



## The Origin of Lunar Mascon Basins

H. J. Melosh *et al.*  
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same conditions, the  $^{15}\text{N}$ -enriched analog  $\{[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Ti}]_3(\mu_3\text{-}^{15}\text{N})(\mu_2\text{-}^{15}\text{NH})(\mu_2\text{-NH})_2\}$  ( $6\text{-}^{15}\text{N}_2$ ) was obtained (Fig. 1B). The  $^{15}\text{N}$  NMR spectrum of  $6\text{-}^{15}\text{N}_2$  showed a singlet at  $\delta_{\text{N}}$  424.6 and a doublet at  $\delta_{\text{N}}$  101.3 with  $J_{\text{NH}} = 64.0$  Hz, which could be assigned to a  $\mu_3\text{-N}$  nitrido and a  $\mu_2\text{-NH}$  imido unit, respectively. These results suggest that the newly incorporated  $\text{N}_2$  molecule is split into a  $\mu_3\text{-N}$  nitrido unit and a  $\mu_2\text{-NH}$  imido unit, whereas the nitrido unit originally existing in **5** is hydrogenated to a  $\mu_2\text{-NH}$  imido group. No apparent reaction between **5** or **6** and  $\text{H}_2$  (up to 8 atm) was observed at room or higher temperatures (up to  $150^\circ\text{C}$ ). However, when the hydrogenolysis of the trialkyl complex **1** with  $\text{H}_2$  was carried out in the presence of 1 equiv of **5**, the tetranuclear di-imido complex **2** was formed quantitatively (Fig. 1B), possibly through hydrogenation of the nitrido group of **5** with a mononuclear Ti hydride species such as  $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{TiH}_3$  formed in situ by hydrogenolysis of **1** (39). These results could account for the formation of **2** in the hydrogenolysis of **1** with  $\text{H}_2$  in the presence of  $\text{N}_2$  (Fig. 1A), in view of the facile formation of **3** in the hydrogenolysis of **1** in the absence of  $\text{N}_2$  and the high reactivity of **3** with  $\text{N}_2$  to give **5**. Although the origin of the unusually high reactivity of the trinuclear mixed valence Ti(IV)/Ti(III) heptahydride complex **3** is subject to further studies, our findings demonstrate that hydride ligands in a metal hydride cluster can serve as the source of both electron and proton and that multimetallic transition metal hydride complexes can serve as a platform for nitrogen fixation.

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- The hydrogenolysis of **1** under a higher  $\text{H}_2$  pressure (80 atm) at  $60^\circ\text{C}$  led to formation of a larger amount of the octahydride **4** (~20%) and a smaller amount of the heptahydride **3** (~50%).
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- A similar DFT study showed that the reaction of the tetranuclear Ti octahydride complex **4** with  $\text{N}_2$  is less favored, because its LUMO is distributed on the four Ti atoms with competitive orbital contribution and is unsuitable in orbital shape for an overlap with the HOMO of  $\text{N}_2$  (see fig. S26 and table S3 in the supplementary materials).
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- The hydrogenation of the nitrido group of **5** with a mixed alkyl/hydride species formed in situ by partial hydrogenolysis of **1** followed by further hydrogenolysis of the alkyl species could not be ruled out in this case.

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#### Supplementary Materials

www.sciencemag.org/cgi/content/full/340/6140/1549/DC1  
Materials and Methods  
Figs. S1 to S26  
Tables S1 to S3  
Scheme S1  
References (40–50)

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## The Origin of Lunar Mascon Basins

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High-resolution gravity data from the Gravity Recovery and Interior Laboratory spacecraft have clarified the origin of lunar mass concentrations (mascons). Free-air gravity anomalies over lunar impact basins display bull's-eye patterns consisting of a central positive (mascon) anomaly, a surrounding negative collar, and a positive outer annulus. We show that this pattern results from impact basin excavation and collapse followed by isostatic adjustment and cooling and contraction of a voluminous melt pool. We used a hydrocode to simulate the impact and a self-consistent finite-element model to simulate the subsequent viscoelastic relaxation and cooling. The primary parameters controlling the modeled gravity signatures of mascon basins are the impactor energy, the lunar thermal gradient at the time of impact, the crustal thickness, and the extent of volcanic fill.

