Early Lunar Magnetism

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It is uncertain whether the Moon ever formed a metallic core or generated a core dynamo. The lunar crust and returned samples are magnetized, but the source of this magnetization could be meteoroid impacts rather than a dynamo. Here, we report magnetic measurements and $^{40}Ar/^{39}Ar$ thermochronological calculations for the oldest known unshocked lunar rock, troctolite 76535. These data imply that there was a long-lived field on the Moon of at least 1 microtesla ~4.2 billion years ago. The early age, substantial intensity, and long lifetime of this field support the hypothesis of an ancient lunar core dynamo.

Before the Apollo missions, the Moon was often thought to be a primordial undifferentiated relic of the early solar system (*1*) that had never formed a core or generated a magnetic dynamo. Because it was well known that the Moon presently has no global magnetic field (*2*), it was a surprise when the Apollo subsatellites and surface magnetometers detected magnetic fields originating from the lunar crust (*3*), and paleomagnetic analyses of returned samples identified natural remanent magnetization (NRM) (*4*). The magnetization of many samples must have been produced by ancient magnetic fields, but the association of crustal magnetization with impact structures (*5*, *6*) and the identification of NRM in <200-million-year-old impact glasses (*7*) suggest that the field sources could have been impact-generated plasmas (*8*–*11*) rather than a core dynamo (*12*). Determining the source of lunar paleofields is critical for understanding the thermal evolution of the Moon, the limits of dynamo generation in small bodies, and, by implication, the magnetization of asteroids and meteorites.

A key difficulty is that available lunar rocks are often poor recorders of magnetic fields (*13*, *14*). Most highlands samples are brecciated and/or shocked, making it difficult to distinguish between NRM acquired instantaneously during shock-magnetization or from long-lived dynamo fields (*11*). A further complication is that the precise thermal histories of most lunar rocks are unknown. Their magnetization ages have often been assumed to be equal to their radiometric ages (*14*), even

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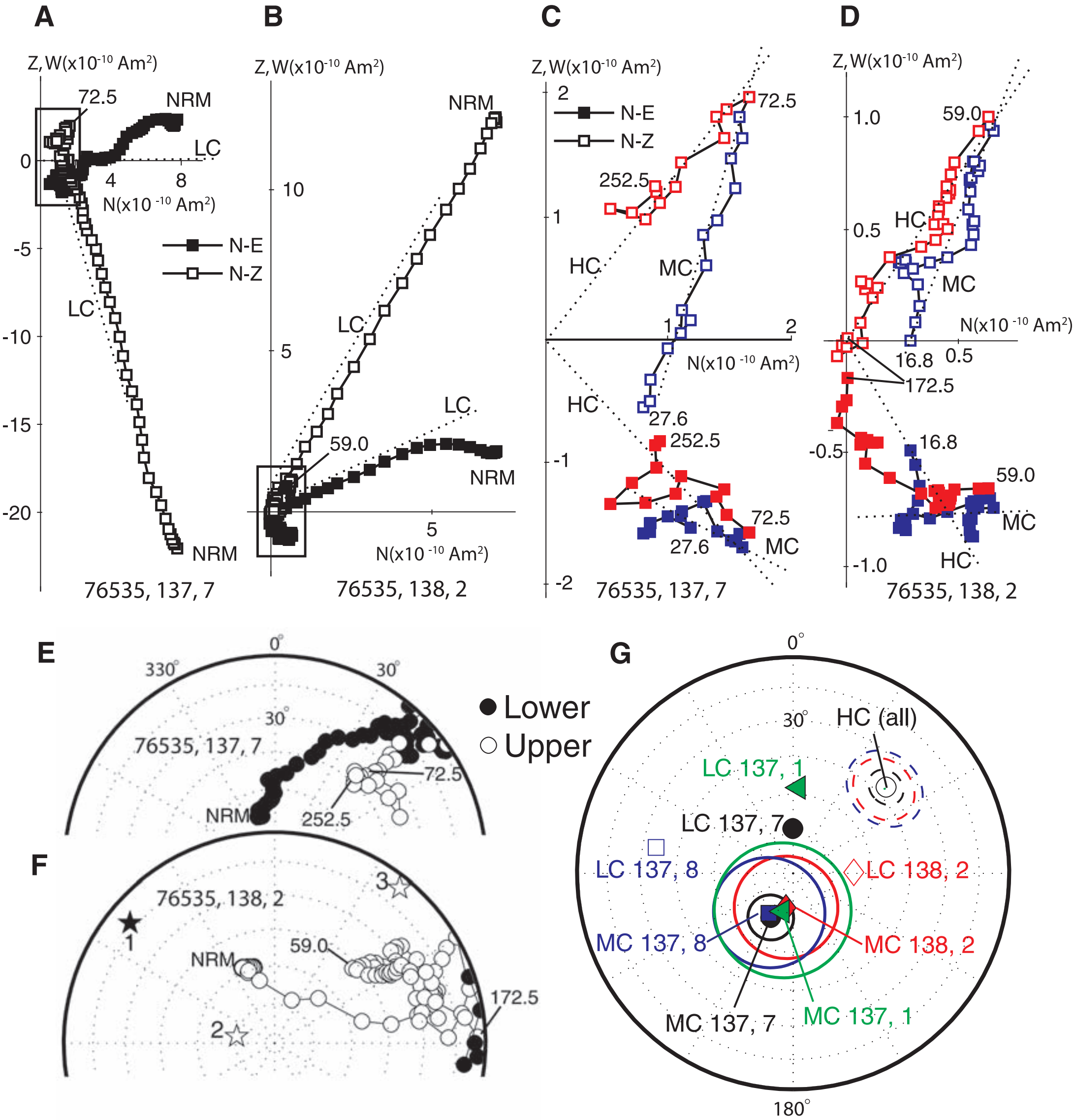


