaert DV, Piani L (2018) Origin and abundance of water in carbonaceous asteroids. *Earth and Planetary Science Letters* 482: 23-32, doi: [10.1016/j.epsl.2017.10.060](https://doi.org/10.1016/j.epsl.2017.10.060)
- McSween Jr. HY and 9 coauthors (2018) Carbonaceous chondrites as analogs for the composition and alteration of Ceres. *Meteoritics & Planetary Science* 53: 1793-1804, doi: [10.1111/maps.12947](https://doi.org/10.1111/maps.12947)
- Palguta J, Schubert G, Travis BJ (2010) Fluid flow and chemical alteration in carbonaceous chondrite parent bodies. *Earth and Planetary Science Letters* 296: 235-243, doi: [10.1016/j.epsl.2010.05.003](https://doi.org/10.1016/j.epsl.2010.05.003)
- Piani L, Robert F, Remusat L (2015) Micron-scale D/H heterogeneity in chondrite matrices: a signature of the pristine solar system water? *Earth and Planetary Science Letters* 415: 154-164, doi: [10.1016/j.epsl.2015.01.039](https://doi.org/10.1016/j.epsl.2015.01.039)
- Piani L, Marrocchi Y, Vacher LG, Yurimoto H, Bizzarro M (2021) Origin of hydrogen isotopic variations in chondritic water and organics. *Earth and Planetary Science Letters* 567: 117008, doi: [10.1016/j.epsl.2021.117008](https://doi.org/10.1016/j.epsl.2021.117008)
- Pignatelli I, Marrocchi Y, Vacher LG, Delon R, Gounelle M (2016) Multiple precursors of secondary mineralogical assemblages in CM chondrites. *Meteoritics & Planetary Science* 51: 785-805, doi: [10.1111/maps.12625](https://doi.org/10.1111/maps.12625)
- Rubin AE, Trigo-Rodríguez JM, Huber H, Wasson JT (2007) Progressive aqueous alteration of CM carbonaceous chondrites. *Geochimica et Cosmochimica Acta* 71: 2361-2382, doi: [10.1016/j.gca.2007.02.008](https://doi.org/10.1016/j.gca.2007.02.008)
- Sakamoto N and 7 coauthors (2007) Remnants of the early solar system water enriched in heavy oxygen isotopes. *Science* 317: 231-233, doi: [10.1126/science.1142021](https://doi.org/10.1126/science.1142021)
- Suttle MD, King AJ, Schofield PF, Bates H, Russell SS (2021) The aqueous alteration of CM chondrites, a review. *Geochimica et Cosmochimica Acta* 299: 219-256, doi: [10.1016/j.gca.2021.01.014](https://doi.org/10.1016/j.gca.2021.01.014)
- Velbel MA, Tonui EK, Zolensky ME (2015) Replacement of olivine by serpentine in the Queen Alexandra Range 93005 carbonaceous chondrite (CM2): reactant-product compositional relations, and isovolumetric constraints on reaction stoichiometry and elemental mobility during aqueous alteration. *Geochimica et Cosmochimica Acta* 148: 402-425, doi: [10.1016/j.gca.2014.10.007](https://doi.org/10.1016/j.gca.2014.10.007)
- Watanabe S and 88 coauthors (2019) Hayabusa2 arrives at the carbonaceous asteroid 162173 Ryugu—a spinning top-shaped rubble pile. *Science* 364: 268-272, doi: [10.1126/science.aav8032](https://doi.org/10.1126/science.aav8032)
- Weisberg MK, McCoy TJ, Krot AN (2006) Systematics and evaluation of meteorite classification. In: Lauretta DS, McSween HY (eds) *Meteorites and the Early Solar System II*. University of Arizona Press, Tucson, pp 19-52
- Young ED, Ash RD, England P, Rumble D (1999) Fluid flow in chondritic parent bodies: deciphering the compositions of planetesimals. *Science* 286: 1331-1335, doi: [10.1126/science.286.5443.1331](https://doi.org/10.1126/science.286.5443.1331)
- Yurimoto H and 5 coauthors (2008) Oxygen isotopes of chondritic components. *Reviews in Mineralogy and Geochemistry* 68: 141-186, doi: [10.2138/rmg.2008.68.8](https://doi.org/10.2138/rmg.2008.68.8)

