Our studies are highly interdisciplinary, but are focused on the processes and products of early planetary and asteroidal differentiation, especially the genesis of the ancient lunar crust. The compositional diversity that we explore is the residue of process diversity, which has strong relevance for comparative planetology.

Most of the accessible lunar crust consists of materials hybridized by impact-mixing. Our lunar research concentrates on the rare pristine (unmixed) samples that reflect the original genetic diversity of the early crust. Among HED basalts (eucrites and clasts in howardites), we distinguish as pristine the small minority that escaped the pervasive thermal metamorphism of the parent asteroid’s crust. We have found a correlation between metamorphically pristine HED basalts and the similarly small minority of compositionally evolved “Stannern trend” samples, which are enriched in incompatible elements and titanium compared to main group eucrites, and yet have relatively high mg ratios. Other topics under investigation included: lunar and SNC (martian?) meteorites; igneous meteorites in general; impact breccias, especially metal-rich Apollo samples and polymict eucrites; siderophile compositions of the lunar and martian mantles; and planetary bulk compositions and origins.

The Moon

Warren [2004a] produced a comprehensive review of lunar geochemistry for the Treatise on Geochemistry. Besides summarizing a great deal of past work, this review included some data “synthesis” that led to new interpretations. For example, calculations revealed the implausibility of regarding the εNd results for ferroan anorthosites as representative of their igneous petrogenesis. From scrutinizing the data base for lunar highland rock ages and siderophile-element compositions, Warren [2004a; also 2003] noted that a popular version of the “cataclysm” hypothesis of lunar cratering history (i.e., the hypothesis that invokes a “spike” at ~3.9 Ga) rests on a dubious assignation of 3.9 Ga as the age of Nectaris. Actually, a large class of Apollo 16 impact melt breccias, spatially associated with the Descartes Highlands and thus probably of Nectaris origin, consistently yield ages closer to 4.1 Ga.
Warren et al. [2005; also Warren and Kallemeyn, 2002; and Warren and Bridges, 2004] have analyzed a variety of “new” lunar meteorites. Several of these rocks are difficult to classify. Dhofar 081 is basically a fragmental breccia, but much of its groundmass features a glassy-fluidized texture indicative of localized shock melting. Also, much of the matrix glass is swirly-brown, suggesting a possible regolith derivation. We interpret DaG 400 as an extremely immature regolith breccia consisting mainly of impact-melt breccia clasts; and Dhofar 026 as an unusually complex anorthositic impact-melt breccia, with scattered ovoid globules that formed as clasts of mafic, subophitic impact melt. The presence of mafic crystalline globules in a lunar material, even one so clearly impact-heated, suggests it may have originated as a regolith. Our new data, and a synthesis of literature data, suggest a contrast in Al₂O₃-incompatible element systematics between impact melts from the central nearside highlands, where Apollo sampling occurred, and those from the general highland surface of the Moon. Impact melts from the general highland surface tend to have systematically lower incompatible element concentration, at any given Al₂O₃ concentration, than those from Apollo 16. In the case of Dhofar 026, both the bulk rock and a comparatively Al-poor composition (14 wt% Al₂O₃, 7 µg/g Sm) extrapolated for the globules, manifest incompatible element contents well below the Apollo 16 trend. Impact melts from Luna 20 (57°E) distribute more along the general highland trend than along the Apollo 16 trend. Siderophile elements also show a distinctive composition for Apollo 16 impact melts: Ni/Ir averaging 1.8× chondritic. In contrast, lunaite impact-melt breccias have consistently chondritic Ni/Ir. Impact melts from Luna 20 and other Apollo sites show average Ni/Ir almost as high as those from Apollo 16. The prevalence of this distinctive Ni/Ir ratio at such widely separated nearside sites suggests that debris from one extraordinarily large impact may dominate the megaregolith siderophile component of a nearside region ≥2300 km across.

