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CONTRASTS ON THE DETECTION OF THE SOLAR NEBULA’S OXIDATION STATE THROUGH ASTEROID OBSERVATIONS. P. A. Abell1,2, M. J. Gaffey2-3, and P. S. Hardersen2-3. 1Planetary Astronomy Group, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Mail Code KR, Houston, TX 77058, paul.a.abell1@jsc.nasa.gov, 2Department of Space Studies, Box 9008, University of North Dakota, Grand Forks, ND 58202, gaffey@space.edu; hardersen@volcano.space.edu, 3Visiting Astronomer at the Infrared Telescope Facility, which is operated by the University of Hawai’i under contract from the National Aeronautics and Space Administration, Mauna Kea, Hawai’i 96720.

Introduction: Asteroids represent the only in situ surviving population of planetesimals from the formation of the inner solar system and therefore include materials from the very earliest stages of solar system formation. Hence, these bodies can provide constraints on the processes and conditions that were present during this epoch and can be used to test current models and theories describing the late solar nebula, the early solar system and subsequent planetary accretion. From detailed knowledge of asteroid mineralogic compositions the probable starting materials, thermal histories, and oxidation states of asteroid parent bodies can be inferred [1, 2]. If such data can be obtained from specific mainbelt source regions, then this information can be used to map out the formation conditions of the late solar nebula within the inner solar system and possibly distinguish any trends in oxidation state that may be present.

Limitation of meteorite studies: Terrestrial meteorite collections provide evidence that a wide range of oxidation states existed within the late solar nebula. However, the terrestrial meteorite collections are a biased and incomplete sample of the material that exists in the main asteroid belt and the locations of very few of the specific meteorite parent bodies are actually known. Mean motion and secular resonances that preferentially deliver asteroidal material to Earth-crossing orbits, can also act as effective barriers to the delivery of material from certain locations within the mainbelt [3]. Hence, a number of objects in the outer mainbelt will not contribute significant amounts (or possibly any) material into Earth-crossing orbits. Similarly objects in the inner belt, but located relatively far from a resonance, will contribute only weakly to the Earth approaching meteoroid population, and even then will still exhibit strong strength-related biases. Therefore, in order to understand the various formation mechanisms, thermal histories, and oxidation states within the asteroid belt, it is necessary to rely on information obtained by remote observation of asteroids in addition to laboratory studies of meteorites.

Visible and Near-IR observations: This wavelength region (~ 0.3 to 2.5 microns) is where the most common solar system materials have diagnostic absorption features. Mineral species such as pyroxene, olivine, feldspar, phyllosilicates, and spinel all have been detected on the surface of mainbelt asteroids through reflectance spectroscopy [1]. High signal-to-noise visible and near-IR spectroscopic observations can be used to constrain the mineralogies of asteroids. Laboratory calibrations and previous spectral studies of meteorites have provided the means to determine the abundance and chemistries of the minerals detected on the surfaces of asteroids [4 – 9]. Therefore using these calibrations, detailed spectroscopic studies of mainbelt asteroids have been able to provide insights into the diverse assemblages and thermal histories that can exist even within one taxonomic group of objects [e.g., 10].

Constraints on the oxygen state: Recent spectroscopic studies have demonstrated that it is possible to determine mineral chemistries and assemblages that constrain the oxidation state of the original asteroid parent body [11]. Hardersen et al. (2005) have shown that several M-type asteroids have absorption features indicative of mafic silicates on their surfaces. These silicates have been identified by Hardersen et al. (2005) as iron-poor orthopyroxenes which suggests that the parent bodies of these objects formed in reducing conditions. This suggests that the regions where the asteroids formed either had low intrinsic oxygen fugacities or that their parent bodies contained sufficient amounts of reducing agents (e.g., carbon) to reduce iron-bearing silicates during igneous processing [11].

Conclusion: The study outlined here is just a brief illustration of how detailed asteroid spectroscopic investigations can help constrain the oxidation state of the solar nebula and supplement the laboratory investigation of meteorites.

Oxidation/Reduction processes in Primitive Achondrites. G.K. Benedix¹ and T.J. McCoy², ¹Washington University, Dept. of Earth and Planet. Sci., Saint Louis, MO 63130 USA (gbenedix@levee.wustl.edu); ²Dept. of Min. Sci., National Museum of Natural History, Smithsonian Institution, Washington, DC 20560-0119 USA.

Introduction: Primitive achondrites are characterized by having a bulk chondritic composition and non-chondritic texture [1]. They fall between enstatite and ordinary chondrites in mafic silicate compositions (Fig. 1). They include the winonaites/IAB iron and acapulcoites/lodranites [2]. Because of their unique textural and chemical features, the underlying goal of most studies of these groups is to understand the processes that modified chondritic bodies into fully-differentiated planetesimals (core, mantle and crust). Their intermediate oxidation state suggests either a significant role for oxidation/reduction during metamorphism and partial melting or a range of precursor oxidation states not fully sampled by chondrites. Here we discuss the relative influence of these processes on reduction/oxidation and suggest mechanisms by which these studies can be extended to asteroid studies.

Processes: Textural evidence for metamorphism and partial melting abounds in both the winonaites/IAB [3, 4] and acapulcoites/lodranite [5, 6] groups. We have examined the role of oxidation/reduction during parent body processes from both an experimental and thermodynamic viewpoint.

Recent experiments heated the H chondrite Kernouve to partial melting temperatures under reducing conditions [8]. While some of the features of primitive achondrites (e.g., magnesian olivine and chromite compositions) were produced, other features would have required either unrealistically high temperatures (e.g., pyroxene reduction) or occurred through reactions (e.g., chromite-sulfide) that have not been observed in primitive achondrites. These experiments suggest that simple reduction of an oxidized precursor chondrite likely did not produce primitive achondrite.

The conclusion is supported by closure temperatures and \( fO_2 \) calculated from orthopyroxene/clinopyroxene and olivine/chromite mineral pairs in the range of ~900 to 1100°C and ~590 to 700°C respectively [7]. Several winonaites/IABs record oxygen fugacities in the range from 2.5 to 3 log units below the Fe-FeO oxidation buffer at both temperatures. This strongly suggests that reduction did not occur during cooling and metamorphism after peak heating. Further, the opx/cpx closure temperature is close to the peak temperature, suggesting that the precursor material of these meteorites was reduced.