Figures

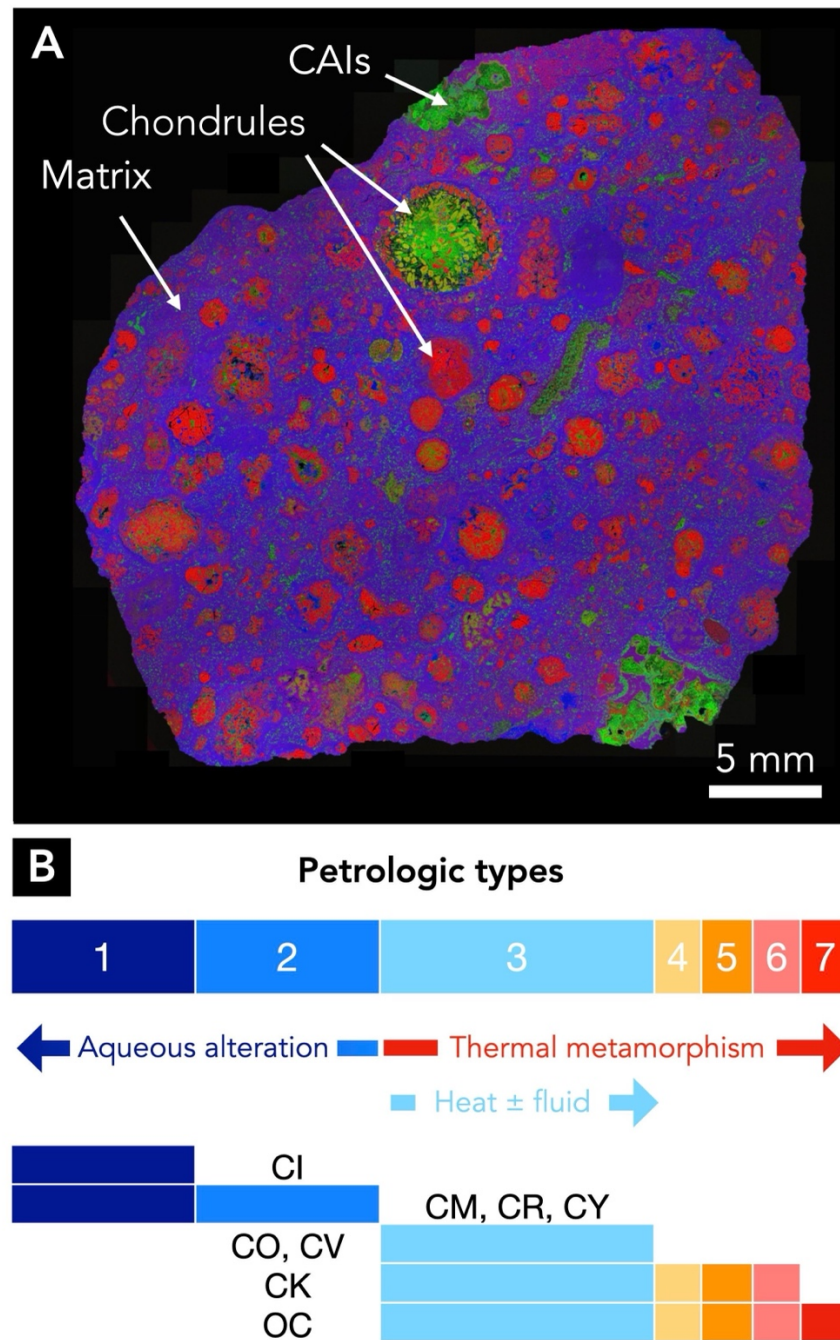


FIGURE 1. Dominant components of chondrites and their classification. **(A)** False-color map of the CV chondrite Allende (Mg: red, Ca: green, and Fe: blue), revealing the distribution of chondrules and CAIs embedded in a fine-grained matrix. IMAGE COURTESY OF RYAN OGLIORE. **(B)** Schematic representation of the chondrite classification (ADAPTED FROM WEISBERG ET AL. 2006). The role played by thermal metamorphism increases from type 3 to 7 while the degree of aqueous alteration increases from type 3 to 1. OC: ordinary chondrite. CV, CO, CM, CR, CY, and CI: carbonaceous chondrite groups.