Highland polymict breccia lunaites and other KREEP-poor highland regolith samples manifest a strong anticorrelation between Al₂O₃ and mg. The magnesian component probably represents the chemical signature of the Mg-suite of pristine nonmare rocks, in a “pure” form unaltered by the major KREEP-assimilation common among Apollo Mg-suite samples. The average composition of the ferroan anorthositic component is now well constrained at Al₂O₃ ~ 29-30 wt% (implying about 17-19 wt% modal mafic silicates), in good agreement with the composition predicted for flotation crust over a “ferroan” magma ocean.

Lunar meteorite Yamato-983885 is a highland regolith breccia with mineral compositions similar to those of another Yamato lunaite regolith breccia, Y-791197. We [Warren and Bridges, 2004] studied it petrographically and analyzed a 220-mg bulk-rock chip. We found exceptionally high concentrations of siderophile elements Ni, Ir and Au (e.g.,
Ir = 22 ng/g), in approximately chondritic proportions to one another. In a ~1 cm² thin section, we identified ~15 glassy regolith spherules and spherule fragments. These spherule-abundance and siderophile results imply at least moderate regolith maturity, for a lunar regolith breccia. If Y-983885 and Y-791197 were paired, we would not expect to find a very high degree of compositional-petrologic disparity between them. Most significant for testing the Y-983885 - Y-791197 pairing hypothesis is a whopping disparity in the levels of incompatible (KREEP-associated) trace elements. Like most lunaite highland regolith breccias, Y-791197 is very KREEP-poor, with a mass-weighted literature mean Th concentration of just 0.33 μg/g. Incompatible elements are consistently ~5 times more enriched in Y-983885 than in a literature average for Y-791197. This degree of compositional disparity exceeds what could reasonably be expected from heterogeneity within a single moderately mature lunar regolith breccia.

A close precedent for the composition of Y-983885 is the average soil from the prototypical nearside highland site, Apollo 16. However, the Y-983885 regolith is significantly less anorthositic than that at Apollo 16. Y-983885 is in many respects similar to the KREEPy Calcalong Creek regolith breccia lunaite, especially in terms of major elements and mafic-associated elements such as Mn, Cr, Sc and V. An evolved (KREEP?) component is also evident in the petrography of Y-983885. For example, one of the largest clasts found (~400 x 200 μm) consists of roughly (in vol%) 40% ilmenite, 25% mesostasis, 20% Na-rich plag (An51-62), 10% K-feldspar, ~4% intergrowth of K-spar with silica, and ~2% merrillite.

Warren [2005; also Warren, 2004b] discussed implications of these and other recent results for lunaites, for calibration of the bulk-Moon Th map and estimation of the bulk-Moon composition. The Lunar Prospector GRS team (D. Lawrence et al.) initially calibrated their Th and K data sets entirely on the basis of a priori assumptions about physical parameters such as the thorium atom density, the calculated gamma-ray production rate, and the mass attenuation coefficient for 2.6-MeV g-rays in the lunar regolith. Based on comparison with ground truth from lunar samples, including lunar meteorites, it became apparent that this calibration was not very good. Not all of the sources of error are easily identified, but among them is surely the assumption by Lawrence et al. that the individual pixel with the lowest counting rate anchors the calibration at 0 μg/g Th. As discussed by Warren [2005; also a 2000 LPSC abstract], this assumption inevitably led to an erroneous calibration, because each of the thousands of pixels that covered typical farside highlands, which are known to be extremely Th-poor based on statistics for lunar meteorites) has a considerable statistical uncertainty in its count rate. The counterintuitive implication is that in
an accurate calibration, the individual pixel with the lowest count rate should have a nominal Th concentration less than zero [Warren, 2005].