Reduced Precursor: While relict chondrules in primitive achondrites point to a chondritic precursor, the identity of that precursor remains elusive. We suggest that association with carbonaceous chondrites and, specifically, with metal-rich carbonaceous (e.g., CR-like) chondrites may be appropriate. The negative \( \Delta^{17}O \) of primitive achondrites would – almost by definition – point to a carbonaceous chondrite precursor. Further, the CR chondrites share many of the properties (e.g., intermediate mafic silicate compositions, metal-rich) seen in primitive achondrites. While an exact link may not be possible, further study of this postulated link seems warranted.

Implications for Asteroid Spectroscopy: Asteroid spectroscopy may provide a tool for understanding the full range of oxidation states in the solar nebula. The olivine:pyroxene ratio and mafic silicate compositions change systematically with oxidation state and their simultaneous solution, particularly for pyroxene composition which is resistant to parent body reduction, might provide a measure of the range of oxidation states.


Figure 1. Fs (mol%) of low-Ca pyroxene plotted vs. Fa (mol%) of olivine for the primitive achondrite groups Acapulcoites/Lodranites (blue diamonds) and Winonaites/IAB Irons (yellow triangles). These groups have Fs and Fa that fall between enstatite (square) and ordinary (circles) chondrites in composition.
LOW-TEMPERATURE CHEMICAL PROCESSING ON ASTEROIDS. P. A. Bland, Dept. Earth Sci. 
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Background: In terms of their chemistry, carbonaceous chondrites (CCs) are amongst the most primitive materials available to us. But it has become clear that their mineralogy is highly altered. Initially, the abundant magnetite found in some CCs was thought to be a nebula condensate [1], or, together with clay minerals, the product of aqueous alteration that occurred in the solar nebula by the reaction of water vapour and anhydrous minerals [2]. Evidence now suggests that aqueous alteration occurred in the meteorite parent body [3-8]. Theoretical work [9] showed that hydration reactions in the nebula would have been kinetically inhibited (although recent studies argue against this [10,11]). Compelling evidence for aqueous processing on asteroids includes alteration products that bridge matrix components, magnetite morphology consistent with precipitation from a liquid phase, altered zones around chondrules, and the presence of carbonates [12]. Modelling [9] suggests that CC parent bodies accreted water in the form of ice. Transformation of ice into liquid water could have taken several possible routes, either hydrocryogenic alteration, or melting due to external or internal heat sources (plausibly, the decay of short lived radionuclides).

Chemistry: CI chondrites have compositions that are within 10% of the solar photosphere for most elements [13]. Early analyses of gram-samples of meteorite from other CC groups showed uniform volatility-controlled depletions compared to CI in elements with condensation T <1350K [14]. All these rocks experienced varying degrees of aqueous alteration. To preserve solar abundances in elements which are easily mobilised in fluids it was postulated that aqueous processing in asteroids was isochemical [3,4,15]. More recent data indicates isochemical alteration on very short length scales. INAA analyses of 10-100mg aliquots [16] shows remarkable reproducibility between samples, and no evidence for element mobility. LA-ICP-MS analyses [17] of 80µm areas of matrix in C3 chondrites indicates minimal exchange between chondrules and matrix on this scale (although some aqueous mobility is apparent in C2s). These geochemical studies are apparently at odds with studies of chondrite petrography which find evidence for metasomatism around chondrules and CAIs in ordinary chondrites [18], CVs [19] and CRs [20].

Oxygen isotopes: Popular models invoke an initial phase of nebula interaction between solid and gaseous reservoirs, followed by parent body aqueous alteration involving simple exchange between a static fluid and anhydrous phases in a closed system [21]. More recently, continuum modelling has shown that the oxygen isotope diversity amongst the CC groups may be explained by as asteroidal process: down-temperature fluid flow and attendant aqueous alteration on a canonical CC parent asteroid [22].

Summary: A means of reconciling geochemical and petrographic studies in CCs involves considering the length-scale over which aqueous metasomatism took place: element mobility occurred, but in C3s it was restricted to zones within ~100-200µm of anhydrous chondrules. In C2s and C1s fluid transport did not occur over distances >>100µm. Oxygen isotope data can also be interpreted as consistent with closed system, isochemical alteration [21]. Numerical modelling of asteroidal alteration suggests flow of pore water may have been limited in parent bodies <80km diameter [23]. The available data therefore appear to be consistent with an environment where fluid flow was minimal, alteration was isochemical, and CC parent bodies were not more than a few 10’s km in diameter.

ON THE FORMATION LOCATION OF ASTEROIDS AND METEORITES. W. F. Bottke and D. Nesvorny.
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Despite the advances made by the planetary science community over the last several decades, there are still fundamental questions about the origin and evolution of asteroids and meteorites. Here we concentrate on the iron meteorites, which currently dominate the fraction of distinct parent bodies represented in our meteorite collection (i.e., 27 chondritic, 2 primitive achondritic, 6 differentiated achondritic, 4 stony-iron, 10 iron groups, and 50 ungrouped irons; Meibom and Clark 1999; Burbine et al. 2002). Chemical and petrographic evidence indicates nearly all iron meteorites came from the cores of distinct differentiated asteroids; they cannot be explained away as impact melts or as fragments produced by the disruption of a few large differentiated bodies like D=530 km asteroid (4) Vesta (Scott 2002). Moreover, cooling rate and textural data suggests that many iron meteorites came from small parent bodies (e.g., 20 < D < 400 km; Mittlefehldt et al. 1998). Collectively, we infer from these constraints that differentiated asteroids and the geologic processes that formed them were once common in the solar system.

These data, however, stand in stark contrast to what observations of main belt asteroids tell us about planetesimal evolution. Despite intense searches (e.g., Burbine and Binzel 2002; Bus and Binzel 2002a,b), the only intact differentiated asteroid found to date is (4) Vesta. Fragments of differentiated bodies, however, have been identified. Observations suggest 22 A-type asteroids (out of a sample of 950) may represent mantle fragments (Burbine et al. 2002). (1459) Magnya, a D=30 km V-type asteroid located in the outer main belt, may sample the crust of a non-Vesta differentiated asteroid (Lazaro et al. 2000; Michtchenko et al. 2002), but the number of these objects (1 known so far) is far lower than our expectations based on the iron meteorite record. Observations of asteroid families, which are the remnants of disrupted asteroids, indicate none have spectral signatures consistent with the expected core-mantle-crust of differentiated asteroids (e.g., Cellino et al. 2002). Disrupted differentiated asteroids should produce large quantities of olivine-rich metal-free silicate meteoroids, yet none have been found in our meteorite collections (Burbine et al. 1996). We could easily go on, but the point is clear: our meteorite and asteroid collections appear to be telling us two very different stories about the nature and evolution of planetesimals coalescing out of the solar nebula.