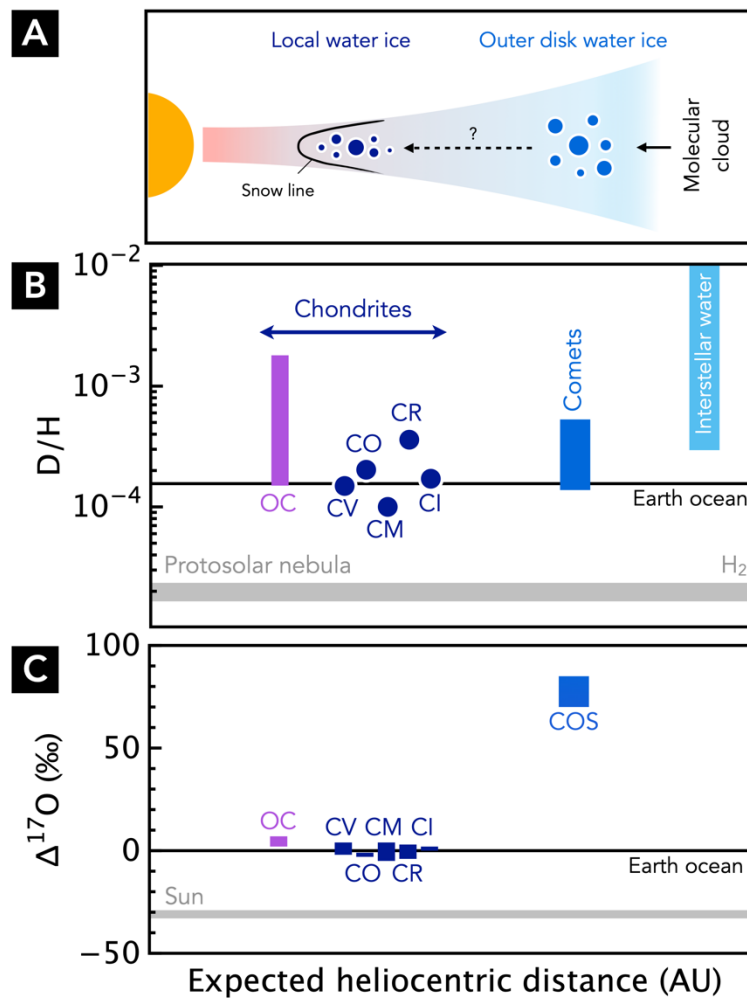


FIGURE 2. Spatial distribution and isotopic compositions of the different water reservoirs in the early Solar System. **(A)** Simplified view of the repartition of the water ice reservoirs in the protoplanetary disk. The snow line represents the distance from the Sun where the temperature is low enough (≤ 170 K) for water ice grains to form. **(B)** Distribution of D/H ratios for water in ordinary (OC) and carbonaceous (CV, CO, CM, CR, CI) chondrites, comets, and interstellar water ice. **(C)** Distribution of mass-independent oxygen isotopic anomalies ($\Delta^{17}O$) recorded by secondary minerals in chondrites. Cosmic symplectite (COS) is an assemblage of ^{16}O -poor magnetite and pentlandite.