As Warren [2005; also a 2000 LPSC abstract] showed, using Apollo and Luna samples of documented collection location for ground truth, a miscalibration of ~1.6 μg/g is inferred for the zero under the initial calibration for Lunar Prospector global Th data. A similar offset of ~1.0 μg/g is implied by comparison with the global regolith Th spectrum as constrained using mainly lunar meteorite regolith breccias. In response to Warren’s [2000 LPSC abstract] critique, as well as a roughly similar critique from the Washington Univ. group (J. Gillis et al.) and a preprint version of Warren [2005], the LP-GRS team (D. Lawrence et al.; T. Prettyman et al.) revised the Th calibration. As discussed in Warren [2005], the newer calibration is much improved, but still too high for the major fraction (80%) of the Moon’s surface with <3 μg/g of Th, based on comparison with Apollo and Luna samples of documented collection location and with the global regolith Th spectrum as constrained using mainly lunar meteorite regolith breccias. In the revised calibration by Prettyman et al, the LP-GRS data imply the average global surface Th = 1.58 μg/g. However, that calibration yields implausibly high concentrations for the three most Th-poor documented sampling sites; it extrapolates to a nonzero Lunar Prospector Th, ~0.7 μg/g, at zero sample Th; and it results in a misfit toward too-high Th when compared with the global regolith Th spectrum as constrained using mainly lunaite regolith breccias. Another problem is manifested by Th vs. K systematics. Ground truth data plot consistently to the high-Th/K side of the Prospector data trend, offset by a factor of 1.2. Warren [2005] proposed a new calibration that represents a compromise between the Th levels indicated by ground truth constraints and the Prettyman et al. calibration. Conservatively assuming that the Th vs. K issue is mostly a K problem, the average global surface Th is estimated to be ~1.35 μg/g, in agreement with older Apollo data.

Warren [2005] noted that the revised Lunar Prospector GRS calibration for Th only the Moon’s remarkable global asymmetry in KREEP abundance is even more pronounced than previously supposed. The surface-Th concentration ratio between the hemisphere antipodal to the Procellarum basin and the hemisphere centered on Procellarum is reduced to 0.24 in the new calibration. This extreme disparity is most simply interpreted as a consequence of origin of Procellarum at a time when the Moon still contained at least a thin residual layer of globe-wide magma ocean. Allowing for diminution of Th with depth, the extrapolated bulk-crustal Th is ~0.73 μg/g. Warren [2005] found that further extrapolation to bulk-Moon Th yields ~0.07 μg/g, nearly identical to the consensus estimate for Earth’s primitive mantle. Assuming chondritic proportionality among refractory lithophile elements implies Al₂O₃ ~ 3.8 wt%. Warren [2005] also noted that the Moon’s bulk-mantle mg ratio is only weakly constrained.
by seismic and mare-basaltic data. KREEP- and mare-free lunaite regolith samples, other
thoroughly polymict lunar meteorites, and a few KREEP-free Apollo highland samples
manifest a remarkable anticorrelation on a plot of \( \text{Al}_2\text{O}_3 \) vs. \( \text{mg} \). This trend implies that an
important component of the Moon is highly magnesian. The bulk Moon is inferred to have an
Earth-like oxide \( \text{mg} \) ratio of \( \sim 87-88 \text{ mol}\% \). The close resemblance between the bulk Moon
and Earth’s primitive mantle extends to moderately volatile elements, most clearly Mn.
Unless major proportions of Cr and V are sequestered into deep mantle spinel, remarkably
Earth-like depletions (vs. chondrites) are also inferred for bulk-Moon Cr and V.