Fig. 1. NRM in troctolite 76535. (**A** to **D**) Two-dimensional projection of the NRM vector during AF demagnetization. Closed symbols represent end points of magnetization projected onto the horizontal N and E planes, and open symbols represent end points of magnetization projected onto the vertical N and Z planes. Peak fields for selected AF steps are labeled in mT. Dashed lines are component directions determined from principal component analyses (PCA). (A) AF demagnetization of 76535,137,7 up to 252.5 mT and its LC component. (B) AF demagnetization of 76535,138,2 up to 172.5 mT and its LC component. (C) Zoom of boxed region in (A), showing data for the MC (blue) and HC (red) components. Data points are from averages of a total of 185 AF measurements. The HC direction is anchored to the origin. (D) Zoom of boxed region in (B), showing data for the MC (blue) and HC (red) components. Data points are from averages of a total of 1450 AF measurements. The HC direction is anchored to the origin. (**E**) Equal-area projection of the remanence directions shown in (A). (**F**) Equal-area projection of the remanence directions shown in (B) and first, second, and third principal axes of the anisotropy of remanence ellipsoid (stars), calculated with a 100-μT bias field ARM in a peak AF field of 57 mT. (**G**) LC, MC, and HC components obtained from PCA of four subsamples studied (four symbols/colors), rotated so that all HC directions overlap with the HC direction of 137,7. Circles indicate maximum angular deviations.

though thermal events that can remagnetize rocks may have no effect on most geochronometers.

Here, we report a magnetic study of an unshocked ancient rock with a well-constrained thermal history, troctolite 76535. We applied $^{40}Ar/^{39}Ar$ thermochronological constraints (*15*) in conjunction with paleomagnetism to determine when 76535 was last remagnetized and to constrain the nature and duration of the recorded paleofields. Because of the putative late heavy bombardment at ~3.9 billion years ago (Ga), there are few lunar rocks with $^{40}Ar/^{39}Ar$ ages older than ~4.0 billion years and no paleomagnetic analyses from before this time. However, it is during this early epoch when a convecting core dynamo is most thermally plausible (*16*). 76535 is the only known unshocked (*17*–*19*) whole rock from this epoch (*20*).

76535 was found in a rake sample from the ejecta blanket of a 10-m-diameter impact crater (*21*). Four different chronometers (U/Pb, Th/Pb, Sm/Nd, and $^{40}Ar/^{39}Ar$) yielded indistinguishable ages of 4.2 to 4.3 billion years (*22*–*26*). Its Rb/Sr age is less certain because of spurious effects associated with olivine separates, ranging between 4.61 to 4.38 Ga (*24*, *27*). The rock contains the ferromagnetic Fe-Ni-Co minerals kamacite and taenite as free grains and as inclusions of oriented linear arrays and needles (with axial ratios up to 45:1) in plagioclase (*17*–*19*). An unsuccessful Thellier-Thellier paleointensity experiment on 76535 (*14*) indicated that it contains a highly stable NRM composed of at least two components and that its Curie point is >780°C. The Co content of its iron metal, up to 6 weight percent, among the largest measured for any lunar sample (*17*, *28*), would indicate a Curie point of ~850°C (*29*).