High-resolution gravity data obtained from NASA's dual Gravity Recovery and Interior Laboratory (GRAIL) spacecraft now provide unprecedented measurements of the gravity anomalies associated with lunar

impact basins (1). These gravity anomalies are the most striking and consistent features of the Moon's large-scale gravity field. Positive gravity anomalies in basins partially filled with mare basalt, such as Humorum (Fig. 1), have been

known since 1968, when lunar mass concentrations, or "mascons," were discovered (2). Mascons have subsequently been identified in association with impact basins on Mars (3) and Mercury (4). Previous analysis of lunar gravity and topography data indicated that at least nine such mare basins possess central positive anomalies, exceeding that attributable to lava emplacement

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alone (5). This result is confirmed with GRAIL observations over basins that lack basaltic infilling, such as Freundlich-Sharonov (Fig. 1), which are also characterized by a central positive free-air gravity anomaly surrounded by a concentric gravity low. These positive anomalies indicate an excess of subsurface mass beyond that required for isostatic (mass) balance—a “superisostatic” state. Mascon formation seems ubiquitous in lunar basins, whether mare-filled or not, despite their formation by impacts (a process of mass removal that leaves a topographic low, which normally implies a negative gravity anomaly), making mascons one of the oldest puzzles of lunar geophysics. Their elucidation is one of the goals of the GRAIL mission.

The gravity anomaly structure of lunar mascon basins was previously attributed to mantle rebound during collapse of the transient crater cavity (5, 6). This process requires a lithosphere beneath the basin capable of supporting a superisostatic load immediately after impact, a proposal that conflicts with the expectation that post-impact temperatures were sufficiently high to melt both crustal and mantle rocks (7). Alternatively, it was proposed (8) that mascons are created by flexural uplift of a thickened annulus of subisostatic (a deficiency of the subsurface mass required for isostasy) crust surrounding the basin, concomitantly lifting the basin interior as it cooled and the underlying lithosphere became stronger. This alternative model emphasizes the annulus of

anomalously low gravitational acceleration surrounding all mascons (Fig. 1) (1, 9, 10), a feature previously attributed to thickened crust (5, 6) or perhaps brecciation of the crust during impact. Many mascons also exhibit an annulus of positive gravitational acceleration surrounding the annulus of negative gravity anomaly, so the gravity structure of most lunar basins resembles a bulls-eye target (Fig. 1).

The role of uplift in the formation of mascon basins has been difficult to test because little is known about the mechanical state of basins immediately after cavity collapse. Here, we couple GRAIL gravity and lunar topography data from the Lunar Orbiter Laser Altimeter (LOLA) (11) with numerical modeling to show that the gravity anomaly pattern of a mascon is the natural consequence of impact crater excavation in the warm Moon, followed by post-impact isostatic adjustment (12) during cooling and contraction (13) of a voluminous melt pool. In mare-filled basins, this stage in basin evolution was followed by emplacement of mare-basalt lavas and associated subsidence and lithospheric flexure.