**Martian Meteorites**

Warren et al. [2004] followed up on our discovery of the Los Angeles shergottite by
assessing mineralogical and petrological contrasts between the two stones of this extremely
ferroan and Cr-poor martian meteorite. The two stones are similar in many characteristics,
strongly suggesting that they originated from a single flow or shallow intrusion. However,
stone 2 is more ferroan and enriched in late-stage materials than its larger, and more widely
studied, sibling. Stone 2 has a far higher abundance (~25 vol\%) than stone 1 (10 vol\%) of
combined “opaques,” meaning not only conventional opaque minerals but also, and more
abundantly, fine-grained symplectitic intergrowths of fayalite + ferroan augite + silica
(interpreted as pyroxferroite breakdown material, PBM). The bulk composition of the PBM is
close to that of stoichiometric pyroxferroite, with roughly 45 wt% FeO. Extensive zonation
within the pyroxenes of both stones is consistent with origin by closed-system fractional
crystallization of the parent basaltic melt(s). However, the compositional and modal disparity
between the two stones suggests that they formed in an environment where at least mild
decimeter-scale differentiation occurred. Probably in both stones crystallization began from
similar melts with \( \text{mg} \sim 27-28 \text{ mol}\% \), but during crystallization significant migration of the
melt component occurred, perhaps by crystal settling and/or filter pressing. Stone 2 acquired
an enhanced proportion of residual melt, and thus higher proportions of late-stage materials
such as PBM, oxides, and phosphates. Within the PBM, clinopyroxene poikiloblastically
encloses fayalite and silica. At least some of the PBM had already formed by decomposition
of pyroxferroite, before the major shock that caused the very scarce brecciation within Los
Angeles. However, the low abundance of fractures within PBM, in comparison to pyroxene
and some other minerals, may be an indication that the textures of PBM regions typically did
not assume their final detailed configuration until after the last major shock. The steep slope
of a pyroxene \( \text{mg} \)-Cr correlation suggests that igneous crystallization occurred at higher \( \text{fO}_2 \)
in Los Angeles than in otherwise similar shergottites such as QUE94201, Shergotty and
Zagami.
During the grant period, Warren continually compiled geochemical data for martian meteorites (and analyzed “new” martian meteorites), and this work has since contributed to a comprehensive review of the geochemistry and petrology of martian meteorites by Bridges and Warren [2004]. In this paper, we proposed a new subclassification of the shergottites. Shergottites are customarily subclassified on mineralogical grounds. To date, about 9 basaltic shergottites have been discovered, 8 olivine-phyric shergottites, and 6 peridotitic (“herzolitic”) cumulates. We suggested a more genetically significant way of subclassifying shergottites based on geochemistry. There are again three groups, which we define as highly depleted shergottites (HDS), moderately depleted shergottites (MDS), and slightly depleted shergottites (SDS). Even the SD shergottites (which constitute the most numerous subclass) are in some respects depleted vs. chondrites, but the depletions are only very mild in comparison to HD shergottites. These geochemical subclasses correlate only loosely with the mineralogical subclasses. Most HDS are olivine-phyric; but HDS QUE94201 is a basaltic melt-rock. Most MDS are cumulate peridotites; yet EET79001 contains two lithologies (basaltic and phryc-xenocrystic), both MD. Most of the SDS are basaltic without conspicuous phenocrysts; yet NWA1068 is olivine-phyric.

The ratio $La/Lu$ ($Lu$ being the heaviest REE) is particularly diagnostic. The HDS subtype have $La/Lu$ consistently close to $0.12 \times CI$; the SDS subtype have $La/Lu$ consistently close to $1.0 \times CI$; and the MD peridotitic shergottites have intermediate $La/Lu$ (despite their cumulate nature, the MD peridotitic shergottites have REE patterns lower but roughly parallel to the patterns of their parent melts). These trace-element signatures of highly diverse extents of depletion are paralleled by isotopic variations. For example, initial $^{87}Sr/^{86}Sr$ ratio, normalized to the typical shergottite age of 175 Ma, is consistently close to 0.701 among highly depleted shergottites, close to 0.722 among SD shergottites, and close to 0.711 among the MD shergottites. A similar pattern is manifested using $\varepsilon Nd$ in lieu of $^{87}Sr/^{86}Sr$. As noted by other workers, the shergottite depletion signatures also correlate with oxygen fugacity.