To determine if 76535 has a record of lunar magnetic paleofields, we conducted nondestructive alternating field (AF) demagnetization of six unoriented polycrystalline chips. AF data for our four most carefully controlled samples (137,1; 137,7; 137,8; and 138,2) demonstrate that the NRM consists of low coercivity (LC), medium coercivity (MC), and hard coercivity (HC) components [supporting online material (SOM) text]. The LC component, blocked below ~12 mT, is apparently a combination of viscous remanent magnetization and an isothermal remanent magnetization (IRM) with a non-unidirectional orientation relative to the MC and HC components (Fig. 1, A and B, and figs. S1 and S2), resembling that observed in many other Apollo samples (*14*, *30*) and meteorites (*31*). The MC component is much weaker than the LC component and extends from ~15 mT to between 45 and 83 mT (Fig. 1, C and D, and figs. S1 and S2, blue). A final HC component trends to the origin from 45 to between 83 and >250 mT, suggesting that it is the final primary component (Fig. 1, C and D, and figs. S1 and S2, red). The angular distances between the MC and HC components for all four subsamples after correction for anisotropy of remanence are similar (142° to 149°) and are consistent with the two components being unidirectional across the 76535 parent rock (Fig. 1G). The high coercivities of NRM are also consistent with the pseudo–single-domain state of the iron in plagioclase-rich subsamples (fig. S11). The inferred paleointensities (SOM text) for the MC and HC components obtained using the anhysteretic remanent magnetization (ARM) and IRM methods are at least 0.3 to 1 μT and possibly an order of magnitude larger (for comparison, the intensity of Earth's dynamo field at the Earth's surface is ~50 μT). Such paleointensities are far larger than that expected from external sources like the Earth, sun, protoplanetary disk, or galaxy from 4.3 to 4.2 Ga (SOM text) but are consistent with fields generated by meteoroid impacts and a lunar core dynamo.

The latter two possibilities can be distinguished by use of a diversity of petrologic and geochronologic data on 76535. The complete lack of shock features in 76535 [peak shock pressures of <5 GPa (*17*)] argues against isothermal shock remanent magnetization (SRM) [which for these pressures typically blocks below coercivities of <~30 mT (*32*, *33*)], as well as the possibility of shock-produced thermoremanent magnetization (TRM) [the temperature increase for any shock of <5 GPa is negligible (*34*, *35*)]. The low ratio of NRM to saturation IRM above 15 mT rules out magnetization by impact-generated (*36*) and artificial IRM fields. These data indicate that nonshock TRM is the most likely explanation for the MC component and much of the HC component (*37*).

Petrologic analyses suggest that 76535 experienced only two cooling events that could have blocked TRM (Fig. 2). The rock crystallized as a cumulate at ~45 km depth (*17*, *18*, *38*), and multiple thermobarometers indicate that it later experienced prograde metamorphism to peak temperatures of >800° to 900°C (*38*–*42*). The observed equilibrium compositions of kamacite and taenite indicate that it then cooled slowly (at ~10°C per million years) to at least ~400°C (*17*), over which time five independent geochronometers closed to yield radiometric ages that are indistinguishable within their uncertainties of 50 to 100 million years ago (Ma). Observations of Fe-Mg ordering in 76535 orthopyroxene indicate that after excavation, it was heated again to at least 500°C and then cooled more rapidly to ~–20°C (the lunar near-surface temperature) over a period of ~10,000 years, probably in an ejecta blanket at ~200 m depth (*39*). Extrapolation of measurements of the diffusivity of Ni in taenite (*43*, *44*) and the observation that the 400°C kamacite equilibrium composition was preserved after excavation imply that the peak temperature reached during burial was <500° to 600°C. This prediction is also in agreement with the 600°C temperature inferred from symmetry transitions in 76535 anorthite that formed during rapid cooling