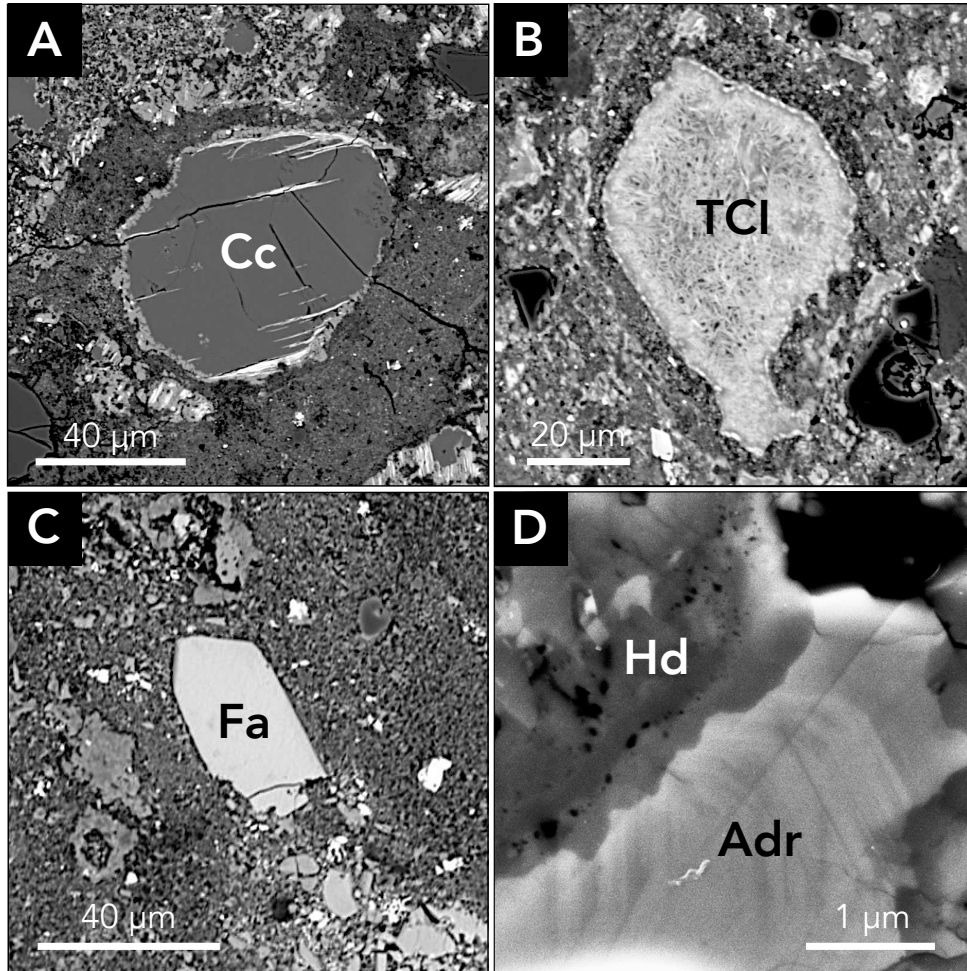


FIGURE 3. Backscattered-electron images of secondary phases in carbonaceous chondrites. **(A)** Ca-carbonate (Cc) from the CM Maribo. **(B)** Tochilinite–cronstedtite intergrowth (TCI) from the CM Boriskino. **(C)** Fayalite (Fa) from the CV Kaba. IMAGE COURTESY OF YVES MARROCCHI. **(D)** Hedenbergite (Hd) and andradite (Adr) from the CV Allende. IMAGE COURTESY OF CLEMENT GANINO.

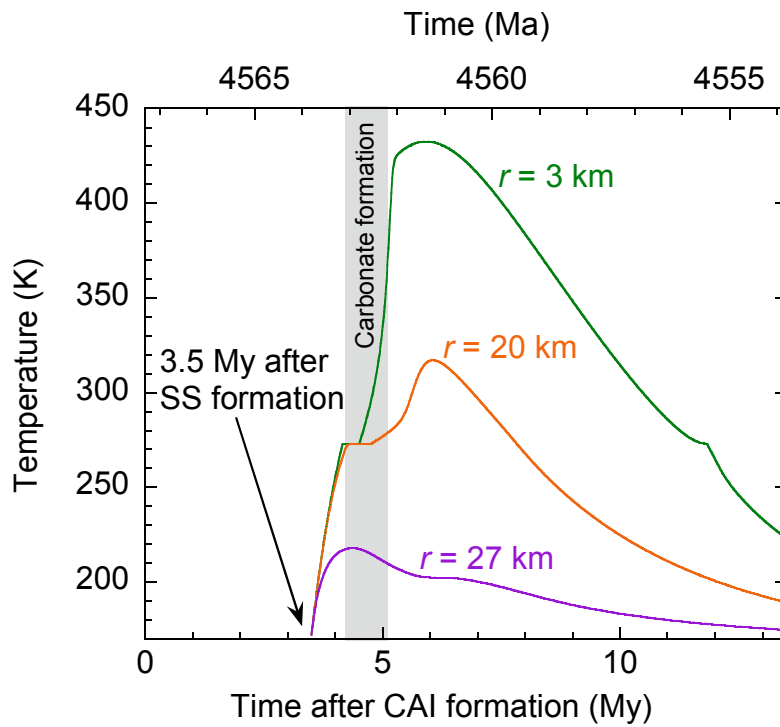


FIGURE 4. Time vs. temperature in an asteroid with a radius of 30 km calculated using the thermal model by Fujiya et al. (2012). The asteroid is assumed to have formed 3.5 My after the birth of the Solar System (SS). The model is based on heat conduction with ^{26}Al as a heat source. The water-ice phase transition and reaction heat of hydration are included. Temperature is given at three depths (r : distance from the center). The vertical gray band shows the age of carbonates in CM chondrites. MODIFIED FROM FUJIYA ET AL. (2012).

