(shown by black arrows in Fig. 3E) (9, 15) exhibits marked correlation with the measured displacements, confirming the quadrupolar nature of elastic forces between colloidal squares. These results imply that the presence of the hole in a colloidal square and, more generally, other modifications to the platelet’s topology are inconsequential to the anisotropy of interactions, as long as the quadrupolar \( n(r) \) symmetry is preserved.

Quadrupolar forces are expected to decay with distance as \(-R^6\) (9, 15). To test if square platelets interact in this manner, we have measured the relative positions of two colloidal squares along \( \theta = \pi/4 \) from initial separations \( R_0 = 14.3 \) and 12.9 \( \mu m \) (Fig. 3F). From a balance of a quadrupolar elastic force \( F_{\text{dip}} = -\kappa_4 R^6 \) with a viscous drag, one obtains the time-dependent particle separation \( R(t) = (R_0^3 - 7\alpha_q t^2)^{1/2} \), where \( \alpha_q = \kappa_4/\xi \). The two sets of data in Fig. 3F can be fit with \( R(t) \) using only one adjustable parameter \( \alpha_q = (1.6 \pm 0.1) \times 10^{-10} \mu m/s \). Taking the average elastic constant \( K \approx 7 \) pN (30), an effective viscosity \( \eta \approx 0.075 \) Pa·s for 5CB, as well as the side length \( 4.5 \mu m \) of the platelet, dimensional analysis gives an estimate of \( \alpha_q \approx 1.6 \times 10^{-10} \mu m/s \), which is in reasonable agreement with these experiments.

Using a drag coefficient \( \xi = 1.9 \times 10^{-5} \) kg/s of a square platelet in 5CB [determined by probing its diffusive motion with video microscopy (Fig. S3)] and \( \alpha_q = 1.6 \times 10^{-10} \mu m/s \), we calculate a maximum attractive elastic force of \(-20 \) nN near contact at \( R = 4.5 \mu m \) and corresponding binding energy \( E = 3 \times 10^{-17} J \approx 7000 k_B T \).

In conclusion, elastic colloidal interactions in NLCs are sensitive to the colloids’ shapes. Equilibrium director field configurations around equilateral polygonal colloids exhibit dipolar symmetry if they have odd \( N \) (i.e., triangles or pentagons) and quadrupolar symmetry if \( N \) is even, giving rise to dipolar and quadrupolar elastic colloidal interactions, respectively. Elastic dipole moments of polygonal platelets orient perpendicular to the far-field director \( n_0 \). Dipole-dipole forces drive their assembly into chains perpendicular to \( n_0 \) if their dipoles are parallel and chains along \( n_0 \) if their dipoles are antiparallel. Although the symmetry of these highly directional elastic forces should not change over a broad range of particle sizes (\(-50 \) nm to tens of microns), the strength can vary substantially. One can envision the design of such interactions for the assembly of colloidal architectures ranging from anisotropic aggregates to new types of colloidal crystals and optical metamaterials with well-defined alignment relative to the far-field director.

References and Notes
19. Materials and methods are available as supporting material on Science Online.
28. Because of a density mismatch of \(-0.2 \text{ g/cm}^3\) between SU-8 and 5CB, particles tend to sediment toward the lower half of the cell and come to rest at a height \(5 \mu m\) at which the repulsive particle-substrate interaction due to the nematic deformations balances gravity \(1/3\).
29. The drag coefficient of a triangular platelet can be estimated as that of a thin disk with the radius \(a\) circumscribing the edges of the triangle: \(\zeta = 32\pi a/3\). Using a representative value of shear viscosity \(\eta = 0.075\ \text{Pa·s}\) for 5CB (9), one finds \(\zeta = 2\times10^{-4}\ \text{kg/s}\). Although this analysis is only approximate, it gives reasonable estimates for platelet colloids, as verified experimentally (19).
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Supporting Online Material
www.sciencemag.org/cgi/content/full/326/5956/1083/DC1
Materials and Methods
Figs. S1 to S3
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Atmospheric Sulfur in Archean Komatiite-Hosted Nickel Deposits
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Some of Earth’s largest iron-nickel (Fe-Ni) sulfide ore deposits formed during the Archean and early Proterozoic. Establishing the origin of the metals and sulfur in these deposits is critical for understanding their genesis. Here, we present multiple sulfur isotope data implying that the sulfur in Archean komatiite-hosted Fe-Ni sulfide deposits was previously processed through the atmosphere and then accumulated on the ocean floor. High-temperature, mantle-derived komatiite magmas were then able to incorporate the sulfur from seabed hydrothermal sulfide accumulations and sulfidic shales to form Neoarchean komatiite-hosted Fe-Ni sulfide deposits at a time when the oceans were sulfur-poor.