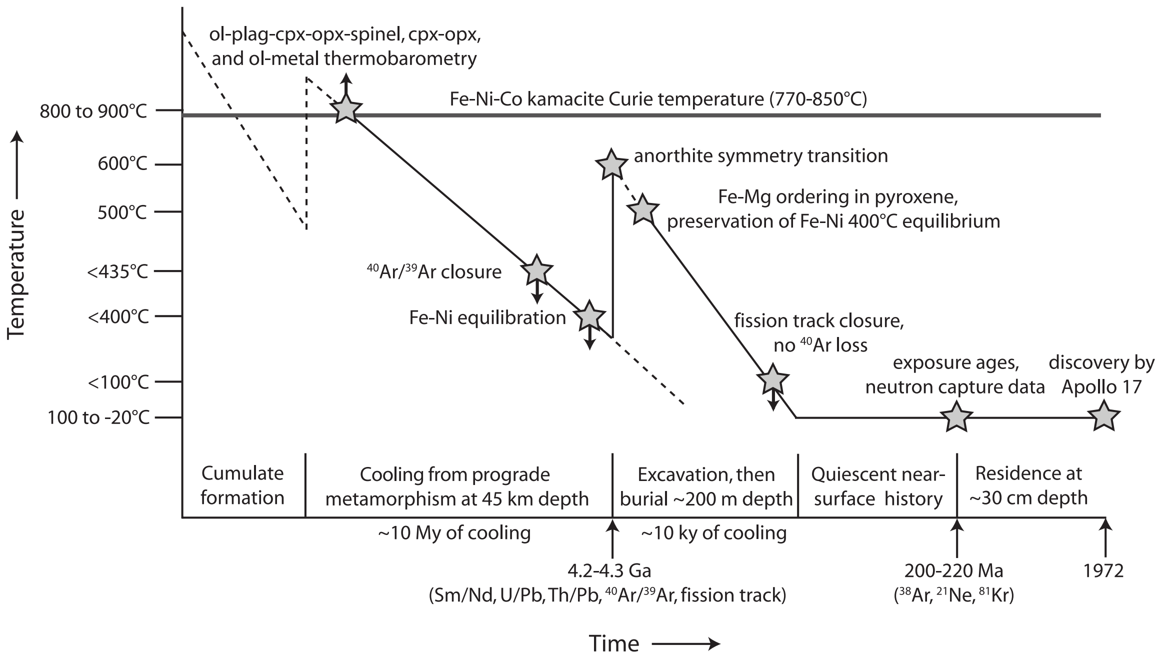


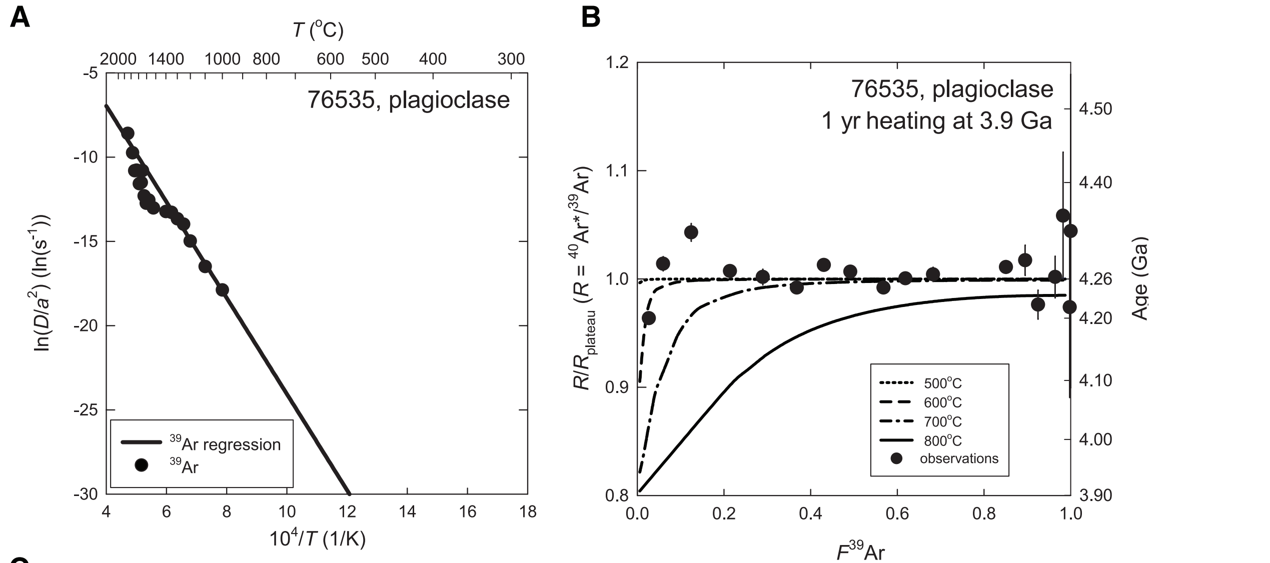
Fig. 2. Thermal history of troctolite 76535, as inferred from a variety of petrologic and geochronometric measurements. Stars and solid lines indicate relatively well-constrained times and temperatures. Dashed lines indicate less-certain time-temperature histories. References for the various data sets described here are found in the main text. Axes are not linearly scaled. My, million years; ky, thousand years.