Given these differences, we believe it is useful to reexamine the origin of differentiated asteroids. Current models suggest planetesimals (and planets) formed throughout the solar nebula. The fractionation observed between different groups of chondrites appears to have resulted from differences in nebular conditions as a function of distance from the sun and, in some cases, differences resulting from sequential formation of planetesimals as a function of time (e.g., McSween et al. 2002). For the latter, consider that radionuclide heating sources with fast decay rates (e.g., 26Al) should have the biggest effect on planetesimals that grow quickly, while accretion models indicate that planetesimal growth rates are highest for objects close to the sun. This information, when coupled to thermal models, predicts that small asteroids are more likely to melt and differentiate if they reside close to the Sun; far from the Sun, only the largest bodies with the right mix of volatiles accrete fast enough to differentiate (e.g., Vesta) (Grimm and McSween 1993; McSween et al. 2002). This scenario, if true, implies that many metamorphized and differentiated planetesimals (and putative meteorite parent bodies) formed < 2 AU (see Wasson and Wetherill 1979 and Wasson 1988).

According to existing planet formation models, the inner solar system planetesimals not accreted by planetary embryos were subjected to both collisional evolution and dynamical scattering events. Preliminary results from our numerical modeling work indicate that throughout the inner solar system, planetary embryos dynamically excite and scatter these planetesimals (and their fragments) away from their feeding zones. We believe this explains the observed spread of S-, C-, and P-type asteroids (D > 50 km) in the main belt (Gradie and Tedesco 1982). In certain cases, intact bodies or, more likely, fragments produced among a < 2 AU planetesimals, become trapped in stable regions like the main belt or Hungaria asteroid populations.

Although these main belt “interlopers” would be subject to Gy of collisional and dynamical evolution, some small fraction would have most likely survived to the present day. Our results indicate the majority of this material would reside in the innermost part of the main belt, making it relatively easy for meteoroids to later escape and reach Earth.

Note that iron meteorite precursors are not only are resistant to disruption events but they also have long dynamical lifetimes against Yarkovsky thermal drag forces (Bottke et al. 2002b). The same cannot be said for basaltic meteorite precursors; few embedded in the main belt 4.5 Ga are likely to be here today. We believe this scenario may explain the so-called meteorite “dunite shortage” without resorting to unphysical collisional models. Finally, our results imply that some meteorites (e.g., winonaites) may sample the long lost planetesimals that formed in the terrestrial planet zone (Wasson and Wetherill 1979).
THE SPECTRAL PROPERTIES OF ANGRITIC BASALTS. T. H. Burbine\(^1\) and T. J. McCoy\(^2\), \(^1\)Astronomy Department, Mount Holyoke College, South Hadley, MA 01075, USA (turbine@mtholyoke.edu), \(^2\)Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC 20560, USA.

**Introduction:** One type of material that tends to be relatively rare in our meteorite collections is basalt. Basalts are rocks rich in calcium-rich plagioclase feldspar and augitic pyroxene that form as solidified lava. One meteorite group, the angrites, is primarily basaltic in origin and make up 0.1% of all meteorite falls. These meteorites are composed predominately of anorthite, Al-Ti diopside-hedenbergite, and Ca-rich olivine. The type specimen, Angra dos Reis, is compositionally anomalous compared to other angrites since it is composed almost entirely of Al-Ti diopside-hedenbergite with only rare plagioclase.

The eucrites are the most common type of meteoritic basalt and appear genetically related to the howardites and diogenites (HEDs). HEDs show continuous variations in mineralogy and chemistry and almost all are believed to have formed on the same parent body. Eucrites contain primarily anorthitic plagioclase and low-Ca pyroxene with augite exsolution lamellae.

Jurewicz et al. \([1]\) found that partial melts of carbonaceous chondritic material resembled either angrites or eucrites, depending on the oxygen fugacity during melting. Relatively oxidizing conditions produced partial melts similar to angrites while relatively reducing conditions produced partial melts similar to eucrites. Iron meteorites are generally believed to represent ~50-70 differentiated parent bodies; however, it is unclear if angritic- or HED-like surfaces were more common. The ~500-km diameter 4 Vesta and a number of much-smaller asteroids (called Vestoids) have reflectance spectra similar to the HEDs. Almost all Vestoids are thought to be fragments of Vesta.

The identification of possible angritic parent bodies was hampered by the fact that the only previously measured angrite, Angra dos Reis \([2]\), has a spectrum unlike any known asteroid. The spectrum of Angra dos Reis is much redder (reflectance increasing with increasing wavelength) than almost all measured asteroids. Recently, the discoveries of two relatively large angrites (D’Orbigny and Sahara 99555) plus previously discovered Antarctic angrites (LEW 86010 and LEW 87051) have allowed for the measurement of the spectral properties of meteorites that may be more typical of the surface compositions of the angritic parent bodies.

**Samples:** Room temperature reflectance spectra for Angra dos Reis, D’Orbigny, LEW 86010, and Sahara 99555 were obtained using the bi-directional spectrometer at the Keck/NASA reflectance laboratory (RELAB) facility located at Brown University. These samples were ground with a mortar and pestle and sieved to particle sizes less than 74 µm for the Angra dos Reis, D’Orbigny, and Sahara 99555 samples and less than 74 µm for the LEW 86010 sample.

D’Orbigny \([3]\) and Sahara 99555 \([4]\) both contain approximately one-third anorthite, one-third Ca-rich olivine, and 20-25% Al-Ti diopside-hedenbergite. LEW 86010 \([5]\) is approximately 20% anorthite, 20% Ca-rich olivine, and 60% Al-Ti diopside-hedenbergite. Angra dos Reis \([6]\) is ~90% Al-Ti diopside-hedenbergite.