Submarine Fe-Ni sulfide deposits hosted in komatiites (mantle-derived ultramafic rocks with high magnesium content) produce ~10% of the world’s annual Ni, making them an important type of ore-bearing deposits (1). Mineralization of komatiite-hosted Fe-Ni sulfides can form either massive ores at the base of, or disseminated/blebbly ores within, komatiite lava flows and sills (fig. S1). Komatiite-hosted massive Fe-Ni sulfide deposits are most abundant during periods of elevated mantle plume magmatism and continental crustal growth. In the Neoarchean and Paleoproterozoic, such events occurred around 2.95, 2.7, and 1.9 billion years ago (Ga), which correspond to global peaks in the abundance of banded iron formations, sulfidic black shales, and volcanogenic massive Fe-Cu-Zn sulfide deposits (2, 3).

Initial efforts to determine the source of sulfur in these deposits suggested that sulfides were transported directly from the mantle (4, 5). It was later proposed based on a wide range of volcanological, stratigraphic, geochemical, sulfur isotopic, thermodynamic, and fluid dynamic constraints that the magmas assimilated sulfur either during ascent or emplacement on the sea floor [see (1) for case studies] because the sulfur content of the mantle is too low (6), komatiites result from high degrees of melting in the mantle, and a negative pressure feedback on sulfur content limits sulfide saturation in mafic magmas (7). Analysis of multiple sulfur isotopes makes it

1086
20 NOVEMBER 2009 VOL 326 SCIENCE www.sciencemag.org
possible to further test sulfur assimilation models. Most Archean sedimentary sulfides show $\delta^{34}\text{S}$ values near that of the mantle (9–12), whereas hydrothermal alteration and metamorphism tend to homogenize variability in primary $\delta^{34}\text{S}$ values (13). Therefore, $\delta^{34}\text{S}$ data alone do not unambiguously constrain the sulfur source for Archean komatiite-hosted Fe-Ni sulfides. However, the products of non–mass-dependent fractionation of sulfur isotopes (14, 15) by photochemical reactions in the Archean oxygen-free atmosphere—oxidized water-soluble sulfur species with negative $\Delta^{33}\text{S}$ values (8) and reduced sulfur species with positive $\Delta^{33}\text{S}$ values—can be readily distinguished from mantle-derived magmatic sulfides (13, 16). For example, it was shown that sulfur from sulfate aerosols was preferentially incorporated into hydrothermally influenced deposits such as banded iron formations, barites, volcanogenic massive sulfides (VMS), and sedimentary exhalative deposits, as well as early diagenetic pyrite nodules in black shales resulting in negative $\Delta^{33}\text{S}$ values (15–21). Sulfur from elemental sulfur aerosols preferentially contributed to disseminated sulfides in sedimentary rocks, including black shales, yielding positive $\Delta^{33}\text{S}$ values (14, 19).

Archean sedimentary rocks are also characterized by highly variable iron isotope signatures that can be reflective of their origin. A range of $\delta^{56}\text{Fe}$ values for banded iron formations, VMS deposits, and black shales has been linked to abiotic and/or biogenic redox-controlled processes in the Archean oceans. In contrast, magmatic minerals and mantle-derived mafic rocks experience little iron isotope fractionation (22, 23).