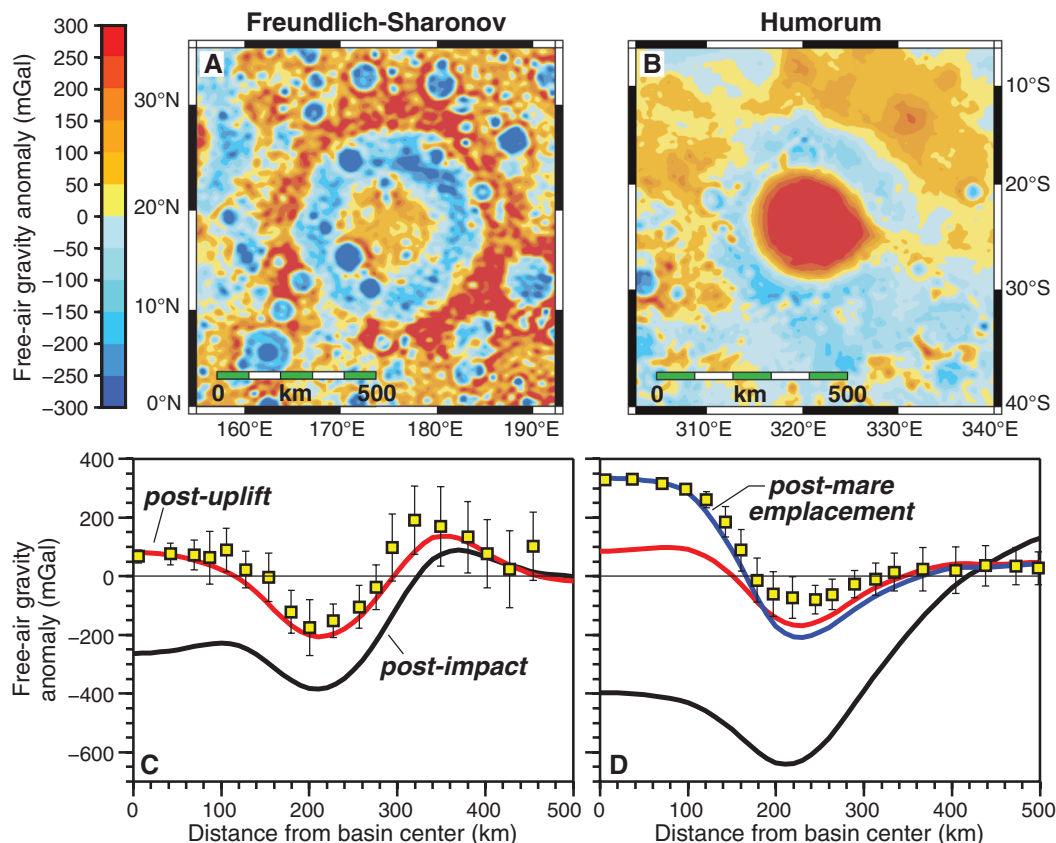
We used the axisymmetric iSALE hydrocode (14–16) to simulate the process of crater excavation and collapse. Our models used a typical lunar impact velocity of 15 km/s (17) and a two-layer target simulating a fractured gabbroic lunar crust (density = 2550 kg/m<sup>3</sup>) (18) and a dunite mantle (3200 kg/m<sup>3</sup>). Our objective was to simulate the cratering process that led to the

Freundlich-Sharonov and Humorum basins, which are located in areas where the crustal thickness is 40 and 25 km, respectively, as inferred from GRAIL and LOLA observations (18). We sought a combination of impactor diameter and lunar thermal gradient that yielded an annulus of thickened crust at a radius of ~200 km, a result which is consistent with the annulus of negative free-air gravity anomaly around those basins.

The dependence of material strength on temperature and pressure has the most marked effect on the formation of large impact basins (19). With little certainty regarding the temperature–depth profile of the early Moon or the diameter of the impactor, we considered impactor diameters ranging from 30 to 80 km and three possible shallow thermal gradients (20)—10, 20, and 30 K/km—from a 300 K surface. To avoid melted material in the mantle, the thermal profile was assumed to follow that for a subsolidus convective regime (0.05 K/km adiabat) at temperatures above 1300 K. We found that impact at vertical incidence of a 50-km-diameter impactor in conjunction with a 30 K/km initial thermal gradient best matched the extent of the annular gravity low and led to an increase in crustal thickness of 10 to 15 km at a radial distance of 200 to 260 km from both basin centers (Fig. 2), despite the differences in initial crustal thickness (21).