**Reflectance Spectroscopy:** The room-temperature reflectance spectra of D’Orbigny, LEW 86010, and Sahara 99555 have similar spectral characteristics. Both have broad features centered near 1 µm and very weak absorption bands centered at ~2 µm. This is in contrast to the strong 2 µm band present in the Angra dos Reis spectrum. The spectra of D’Orbigny, LEW 86010, and Sahara 99555 are relatively red, but not as red as the Angra dos Reis spectrum.

The presence of a 1 µm band but a very weak 2 µm feature is characteristic of some high-Ca pyroxenes where iron is located almost entirely in the M1 site. Calcium is found in the slightly larger M2 site. These pyroxenes have two absorption bands centered at ~0.90 and ~1.15 µm that partially overlap; however, the presence of olivine in these angrites wipes out this structure in the angrite spectra.

**Asteroid Spectra:** Currently, no asteroid has been found to be a suitable spectral match to the angrites. Asteroids classified as Sr in the Bus and Binzel \([7]\) taxonomy have visible spectra that match angrites, but do not spectrally match angrites in the near-infrared. Many asteroids with distinctive olivine absorption bands (such as A types) have similar spectral slopes to the newly measured angrites; however, angrites do not have these distinctive olivine bands.

**Conclusions:** The parent body or bodies of the angrites had to have existed in the asteroid belt, but presently no spectral analogs to the angrites have been identified.

**References:**

\[2\] Gaffey M. J. (1976) *JGR, 81*, 905-920.  
CORRELATION BETWEEN CHEMICAL AND OXYGEN ISOTOPIC COMPOSITIONS IN CHONDRITES. Robert N. Clayton, Enrico Fermi Institute and Departments of Chemistry and of the Geophysical Sciences, University of Chicago, Chicago, IL 60637 (r-clayton@uchicago.edu).

Although there is growing support for the role of isotopic self-shielding in the photolysis of gaseous carbon monoxide as the main process leading to the “anomalous” isotopic fractionation of oxygen in the early solar system, there is no consensus concerning the physical site of this process [1, 2, 3]. Many recent SIMS studies of refractory inclusions (CAIs) and chondrules have elucidated the mineralogical, chemical, and spatial systematics, which may provide constraints on P,T conditions and timescales for condensation, melting, evaporation, and alteration processes. It is well-established that the primary formation of CAIs involved condensation from a gas of solar chemical and oxygen isotopic composition. An 16O-rich solar isotopic composition, with δ18O and δ17O both near −50‰ relative to SMOW, is implied from the meteorite data [1], and from solar atoms implanted in lunar soil grains [4]. Primary condensates were subsequently altered isotopically by exchange with a gas, probably H2O [2, 3] or atomic O [5], which had been enriched in 18O and 17O by the photochemical process. A clue to the conditions of this secondary process may come from correlations of oxygen isotope abundances with chemical properties related to oxidation reactions, such as the ferrous iron content of chondritic silicates. Such correlations have been seen in chondrules, rims, and crystals in several contexts: in chondrules and their rims in Allende [6], in whole chondrules in Allende [7], in isolated olivine grains in Allende [8], in chondrules in ALH 77007 [9], in relict and host olivine in porphyritic chondrules in Y 81020 [10]. These correlations all show enrichments in 17O and 18O associated with increases in oxidized (ferrous) iron. The examples cited all occur in carbonaceous chondrites, in which the oxygen isotope data fall on or near a slope-1 line in the three-isotope diagram, implying incomplete (non-equilibrium) exchange between a 18O-rich condensed object and a 16O-poor gas species. A similar oxygen-iron correlation is observed in whole-rock analyses of ureilites, which are thought to have carbonaceous-chondrite-like precursors [11].

The correlation between oxygen isotopic composition and the oxidation state of iron is less clear for unequilibrated ordinary chondrites. There is still an isotopic distinction between refractory forsterite cores and FeO-rich rims [12], but an early study of whole chondrules [13] showed no correlation between Δ17O and Fa in six chondrules from Hallingberg and Semarkona. Furthermore, the range in isotopic compositions for these L3 chondrites is much smaller than that in carbonaceous chondrites, and the data define a shallower slope, near 0.7. These features suggest a more complete approach to isotopic equilibrium for ordinary chondrite chondrules that for carbonaceous chondrite chondrules: probably a parent-body effect.

The observed correlations between oxygen isotopic compositions and ferrous iron content (both non-equilibrium properties) in chondrules in carbonaceous chondrites argue in favor of the acquisition of both properties in the same event: chondrule formation. In the photochemical scenarios of [2, 3], the 16O-poor reservoir is segregated from the nebular gas as water ice, and its formation is decoupled from the chondrule-forming process. In the X-wind scenario [1, 4], the photochemical formation of atomic 17O and 18O is directly responsible for the chondrule chemical and isotopic compositions.

EFFECT OF IN-SITU AQUEOUS ALTERATION ON THERMAL MODEL HEAT BUDGETS. B. A. Cohen¹ and R. F. Coker², ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131 (bcohen@unm.edu) ²Los Alamos National Laboratory, Los Alamos, NM 87545.

Introduction: CM chondrites experienced relatively low-temperature aqueous alteration, at least some of which happened on their parent body. The conditions under which aqueous alteration occurred are: fluid temperatures of 0-25°C [1], from the time of asteroid formation up to 15 Myr [2-4] and mobility over scales of only tens of µm [5, 6].

Asteroid thermal models [7] have been successful in describing high-temperature parent-body processing, but no models yet completely characterize CM-type parent bodies. We continue to use our thermal model [8], which addresses the characteristics and physics of the liquid water phase, to develop scenarios that produce liquid water consistent with observed thermal and spatial constraints in CM meteorites.

In-situ alteration budgets: Exothermic alteration reactions (represented by a simple serpentinization reaction) are the chief cause of thermal runaway in our previous work. To further explore the effect of this heat source, we created scenarios that begin with serpentine in the parent body, which might be from aqueous activity in the nebula [9] or in previous parent bodies. We began these runs with 25%, 35%, and 45% initial serpentine by volume and included only enough initial reactants (forsterite and enstatite) to create ~50% total serpentine (the difference in initial serpentine among runs is made up in inert rock).