The diversity of depletion characteristics among shergottites has often been interpreted as a manifestation of varying extents of assimilative mixing between primary, HD-type basalt and a putative enriched (high $La/Lu$, REE-rich, Sr-rich, etc.) material. The setting for the assimilative mixing and the detailed composition of the enriched component are speculative; the assimilated material is often referred to simply as “crust.” Nyquist et al. have proposed a roughly quantitative model in terms of Sr and Nd, including isotopic ratios. However, these authors did not model $La/Lu$ (or any analogous ratio such as $La/Yb$). Bridges and Warren [2005; also Warren and Bridges, 2005] showed that a mixing model based on the assumptions of Nyquist et al. for Nd, Sr and $^{87}Sr/^{86}Sr$ in the crust and HD-basalt components,
augmented with an assumption that the La/Lu of the crust component was equivalent to lunar KREEP in terms of REE pattern (i.e., La/Lu = 2.28 × CI chondrites) yields a marginally satisfactory fit to most of the shergottite compositions, the main exception being EET79001. However, this model yields (by extrapolation from all the other assumed parameters) a dubiously low Sr concentration for the HD-basalt component, which translates into relatively high (crust-dominated) $^{87}\text{Sr}/^{86}\text{Sr}$ at any given La/Lu position along the mixing curve. No known shergottite analysis has Sr < 20 μg/g. The mass-weighted mean of two precise analyses for QUE94201 is 48 μg/g, and the only other applicable result (most HD shergottites have suffered warm-desert weathering) is 20 μg/g for Y980459. More realistically, the average HD composition has Sr ~ 35 μg/g. The mixing parabolas are also sensitive to the assumed La/Nd and Lu/Nd (and thus La/Lu) ratios of the enriched component. In 35 μg/g models, the proportion of the enriched component that has to be added to the HD end-member to reach the SD shergottites is ~17 wt%; in the 19 μg/g model, it is ~10 wt%. Only the model with flat La/Lu comes close to matching the combination of low La/Lu and relatively high initial $^{87}\text{Sr}/^{86}\text{Sr}$ observed in the two distinct (but similar) EET79001 lithologies. An approximately flat REE pattern for an otherwise highly enriched component is hardly expected as a typical outcome from planetary igneous differentiation. It seems more likely that the model is oversimplified; MD and SD shergottites are not simple dilutions of HD matter by a single, uniform "crust" component.

**Ureilites**

Ureilites, the second most abundant type of achondrite, formed as partial melt restites (olivine + pyroxene + minor, 0.2-6 wt%, carbon) in the mantles of carbonaceous asteroids. Warren [2004c] studied the petrology of unusual Cr-silicates in the NWA766 ureilite. He showed that this extraordinary phase is not, as previously supposed, a Cr-garnet. It is instead a phase with olivine-like stoichiometry, in which the Cr is preponderantly divalent (Cr$^{2+}$). Enrichments of Cr, presumably mainly divalent, were also found in the reduced rims of olivines in NWA766 and various other ureilites. Warren [2004c] also used mainly literature data to show that the smelting reaction (basically C + MgFeSiO₄ = MgSiO₃ + Fe + CO) popularly invoked as a key aspect of ureilite igneous petrogenesis, putatively accounting for the ureilites' highly diverse mafic-silicate-core mg ratios, in fact could not have played a major role. Far too much volume of CO (or CO₂) gas has too form, and too much Fe-metal has to form (and yet not be lost — based on consistely moderate-high siderophile concentrations), to account for the observed mg diversity. Moreover, an expected anticorrelation between mg and carbon is not observed.
Warren [2004d; also Kallemeyn and Warren, 2005] used siderophile trace element data acquired for various ureilites over many years to constrain the process of incipient asteroidal core formation. Degrees of melting were sufficient to virtually eliminate plagioclase from the entire ureilite milieu; at temperatures of ~1210-1300°C. At about the same time the ureilites underwent this partial melting, they acquired moderate to major depletions in siderophile elements. Natural siderophile variations are notoriously untidy, but collectively the many ureilite samples can potentially furnish important insight into the early stages of core formation. Ureilites have Ni, Au and Ir concentrations that are very high in relation to NAA detection limits, so analytical precision should be excellent. Os is also easily detected, given a favorable counting schedule; Ru and some interesting moderately siderophile elements such as As and Se are doable but more challenging. Combined with literature data, we now have constraints for Ir in 44 ureilites; with similar tallies for Ni (47) and Au (39).