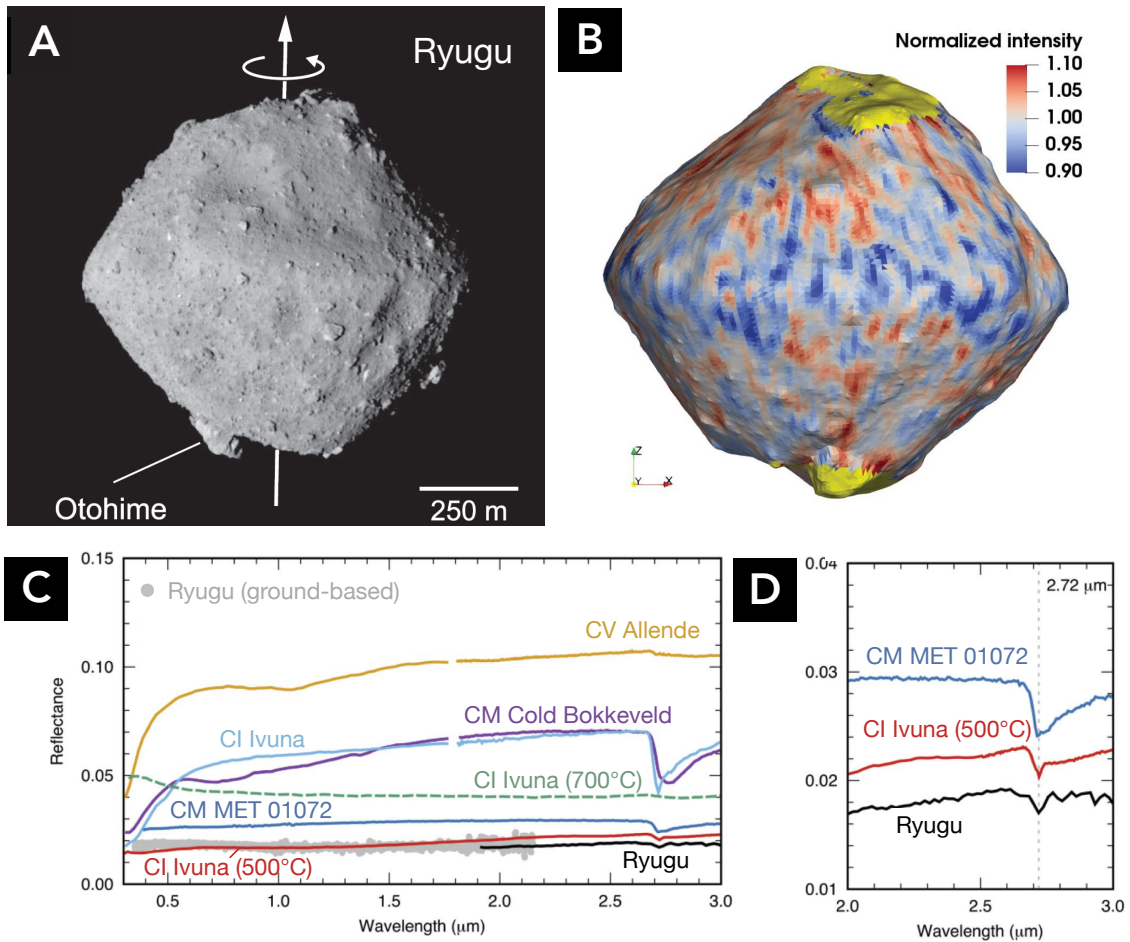


FIGURE 5. Observation of asteroid Ryugu by the Hayabusa2 spacecraft. **(A)** Visible light images of Ryugu taken with the Optical Navigation Camera–Telescopic (ONC-T) from 20 km altitude on July 10, 2018. **(B)** Normalized intensity of the 2.72- μm feature obtained with the Near-Infrared Spectrometer (NIRS3) projected onto the shape model of Ryugu. The yellow areas represent unobserved regions. **(C)** Comparison between the reflectance spectra of Ryugu’s surface and that of chondrites. **(D)** Enlargement of the NIRS3 wavelength range in **(C)**. ADAPTED FROM WATANABE ET AL. (2019) AND KITAZATO ET AL. (2019).