As expected, in all three cases, the peak temperature at the center of a 20-km parent body is lower than achieved previously (<330K). The peak temperature as a function of radius is shown in Fig. 1 for the 25% initial serpentine run. Since this run undergoes more reactions, it has the largest heat budget. However, even in this case, only the central 5 km reaches the melting temperature of ice so that the volume of the body further altered to ~50% serpentine is only approximately the central 1/6 of the asteroid volume. This total volume doesn’t change significantly between these three scenarios. In addition, in all three cases, radial transport of water occurs over scales of kms rather than µm. This is due to the hydration reactions, which start in the center of the parent body, generating a strong enough temperature gradient to push both liquid and vapor upwards for kms through the rock pore space. The final serpentine and ice composition of the 25% initial serpentine case is shown in Fig. 2. Excess liquid water is pushed up to the outer radius of reactions where it meets the inward moving cooling wave and freezes, nearly filling up the pore space.

Conclusions: Hydration prior to final parent body formation and evolution is insufficient, in itself, to resolve the mismatch between thermal models and CM meteorite observations. Ongoing simulations are exploring parameters such as macroporosity and kinetics of heat release.

OXIDATION-REDUCTION IN METEORITES: THE CASE OF HIGH-NI IRONS.  C. M. Corrigan1 and T. J. McCoy2, 1Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel MD 20723, 2cari.corrigan@jhuapl.edu; 2National Museum of Natural History, Smithsonian Institution, 10th St. and Constitution Ave. NW, Washington DC, 20560-0119.

Introduction: In recent years, our research group has studied a range of asteroidal processes intimately linked to oxidation-reduction on meteorite parent bodies. These include the formation of oxide-bearing clasts on the aubrite parent body [1], melting of ordinary chondrites in the presence of graphite to understand the formation of primitive achondrites [2] and the formation of vesicular basalts from the eucrite and angrite parent bodies by oxidation to form CO [3]. Our most recent foray into oxidation-reduction and its influence on the formation of meteorites has been the study of high-Ni irons, specifically the Ni-rich ungrouped iron Tishomingo [4]. While we have previously explored the role of fractional crystallization in the formation of high-Ni irons, this work specifically examines the role of oxidation.

Our Previous Work on Tishomingo: Tishomingo is an ungrouped iron meteorite that is both rich in Ni (32.5 wt.%) and poor in phosphorus (<0.01 wt.%). The martensitic structure of Tishomingo is consistent with cooling of a high-Ni, low-P taenite and diffusionless transformation to martensite during cooling to ~80K. Oxygen isotopes in a single SiO2 grain are similar to angrites in δ17O and similar in δ18O and bracketed in δ15O by the CR chondrite Renazzo and the metal-rich chondrite GRO 95551. Chemically, Tishomingo is broadly similar to IVB irons for many siderophile elements. IVB irons are the most Ni-rich of the main groups (15.6-18 wt.% Ni) and share the volatile siderophile element depletion of Tishomingo (Fig. 1). Both fractional crystallization and high-temperature condensation have difficulties explaining the composition of Tishomingo [4].

Oxidation. Oxidation might explain the origin of several features in Tishomingo, including the high-Ni and low-P composition, the presence of SiO2, and the fractionated (Fe/Pd)CI and (W/Ir)CI ratios. A recent study of IVB irons [5] advocated a role for oxidation and further argued that the silicate complement to the oxidized IVB irons might be the oxidized angrites. This is an intriguing suggestion in light of the similarity in δ15O between these groups. This oxidation might occur in either the solar nebula or, as suggested by [5], on the parent body.

In their pioneering work, [6] suggested mechanisms for nebular oxidation at a range of temperatures, including reaction of FeO with H2S, O2 and H2O. Mechanisms for oxidizing the core on the parent body have not, to our knowledge, been proposed. The fundamental problem is how to deliver a large quantity of oxygen to the core of a body during or after differentiation. Foreign sources (e.g., comets) would have to penetrate (and likely disrupt) the mantle. The most likely scenario would seem to be reaction of metal with water during differentiation. In this vein, the CR chondrites are particularly interesting. With a Ni concentration in metal on the order of 10 wt.% [7], ~70% of the Fe in the metal would need to be oxidized to produce a core with ~32.5 wt.% Ni. The metal in CR chondrites (~15 wt.%) would require ~3 wt.% H2O, assuming a simple stoichiometric reaction of FeO+H2O=FeO2+H2. This may be realistic, given the hydrated nature of CR chondrite matrix and the high ratio of matrix to metal (~44:7, in vol.%) [7].

We suggest that the most likely precursor for Tishomingo and IVB irons was a volatile-depleted chondritic core that contained both metal with moderate Ni concentrations and hydrated matrix. Oxidation by reaction of metal with water occurred during melting, producing one or more parent bodies with small, Ni-rich cores that underwent fractional crystallization. The complex interplay of condensation, oxidation and fractional crystallization produced the Ni-rich iron in our collections.

UREILITE ATMOSPHERICS: COMING UP FOR ‘AIR’ ON A PARENT BODY.
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Introduction: The ureilite group is unusual. Petrographically, ureilites appear to be samples of a coherent suite that differentiated on a single parent body. The oxygen isotope ratios of the ureilites vary along a mass-independent fractionation (MIF) trend rather than the mass-dependent trend typical of most differentiated asteroids sample suites. The individual ureilites cannot be linked to one another by mass dependent fractionation of oxygen isotopes. Isolated lithic clasts in an individual polymict ureilite cannot be linked to a common process, by mass-dependent fractionation yet they are, by definition, samples of the same parent body. The MIF trend for oxygen is as fundamental property of ureilites, as the intense redox exchange products visible in all samples. While mixing of heterogeneous precursors might explain the variation of ureilite oxygen isotope ratios, it is implausible that such variation would survive the very high temperature processes implicit in ureilite petrography.

The petrographic/experimental evidence suggests that a “smelting” process may be responsible forming ureilites (e.g. Walker and Grove, 1993; Singletary and Grove, 2003). The smelting reaction can be written as: $\text{Fe}_2\text{SiO}_4 + \text{C} \rightarrow \text{FeSiO}_3 + \text{CO} + \text{Fe}$. (A comparable reaction exists for CO$_2$). The reaction consumes graphite to reduce silicate FeO to Fe metal with CO/CO$_2$ as a by-product. The assumption is made that graphite is the reactant and CO gas, the product, even though both graphite/diamond and metal are present in most ureilites. The reaction, as stated, implies that the only mechanism, affecting the oxygen isotope ratios, is mass dependent fractionation. It provides no explicit explanation for the mass independent effects that are so characteristic of ureilites. However, if the CO acts as an oxidizing agent, in reaction with metal, and is reduced back to graphite, then the gas phase reactions can be exploited.