Using our new data plus literature ureilite data, a plot of Au vs. Ni shows a good, approx. linear correlation ($r = 0.87$), which interestingly extrapolates to a much lower Au/Ni (by a factor of ~2) than the range for carbonaceous chondrites. Au vs. Ir and Ni vs. Ir show much more scatter. But a very strong correlation ($r = 0.95$) is manifested by Au/Ir vs. Ni/Ir, which parallels a trend among carbonaceous chondrites, but is offset (toward lower Ni/Au) by a large and clearly significant factor. Analogous distributions are found if As/Ir, Co/Ir, Se/Ir or Te/Ir are substituted for Ni/Ir, except with these parameters the carbonaceous chondrite and ureilite trends approximately overlap. Evidently, the final levels of Au and Ni among ureilites were established by a different process than the process(es) that had earlier depleted both, but Au more than Ni. Also, the effect of metal removal should be to drive a restite composition toward higher Au/Ir and Ni/Ir (since Ir is the most highly siderophile of these elements), yet the main direction of ureilite differentiation, assuming the precursor materials were chondrite-like, was toward lower Au/Ir and Ni/Ir.

When the grand average composition of all ureilites is normalized to CI and plotted as a function of the elements’ solar nebula 50% condensation $T$, the depletions in elements like Au, Co, Ni and As appear to be in conformity with a loose overall correlation. However, two somewhat siderophile elements (Ge and Zn) are little-depleted even though moderately volatile; instead, Ge and especially Zn plot near C, which is highly volatile (in a solar-nebula setting) and yet only marginally depleted relative to CI. The grand average ureilite composition yields a tidier trend when instead of a measure of volatility, we make the x-axis parameter a measure of affinity of the elements for S-rich metallic melt. The first metal-rich melts presumably contained about 20-30 wt% S, as an inevitable consequence of the Fe-FeS eutectic relationship. N. Chabot and her colleagues have constrained the relevant partitioning
relationships for many elements. The available data manifest an impressive match between ureilite observed compositions and a model assuming that the major yet not exhaustive depletions of typical ureilites arose by down-seepage of small proportions of S-rich metallic melt. Such a model seems plausible from the perspective of independent constraints on the nature of ureilite partial melting. The virtually complete removal of plagioclase implies that a total of (at least) 20-25 wt% of silicate melt was ultimately extracted. Application of compaction theory to the scenario of asteroidal partial melting suggests that the melt could never escape in time (before the decay of $^{26}$Al and/or other short-lived primordial heat sources) by steady, low-$f$ percolation. Thus, paradoxically, melt build-up to high-$f$ "batch" partial melting would be a more temporally efficient melt removal mechanism. Moreover, the incompatible element levels of typical ureilites militate for a melting style much closer to batch (a.k.a. "equilibrium") melting than to fractional fusion.

**Eucrites**

Warren [2002; 2003] continued to amass data for "new" HED meteorites, with particular emphasis on the tiny minority that possess unequilibrated mafic silicates, i.e., that escaped the near-ubiquitous thermal metamorphism of the HED-asteroidal crust(s). Following the pioneering work of H. Takeda, these eucrites are termed "pristine." Northwest Africa 1000 [Warren, 2002] is petrologically highly complex. It is extraordinarily shocked (much of its former plagioclase is now Maskelynite); many of its large, unequilibrated pyroxenes are crisscrossed by fayalite-rich veins; and it was substantially weathered in the north African desert. Like most of the "pristine" (unequilibrated) eucrites, NWA1000 has uncommonly high concentrations of incompatible trace elements. Yamato 981651, in contrast, has normal-low concentrations of incompatible elements [Warren, 2003]. However, Y-981651 appears petrographically to be an impact melt, with a minor proportion (0.5%) of relict, corroded grains of silica, plagioclase, Cr-spinel and pyroxene set in a vesicular, vitrophyric groundmass. The pyroxene zonation trend in Y-981651 is significantly different (initially higher-Wo, and possibly also "flatter" in its Fe,Ca-enrichment path, on the pyroxene quadrilateral) in comparison to all other "pristine" eucrites. The nearest precedent for Y-981651 is Pasamonte. Both of these eucritic impact melts are very poor in siderophile trace elements in comparison to analogous impact melt rocks from the Moon.
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WARREN P. H. (2004c) Lunar Prospector data imply an age of 4.1 Ga for the Nectaris basin, and other problems with the lunar “cataclysm” hypothesis. Third International Conference on Large Meteorite Impacts, Nördlingen, Germany (abstract 4129).