A crucial aspect of the model is the formation of the superisostatic collar of thickened crust surrounding the deep central pool of melted mantle

**Fig. 1.** Free-air gravity anomalies over (A) the mare-free Freundlich-Sharonov basin (radius to the center of the free-air gravity low is 210 km) and (B) the mare-filled Humorum basin (radius to the center of the annular free-air gravity low is 230 km) from GRAIL observations (2). (C and D) Comparison of observed and calculated free-air gravity anomalies for the Freundlich-Sharonov and Humorum basins, respectively. The observed anomalies and associated 1-SD ranges were derived from averages of the data within concentric rings at different radial distances. The black lines represent the predicted gravity anomaly just after impact and transient cavity collapse, from the hydrocode calculation. The red lines represent the predicted anomaly after isostatic response and cooling, a state which is appropriate for comparison with the Freundlich-Sharonov data. The blue line in (D) represents the predicted gravity anomaly after mare emplacement in the Humorum basin and is appropriate for comparison with data from that basin.



rock. The crust is thickened as the impact ejects crustal material onto the cool, strong, preexisting crust. The ejected material forms a wedge ~15 km thick at its inner edge that thins with increasing distance from the center. The preexisting crust is drawn downward and into the transient crater cavity because of a combination of loading by ejecta and inward flow of the underlying mantle, deforming it into a subsisostatic configuration. This arrangement is maintained by the frictional strength of the cool (but thoroughly shattered) crust, as well as by the viscoelastic mantle that requires time to relax. It is the subsequent relaxation of the mantle that leads to a later isostatic adjustment. The result is a thick, low-density crustal collar around the central hot melt pool that is initially prevented from mechanically rebounding from its disequilibrium state. The higher thermal gradient of 30 K/km, somewhat counterintuitively, yields a thicker subsisostatic crustal collar than the thermal gradients of 10 and 20 K/km. This difference occurs because the weaker mantle associated with a higher thermal gradient flows more readily during the collapse of the transient crater, exerting less inward drag on the crustal collar, which consequently experiences less stretching and thinning.

Calculations suggest that the impact into relatively thin crust at Humorum basin fully exposed mantle material in the central region of the basin (Fig. 2B), whereas a ~15-km-thick cap of crustal material flowed over the central region of the Freundlich-Sharonov basin (Fig. 2A). This crustal cap was warm, weak, lower crustal material that migrated to the basin center during crater collapse (fig. S1). At the end of the crater collapse process, the basins (defined by their negative topography) were 6 to 7 km deep out to 150 km from the basin center, with shallow negative topography continuing to a radial distance of 350 to 400 km, approximately twice the excavation radius. A substantial melt pool, defined as mantle at temperatures above 1500 K, developed in both basins. This melt pool extended out to ~150 km from the basin center and to more than 100 km depth (Fig. 2).

To model the subsequent evolution of the basins, we used the finite element code Abaqus (22, 23). We developed axisymmetric models of the Humorum and Freundlich-Sharonov basins from the hydrocode output, adjusting the thermal structure of the melt to account for rapid post-impact convection and thermal homogenization of the melt pool. The density of solid and liquid silicate material was calculated from the bulk composition of the silicate Moon (21, 24).