CO or CO$_2$ may provide oxygen in a form that enables symmetry dependent gas phase reactions to produce mass-independent enrichment of $^{16}$O relative to $^{17}$O and $^{18}$O (Theimens 1996). The reaction of such mass independent effects interacts with the solid fraction (ureilite matrix) to produce variable amounts of isotopically heavy olivine and pyroxene as well as a C-polymorph. Alternatively if the process occurs in communication with the parent body surface, the presence of a transient CO atmosphere would permit photochemical disequilibrium in the form of self shielding reactions (Clayton, 2005). In this case, the heat source for ureilite melting and the cause of the CO-photolysis reactions is likely the same – intense solar radiation +/- inductive coupling to magnetic fluctuations both associated with X-wind processing. Accretion and differentiation of a ureilite parent asteroid, should be intimately associated with at least partial mass-independent fractionation of oxygen in the parent body ‘atmosphere’. Interaction of the oxygen fugacity buffering reactions and oxygen isotopic signatures of the final lithic fragments seen in the meteorites is an inevitable consequence.

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HIGH TEMPERATURE EFFECTS INCLUDING OXYGEN FUGACITY, IN PRE-PLANETARY AND PLANETARY METEORITES AND ASTEROIDS.

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Introduction: The properties of asteroids are established by early solar system accretion processes. The elemental and isotopic compositions of a meteorite, and by extension its parent body, reflect the composition of the nonvolatile nebular components available at the time of assembly. The chemical state of the elements, in contrast, is a reflection of both these condensable components and, provides a proxy for volatile components such as H₂, H₂O, CO, CO₂, CH₄, SO₂, that are not usually present in the available samples. High temperature processes produce the gross properties of both pre-planetary and planetary asteroids.

Pre-planetary asteroids that have not experienced planetary differentiation are more abundant than the fully differentiated planetary asteroids. Pre-planetary asteroids are most closely associated with chondritic meteorites of various types. Planetary asteroids, or planetoids, are represented by achondrite groups. All stages from zero differentiation, through intermediate states, to complete differentiation, are represented by meteorites.

Processes: Accretionary processes are manifested as impact signatures in all meteorite types. Craters and, of necessity impact processes, are prominent features of most asteroids. While impact is one source of heating, internal processes of radioactive decay and gravitational overturn also produce heat. External heat sources associated with, for example, X-wind effects must also be considered. Thermal effects range from minimal to metamorphic overprints to wholesale melting. The softening effects of melting in the interior are probably essential for planet scale differentiation.

Although oxygen is volumetrically the most abundant element in most preplanetary and planetary samples, it is often assumed to provide a passive ‘framework’ in which cation exchange reactions occur. However, the importance of redox processes in determining the final outcome of both preplanetary and planetary reactions is paramount. Although oxygen is more abundant than most heavier elements the solar system, it is significantly depleted in most available samples relative to nebular abundance. As a result, there is often too little oxygen to balance the charge on most cation species, thus, most meteorite samples are reduced. Much of the original oxygen in the nebula has been incorporated into volatile species that precipitate in low temperature regimes that exist outside the solar system’s frost line (in the outer asteroid belt). Only samples that originate outside the frost-line will have excess oxygen and may therefore be considered oxidized. This fundamental dichotomy will have very far reaching effects in our interpretation of both oxygen chemistry and its isotopic signatures.

Thermal regimes and oxygen fugacity: High temperatures are not exclusive to the inner solar system, but material that has obviously been processed at high temperatures (planets) is most easily observed there. It is tempting to suggest that the majority of differentiated planetoids formed in our inner solar system, but this is probably a gross oversimplification. Oxygen depletion is typically quantified in terms of oxygen fugacity (fO₂). In particular, the chemical state of iron, the most abundant of the multivalent transition elements, is used as a proxy for fO₂. Unlike the water-rich surface of the earth, where Fe²⁺ and Fe³⁺ coexist, the reduced oxygen content of the inner solar system, has forced the coexistence of Fe⁰ and Fe²⁺ with Fe³⁺ much less common. The implied low oxygen fugacity of most meteorites also requires consideration of the oxidation states of other transition elements such as Cr, V and Ti as proxies.

Because iron is a major element in both preplanetary and planetary meteorites, its oxidation state is important to all associated phase equilibria and hence the magmatic and metamorphic evolution of meteorites and their parent asteroids. The buffering effect of iron metal (Fe in excess of available O) constrains many systems but other oxygen buffering reactions are also important. In rare cases, relatively oxidizing reactions such as those buffered at quartz-fayalite-magnetite appear in meteorites where physical separation of Fe metal has occurred previously (e.g. core formation). More commonly, reduced buffers such as C-CO or CO-CO₂ are recognized. Measurement of the products of these oxygen buffering reactions is increasingly important. The development of microanalytical techniques that determine the chemical state of meteoritic systems at the same spatial scale as elemental and isotopic abundance measurements is critical to progress.

Summary: The abundance of oxygen in both preplanetary and planetary meteorites and asteroids and its representation as oxygen fugacity is fundamental. The high temperature evolution of asteroids and planetoids, particularly when melting occurs, is critically dependent on the buffer assemblages originally present. Achondritic meteorites provide very clear examples of this influence but chondritic samples show more extreme variations. If differences between the volatile abundances of inner and outer asteroid belt are reflected in the oxygen fugacity of representative meteorites, a more complete understanding of the links between oxygen isotope signatures and fugacity will be a fundamental tool.
**OXYGEN ISOTOPIC VARIATION OF ASTEROIDAL MATERIALS.** I. A. Franchi, R. C. Greenwood, L. Baker and A. A. Morris  
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**Introduction:** The vast meteorite collections now available reveal a fantastically diverse range of different rock types and minerals that originate from asteroids. This suite contains minerals that have existed prior to the formation of the Solar System, grains which formed from the gas and dust of the solar nebula and minerals that are the result of secondary process once these early formed grains, together with ices, had accreted onto planetisimals. As such these rocks and minerals record a large range in oxygen isotopic compositions, reflecting the location, sources and conditions of their formation. This offers an important tool in tracking the origin and evolution of asteroidal and planetary material. Differential incorporation of these components into the planetisemals has led to oxygen isotopic variations persisting at all scales, even measurable isotopic variations between a large number of asteroids and planets. As such, oxygen isotopic measurements are a useful tool in the determining the relationships between randomly collected and diverse meteorites. However, this is only possible as we develop our understanding of the isotopic variation within individual asteroids and the internal processes which modify the oxygen isotopic signatures.