(*19*, *45*). A final event excavated the rock to a depth of ~30 cm where it remained for much of the last ~220 million years (*23*).

Fission track data (*46*), in conjunction with our calculations using $^{40}Ar/^{39}Ar$ data (*25*), demonstrate that initial excavation took place at ~4.2 Ga. Because the rock was heated to 500° to 600°C after initial excavation, its fission track age (~4.2 billion years, when corrected for annealing at ambient lunar surface temperatures) must have been completely reset at this time [see (*47*, *48*)]. The lack of evidence for Ar loss after 4.2 Ga places a conservative upper bound of heating for ~50 years at 500°C at 3.9 Ga, the time of major basin formation, or several hours at 800°C (Fig. 3) (SOM text). Limits placed on events since 3.9 Ga are even more stringent (Fig. 3C). Therefore, a simple interpretation of these magnetic data are that the HC component was acquired during slow cooling in the deep crust at ~4.2 Ga and the MC component was acquired just after excavation during cooling in an ejecta blanket over ~10,000 years. The cooling rates experienced by 76535 during both events require that the magnetizing fields persisted for far longer than expected for the longest-lived impact-generated fields [just ~1 day for the largest basins (*10*)]. The slow cooling rate for the HC component indicates that the field was stable over millions of years, comparable to superchrons on Earth during the last several hundred million years (*49*).

Although the Ar data are permissive of extremely brief ad hoc heating events (such as those from deposition in shallow ejecta blankets) after 4.2 Ga, we can demonstrate that even if such events took place, the durations of the magnetic fields from such impacts are too short to be a plausible source of the magnetization in 76535. Conductive heating from a hot ejecta blanket would raise the temperature of the ~5-cm-diameter rock (conservatively assuming it has always been no larger than its size as sampled by Apollo 17) from –20°C (ambient subsurface) to 770°C (the minimum Curie temperature) in approximately 1000 s (fig. S12). However, spontaneously generated fields due to plasma currents or motion of charged ejecta are believed to disappear in <~10^2 s for craters <100 km in diameter (*8*, *9*), before the rock could even begin to cool and acquire TRM. Such short thermal events are also unlikely to have occurred during the last 4 billion years because they would require the rock to be in a thin ejecta blanket unrealistically close to the surface (<10 cm) (fig. S12), in contradiction with its exposure age of 220 million years and neutron capture data (*23*, *50*). Even the day-long impact-generated fields that may have been present during major basin formation ~3.9 Ga would require an unrealistically small <~1-m-thick ejecta blanket to permit 76535 to acquire TRM (SOM text). Therefore, the most reasonable remaining origin for the high-coercivity NRM in 76535 is from long-lived magnetic fields like those expected from a core dynamo.

The plausibility of a lunar dynamo has been questioned because of the unconfirmed existence of a fluid metallic core (*51*), the difficulty of sustaining a dynamo at least 600 million years after accretion (*16*, *52*), and large paleointensities of ~100 μT that are difficult to reconcile with theoretical predictions (*51*, *53*). However, recent predictions of the effect of dissipation at a liquid-core mantle boundary on the orientation of the lunar spin axis (*54*) and refined measurements of the tidal Love number (*55*) have provided growing evidence that the Moon even today has a small