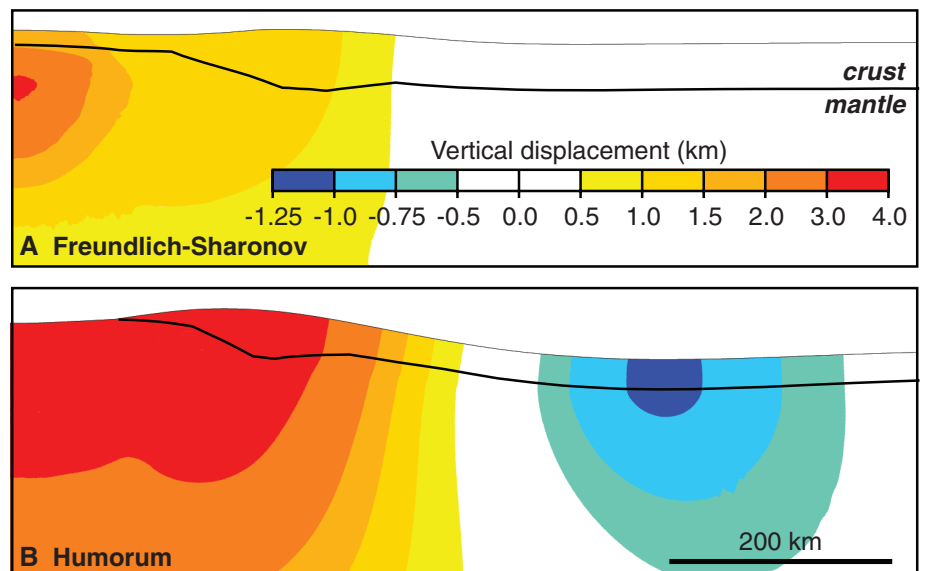
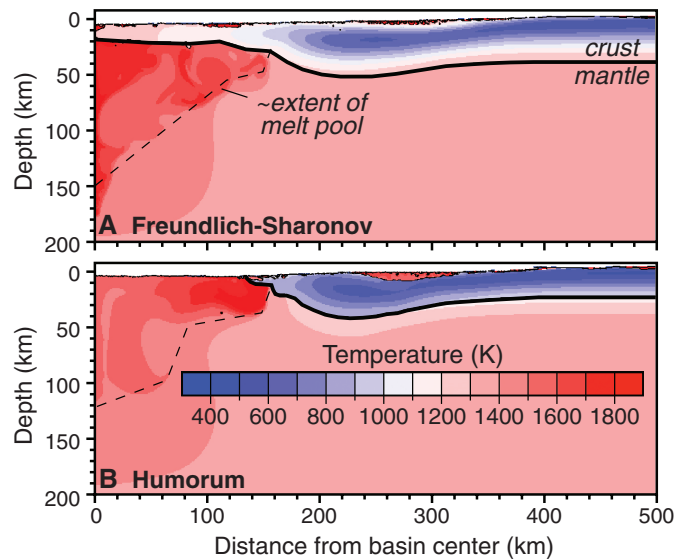
Our models (Fig. 1, C and D) show that the depressed basin topography, the thickened crustal collar, and the lower density of heated material combine to create a substantial negative free-air gravity anomaly at the basin centers (21). The post-impact free-air anomaly is slightly positive outside of the basin owing to ejecta supported by the cool, strong crust and mantle. The overall shape of the modeled post-impact free-air gravity

anomaly is similar to that observed but is much more negative, suggesting that the general pattern of the observed gravity anomaly is the result of the impact, but that subsequent evolution of the basin drove the central anomalies positive.

As the impact-heated mantle beneath the basin cooled, the pressure gradient from its exterior to its interior drove viscoelastic flow toward the basin center, uplifting the basin floor. The inner basin (where the central mascon develops) cannot rise above isostatic equilibrium solely because of forces from its own subsisostatic state. However, mechanical coupling between the inner and outer basin—where the collar of thickened crust was also rising isostatically—provided additional lift to the inner basin floor, enabling it to achieve a superisostatic state. This mechanical coupling is

achieved if the lithosphere above the melt pool thickened sufficiently as it cooled. In the case of the Freundlich-Sharonov basin, the 15-km-thick layer of cool crust provided an initial (if thin) lithosphere from the beginning, which thickened as the underlying mantle cooled. For Humorum basin, the melt pool reached the surface and thus there was initially no lithosphere, although one developed during cooling. Our calculations show that if the viscosity of the mantle outside the melt pool is consistent with dry dunite, its viscoelastic strength would delay isostatic uplift of the basin floor so that lithospheres sufficient for development of a mascon develop over the melt pools in both basins. In addition to these isostatic forces, cooling increases the density of the melt through contraction; given a strong lithosphere that hin-

**Fig. 2.** Vertical cross section of crust and mantle geometry and thermal structure after crater collapse (2 hours after impact) for the (A) Freundlich-Sharonov basin (40-km-thick original crust) and (B) Humorum basin (25-km-thick original crust), according to the hydrocode calculation.



**Fig. 3.** Vertical displacement calculated by the finite element model relative to the initial post-crater-collapse configuration predicted by the hydrocode for the unfilled (A) Freundlich-Sharonov basin and (B) Humorum basin. The deformation is exaggerated by a factor of 10.

ders the sinking of this higher-density material, this process further increases the gravity anomaly at the basin center. The net effect is that isostatic uplift of the surrounding depressed surface topography and crustal collar, combined with cooling and contraction of the melt pool, create the central positive free-air anomaly. The flexural strength that enables the inner basin to rise into a superisostatic state prevents the outer basin from fully rising to isostatic equilibrium, leaving the observed ring of negative free-air anomaly that surrounds the inner basin.