**Interstellar Grains:** Interstellar oxides grains isolated from acid residues of primitive meteorites have oxygen isotopic enrichments/depletions of up to two orders of magnitude in $^{16}$O and $^{18}$O [1]. However, with an abundance of $\approx 0.01$ ppm [e.g. 1] these can have no measurable effect on the macro isotopic variation observed in meteorites. More recently, in situ studies of matrix material in primitive chondrites has revealed higher abundances of oxides (up to 50 ppm) and interstellar silicates up to 130 ppm [2]. These higher abundances raise the possibility that some measurable differences at the macro scale could be the result of differential accretion of such grains, particularly if the original abundance was even higher – e.g. interplanetary dust grains contain up to 400 ppm pre-solar silicates [3].

**Nebula Components:** Primitive meteorites contain high temperature condensates from the solar nebula – CAIs, chondrules and mineral fragments. The earliest formed are the CAIs – with oxygen isotopic signatures enriched in $^{16}$O by over 40% [4]. Chondrules, which formed slightly later than the CAIs, are the dominant component of many primitive chondritic meteorites. The oxygen isotopic signature of chondrules from ordinary, enstatite and carbonaceous chondrites are all different [5] indicating distinct formation histories, spatially and/or temporally. It is clear that the oxygen isotopic signature of both CAIs and chondrules has been affected by secondary processes [e.g. 6,7]. Resolving the primary and secondary signatures is needed to understand the origin of these primitive components, particularly for chondrules where there is less consensus about the nature of their formation.

**Asteroidal Processing:** There is clear evidence of asteroidal processes affecting the primitive materials mentioned above. CM, CI and CR chondrites now contain large amounts of phyllosilicates, carbonates, salts, etc which have been produced by water-rock interaction. Such reactions re-distribute oxygen isotopic signatures and generate large isotopic fractionations, which can be used to determine the conditions at which these secondary minerals formed – providing key information about early asteroidal processes. Such work has led to the development of a number of models describing the oxygen isotopic systematics observed [e.g. 8,9] – but uncertainty persists about the fluid conditions during this process.

At higher temperatures, thermal metamorphism and melting lead to homogenization of oxygen isotopic heterogeneity – eventually generating well defined mass fractionation lines – such as those defined by the HED (possibly from Vesta) and angrite meteorites [10], martian, lunar and terrestrial samples. Where such processes are not sufficiently advanced (primitive achondrites) isotopic heterogeneity persists [e.g. 11,12] which can be used to define local areas of homogenisation (i.e. local reservoirs) and to track the onset of melting.

Introduction: Small planetary bodies accreted within 2.4 Myr of solar system formation [1]. The primitive materials (CAIs, chondrules, matrix) incorporated into these asteroids were altered by a variety of secondary processes, including aqueous alteration, shock metamorphism, thermal metamorphism and melting. Here we look primarily at the role played by thermal metamorphism and melting in altering the oxygen isotope systematics of asteroidal materials.

Metamorphism and melting: Peak temperatures recorded by meteorites range from 400°C in the least altered type 3 chondrites [2], to over 1500°C for achondrites formed during large scale planetary melting [3]. This range can be subdivided as follows: i) thermal metamorphism (400°C to 950°C), ii) limited partial melting (950°C to 1250°C), and iii) extensive partial melting (1250°C to >1500°C). These divisions loosely correspond to the thermal regimes experienced by i) chondrites, ii) primitive achondrites, and iii) differentiated achondrites.

Chondrites (400°C to 950°C): Slow rates of oxygen diffusion in the solid state mean that, where thermal metamorphism was essentially dry, only limited disturbance of primary oxygen isotope signatures took place. Consequently, chondrites preserve important information about nebular processes [4]. However, chondrites are not pristine materials. Recent studies of the ordinary chondrites demonstrate that they have complex histories with low-temperature hydrothermal assemblages being progressively obliterated by later thermal metamorphism [5]. Systematic shifts in oxygen isotopes have been recognized in the CO3 chondrites, with a subtle increase in $\Delta^{17}$O values from grades 3.1 to 3.4 indicating an aqueous fluid phase was present during metamorphism [6]. In contrast, a systematic increase in $\delta^{18}$O values in the enstatite chondrites from type 3 to type 6 is not the result of any simple parent body process [7]. In the carbonaceous chondrites significant difficulties exist in establishing genetic links between unequilibrated (type 3) and equilibrated (type 4 to 6) groups. A genetic relationship has been proposed for the CV3 and CK groups [8], which display a trend of decreasing oxygen isotope variation with increasing grade.

Primitive achondrites (950°C to 1250°C): Eutectic melting occurs at about 950°C in the Fe-FeS system, with silicate partial melting commencing at ~1170°C. Asteroidal materials that experienced these conditions show complete recrystallisation followed by progressive loss of Fe-Ni-S and silicate partial melts [9]. Termed primitive achondrites, these meteorites include the ureilites, acapulcoites and lodranites, aubrites, brachintes, winonaites and associated IAB and IIICD irons. In terms of oxygen isotope systematics they show less heterogeneity than chondrites, but still retain significant levels of variability [10]. Thus, acapulcoites and lodranites display textures indicative of about 1% to 20% partial melting of a single parent body [11]. Their $\Delta^{17}$O values (-0.99% to -1.49%) display a significantly greater range than seen in the differentiated achondrites [10]. Likewise, ureilites display major oxygen isotope variation and scatter about the slope 1 line defined by primitive chondrites [10].

Differentiated achondrites (1250 to >1500°C) At relatively high degrees of partial melting complete isotopic homogenisation takes place, with subsequent mass-dependent fractionation resulting in variation along lines with slope 0.52 on $\delta^{17}$O v. $\delta^{18}$O diagrams [10]. Examples of differentiated achondrites include the HEDs and angrites. Pallasites, mesosideites and IIAB irons show similar oxygen isotope variation to the HEDs and may be fragments from the same parent body [9].