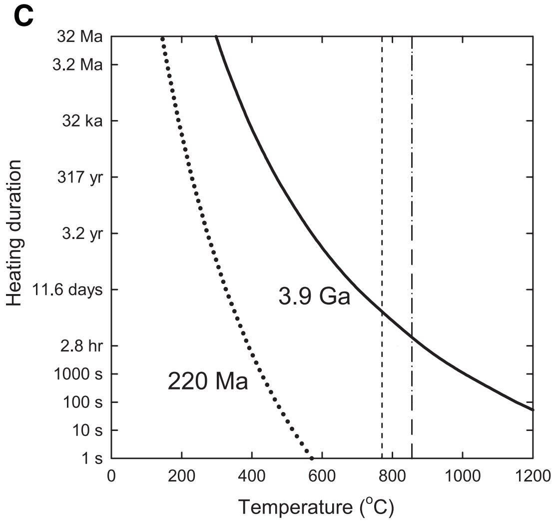


Fig. 3. $^{40}Ar/^{39}Ar$ thermochronological constraints on troctolite 76535. (**A**) Diffusivity as a function of temperature (Arrhenius plot) calculated from ^{39}Ar release data of Husain and Schaeffer (*25*). Circles are the diffusion coefficients calculated following (*56*). The solid line is the model $D(T)/a^2$ obtained from the linear regression to data collected below 1350°C, where D is the diffusivity as a function of temperature T and a is the radius of the diffusion domain. (**B**) Measured and modeled $^{40}Ar^*/^{39}Ar$ ratio evolution spectra. $^{40}Ar^*/^{39}Ar$ ratios, R (normalized to the plateau ratio, $R_{plateau}$). Circles are the $^{40}Ar^*/^{39}Ar$ data of (*25*) with associated uncertainties. The model spectra were calculated with use of a spherical one-domain model with the diffusivity shown in (A) for thermal disturbances at 3.9 Ga lasting for 1 year at various constant temperatures: 500°C (dotted line), 600°C (dashed line), 700°C (dash-dot line), and 800°C (solid line). (**C**) Time-temperature constraints derived from $^{40}Ar^*/^{39}Ar$ data. Shown is an upper limit on the temperature experienced by the rock for a thermal disturbance at 3.9 Ga (solid curve) and 220 Ma (dotted curve) for various assumed heating duration. The short dashed line shows the lower limit on the Curie point derived from the data of (*14*), and the long dashed line shows the best estimate of the Curie point using the Co content of 76535 metal, as measured by (*17*).

(~350-km radius) partially liquid core. Furthermore, the field that magnetized 76535, which is ~300 million years older than that recorded by all previously studied lunar samples, is from the early epoch when the Moon would have most likely had a convecting core due to enhanced heat flow and a possible cumulate overturn event (*52*). Finally, the NRM in 76535 indicates that minimum paleointensities were of order microteslas, consistent with the theoretical expectations for a lunar core dynamo (*53*). Our data and these considerations suggest that at 4.2 Ga, the Moon possessed a dynamo field, and by implication a convecting metallic core.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/323/5912/356/DC1
SOM Text
Figures S1 to S12
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References

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Contribution of Fish to the Marine Inorganic Carbon Cycle

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Oceanic production of calcium carbonate is conventionally attributed to marine plankton (coccolithophores and foraminifera). Here we report that marine fish produce precipitated carbonates within their intestines and excrete these at high rates. When combined with estimates of global fish biomass, this suggests that marine fish contribute 3 to 15% of total oceanic carbonate production. Fish carbonates have a higher magnesium content and solubility than traditional sources, yielding faster dissolution with depth. This may explain up to a quarter of the increase in titratable alkalinity within 1000 meters of the ocean surface, a controversial phenomenon that has puzzled oceanographers for decades. We also predict that fish carbonate production may rise in response to future environmental changes in carbon dioxide, and thus become an increasingly important component of the inorganic carbon cycle.

The inorganic half of the marine carbon cycle includes biogenic reaction of seawater calcium (Ca^{2+}) with bicarbonate (HCO_3^-), producing insoluble calcium carbonate ($CaCO_3$) in the process of calcification (*1*):

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$$

The vast majority of oceanic calcification is by planktonic organisms (*2*). Coccolithophores are considered to be the major contributor, but foraminifera are also included in global carbonate budgets (*3*). Upon death, their carbonate "skeletons" are released and rapidly sink to deeper ocean layers. Based on observations and models, estimates of global production of new $CaCO_3$ range from 0.7 to 1.4 Pg $CaCO_3$-C $year^{-1}$ (*4–7*) (Fig. 1).

It is less widely known that all marine teleosts (bony fish) produce and excrete carbonate pre-

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