Isostatic uplift raised the surface topography of the Freundlich-Sharonov basin by ~2 km at the center of the basin (Fig. 3A). These effects place the final basin depth at just over 4 km, a value which is consistent with LOLA elevation measurements (11, 21). For the Humorum basin, the inner basin was calculated to rise ~3 km (Fig. 3B). This uplift distribution would have left the Humorum basin ~4 km deep before mare fill. Infilling of a 3-km-thick mare unit and associated subsidence brings the floor depth of the Humorum basin to just over 1.5 km deep, modestly deeper than the 1 km depth measured by LOLA (21).

The free-air gravity anomalies of both basins increased markedly after crater collapse as a result of cooling and isostatic uplift. The free-air anomaly of the Freundlich-Sharonov basin is predicted to have risen to a positive 80 mGal in the inner basin and ~200 mGal in the outer basin above the thickened crust, which are figures in excellent agreement with GRAIL observations (Fig. 1C, red line) (1). Furthermore, the model predicts an outer annulus of positive anomalies, which is also in agreement with observations. A similar post-impact increase in the free-air anomaly is observed in our model of Humorum basin (Fig. 1D, red line), although this gravity anomaly cannot be verified because the Humorum basin was subsequently partially filled with mare basalt. Our results support the inference that lunar basins possess a positive gravity anomaly in excess of the mare load (5). As a final step in our analysis, we replaced a mare unit 3 km thick and 150 km in radius (tapered to zero thickness over the outermost 50 km in radial distance) within the Humorum basin. The addition of the mare increases the mascon at the center of the Humorum basin to 320 mGal (Fig. 1D, blue line), matching GRAIL measurements (1).

This basin evolution scenario depends primarily on the energy of the impactor, the thermal gradient of the Moon at the time of the impact, and the thickness of the crust. A high thermal gradient enables weaker mantle to flow more readily during the collapse of the transient crater, resulting in less inward motion and thinning of the crust. In contrast to hydrocode parameters that control crater excavation and collapse, such as the energy of the impactor and the initial thermal gradient, the close match of our predicted free-air gravity anomalies to those observed by GRAIL is not a product of finding a special combination of finite-element model parameters as-

sociated with isostatic uplift and cooling. These processes are controlled by the evolution of the density and viscosity structure in the model, which follow from the mineralogy of the lunar crust and mantle and the evolution of temperature as the region conductively cools.

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#### Supplementary Materials

www.sciencemag.org/cgi/content/full/science.1235768/DC1  
Supplementary Text  
Figs. S1 to S6  
Tables S1 to S4  
References (26–43)

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## Continuous Permeability Measurements Record Healing Inside the Wenchuan Earthquake Fault Zone

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Permeability controls fluid flow in fault zones and is a proxy for rock damage after an earthquake. We used the tidal response of water level in a deep borehole to track permeability for 18 months in the damage zone of the causative fault of the 2008 moment magnitude 7.9 Wenchuan earthquake. The unusually high measured hydraulic diffusivity of  $2.4 \times 10^{-2}$  square meters per second implies a major role for water circulation in the fault zone. For most of the observation period, the permeability decreased rapidly as the fault healed. The trend was interrupted by abrupt permeability increases attributable to shaking from remote earthquakes. These direct measurements of the fault zone reveal a process of punctuated recovery as healing and damage interact in the aftermath of a major earthquake.

The initiation and propagation of earthquakes depend critically on the hydrogeologic properties of the fault zone, including the fracture-dominated damage zone (1–6). Fault zone permeability serves as a proxy for fracturing and healing, as the fault regains strength

during one of the most unconstrained phases of the earthquake cycle (7). In addition, permeability and storage help to govern the pore pressure and effective stress on a fault. Because earthquakes generate fractures in a damage zone around a fault, it is reasonable to expect that after a large