Conclusions: Meteorites provide clear evidence of widely varying thermal conditions within asteroids in the early solar system. With increasing temperature there is a progressive loss of primary oxygen isotope variation, complete homogenization occurring at high degrees of partial melting.

Opaque assemblages (OAs), also called Fremdlinges, are complex objects that normally contain Fe-Ni metals, magnetite, sulfides, phosphates, silicates, Pt-metal nuggets and their oxides. OAs occur in Ca-Al-rich inclusions (CAIs), chondrules, and matrix of carbonaceous chondrites [1-10]. The unique and complex mineral components of OAs indicate that they formed at a wide temperature range and under highly variable redox conditions [1]. Oxygen isotopes of OAs, unavailable until now, can help us understand the origin of these objects and provide us insights about the early processes in solar nebula or on asteroid bodies.

The OAs (~100 to ~350 µm in sizes) from the Ningqiang carbonaceous chondrite were observed in its chondrules and matrix. The morphology, texture, and mineralogy of these OAs closely resemble those of CAI OAs [10]. Briefly, they appear as round to oblate spheroids. Major mineral phases are magnetite, Ni-rich metal, troilite/pentlandite, and whitlockite. Minor phases include silicates (olivine and pyroxene) and mesostasis (mixture of silicates and phosphates). Os-Pt-rich Fe-Ni grains (~150 nm in sizes) are rare and appear only in magnetite.

In situ oxygen isotopic compositions were obtained for 12 magnetite and 1 whitlockite grains from 5 Ningqiang OAs. Eight olivine grains adjacent to the OAs were also analyzed. The results are plotted in Fig. 1. Oxygen isotopic compositions of magnetite show variations both among OAs (~16‰ in δ18O) and within one OA (~9‰ in δ18O) of a compound olivine chondrule. All the magnetite data fall along a regression line with a slope of 0.51, which is parallel to the terrestrial fractionation (TF) line with an offset of -2.9‰ in Δ17O. Oxygen isotopic composition of the whitlockite grain falls close to the magnetite regression line (Fig. 1). Oxygen isotopic heterogeneity exists in olivine grains within and among chondrules. The olivine data points plot below the magnetite regression line but above the carbonaceous chondrite anhydrous mineral (CCAM) line. A regression line through olivine data has a slope of -0.7. Magnetite has higher Δ17O values than its adjacent olivine. In the OA of a compound olivine chondrule, the average Δ17O of magnetite is (-2.7±0.5)‰, much higher than that of adjacent olivine (-6.1±0.5‰).

It has been proposed that OAs could have formed by: 1) direct nebular condensation [2, 3, 6], 2) crystallization from immiscible metallic-sulfide-oxide liquids during CAI and chondrule formation [7, 8], and 3) low temperature oxidation of preexisting metal alloys [4, 8, 9]. The oxygen isotopic compositions of OAs in chondrules and matrix from Ningqiang present conclusive evidence that OAs formed by aqueous alteration of metal alloy precursors on parent bodies. Therefore, OAs do not represent the oldest solids in the solar nebula, instead, they provide constraints on secondary processes on asteroidal bodies.

WATER DISTRIBUTION IN THE ASTEROID BELT. E. S. Howell, Arecibo Observatory, Arecibo PR 00612, USA, (ehowell@naic.edu), A. S. Rivkin, Dept. Earth, Atm. and Planetary Sciences, MIT, Cambridge, MA 02139, USA, F. Vilas, NASA JSC, Houston, TX 77058, USA.

Water is abundant in the solar system, reactive, and a sensitive thermal tracer in asteroids. We learn a great deal about the formation conditions and thermal history of asteroids by measuring where the water is and is not. Water ice was presumably incorporated into at least the middle and outer belt asteroids. If these objects were heated, melting the ice, the water would quickly react with any silicate minerals forming phyllosilicates, containing structural hydroxyl groups and possibly also interlayer water molecules. We see the spectral signatures of these hydrated minerals in the reflectance spectrum of asteroids at 3 microns. The 3-micron absorption feature is a very useful diagnostic spectral feature on asteroids (Lebofsky et al., 1981; Jones et al., 1990). It has been suggested that the 3-micron band could be produced by effects unrelated to water/OH, but all of the alternative interpretations proposed make predictions that are not supported by the observations (Rivkin et al., 2003). In spite of improved infrared instrumentation, it remains difficult to observe the 3-micron band from the ground because of strong atmospheric absorption. Another spectral feature that is easier to observe, and can be detected by smaller telescopes on fainter objects, is the 0.7-micron phyllosilicate feature (Vilas and Gaffey, 1989; Howell et al., 2002). This absorption band is a Fe$^{2+}$-Fe$^{3+}$ charge transfer band in iron-bearing phyllosilicates. Although there is clearly a correlation between the 0.7 and 3-micron features, there are inconsistencies as well. Hiroi et al., (1996) showed that mild heating subsequent to aqueous alteration can explain objects that have the 3-micron feature but not the 0.7 feature. However, the 0.7-micron feature should never be present without the 3-micron feature, at the same rotation phase. Our observations bear this out: In all cases we have found the 3-micron band present on objects with a 0.7-micron band at the same rotation phase.

If the 0.7-micron band is seen, Fe-bearing hydrated minerals are present. However, if it is not seen, no conclusion can be drawn about the hydration state. In a fairly small sample (though not unbiased) about half of the objects without the 0.7-micron band did have the 3-micron band, the other half did not. Our observations of the 0.7-micron absorption band at different rotation phases reveals that a large fraction of hydrated asteroids do show variations in the spectral band occurrence and depth on different faces. On a compositionally heterogeneous asteroid, we might expect to see hydrated spots exposed on the surface at some places and not others. However, thermal models suggest that, since aqueous alteration is exothermic, once it starts, the entire body becomes hydrated: Hydration is expected to be homogeneous. Our observations clearly show variability in hydration. This conflict could be resolved if the hydration reaction is limited by the amount of water available. These observations are primarily of larger asteroids (D $>$ 100 km). We do not (yet) know the spatial scale of the hydrated areas, or whether the patchy exterior necessarily implies a heterogeneous interior. We are pursuing observations of smaller asteroids that will answer these questions and help constrain aqueous alteration models.

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