Here, we combine $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ analyses to determine the source(s) of sulfur in Archean komatiite-hosted Fe-Ni sulfide deposits. Samples were collected from the ~2.71-Ga Agnew-Wiluna and Norseman-Wiluna greenstone belts of Western Australia and the time-equivalent Abitibi greenstone belt, Canada (24). The samples represent massive, blebby, and disseminated komatiite-hosted Fe-Ni sulfides, sulfide black shales, and massive sulfide lenses in felsic metavolcanic and volcanioclastic sedimentary rocks underlying the komatiite sequences. The isotope signatures of Fe-Ni sulfide deposits were then compared with those of possible sulfur sources in host rocks such as sulfidic organic matter–rich shales and massive sulfide lenses (24) to determine their origin.

The magmatic komatiite-hosted Fe-Ni sulfides show significant ranges in sulfur isotope values, which can be directly compared with those of sulfur-rich crustal lithologies (Fig. 1). The magmatic Fe-Ni sulfides have a 10.6 per mil (‰) range in $\delta^{34}\text{S}$ values that overlaps with the $\Delta^{33}\text{S}$ range of sulfidic black shales and VMS deposits. The volcanogenic massive sulfides have consistently negative $\Delta^{33}\text{S}$ values as low as $-0.7$‰, within the range of values obtained for Archean hydrothermal barites and sulfides (14–18, 20, 21). In contrast, sulfidic black shales underlying komatiite-hosted Fe-Ni sulfide deposits have near 0‰ values, which can be directly compared with most Archean sedimentary rocks.

### References

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**Fig. 1.** $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ data for the studied samples and fields for mantle sulfur and Neoarchean VMS deposits. $\delta^{34}\text{S}$ values for mantle sulfur are from (12) and those for Neoarchean VMS deposits are from (33). $\Delta^{33}\text{S}$ values for the Archean mantle are inferred from (13, 16) and those for the Neoarchean VMS deposits are from the current study and (15, 16, 18, 21).

**Fig. 2.** $\Delta^{32}\text{S}$ and $\delta^{56}\text{Fe}$ data. The range of $\Delta^{32}\text{S}$ values for magmatic mantle-derived Fe-S and Neoarchean VMS deposits is from Fig. 1. $\delta^{56}\text{Fe}$ values (0.09 ± 0.05%) for the bulk silicate Earth (23) were expanded down to $-0.35$% based on a fractionation factor between pyrrhotite and peralkaline rhyolitic melt (26) to infer the iron isotope composition of magmatic mantle-derived Fe-S. We assume that the fractionation factor for pentlandite is similar or very close to the one for pyrrhotite. The origin of Fe-Ni sulfides with positive $\delta^{56}\text{Fe}$ values (up to 0.4‰) and negative $\Delta^{33}\text{S}$ values (down to $-0.6$‰) is enigmatic; however, assimilation of in situ sulfidized iron oxides may explain their iron and sulfur isotope systematics. The range of iron isotope composition of Neoarchean VMS deposits (–2.4 to 0.0‰) is very close to that of modern submarine VMS deposits (–2.1 to $-0.1$‰) (25).
Archean seawater or high-temperature hydrothermal fluids. In contrast, the $\delta^{56}\text{Fe}$ values for Fe-Ni sulfide samples display a limited range from $+0.4$ to $-0.4\%$. This range is much smaller than that in both the VMS and shale-hosted sulfides and might reflect either minor crustal iron contribution to iron-rich komatiite magmas or high-temperature iron isotope fractionations. Indeed, recent experimental studies (26) have demonstrated a significant iron isotope fractionation between pyrrhotite and peralkaline rhyolitic melts ($\Delta^{56}\text{Fe}_{\text{Fe,Ni-sulfide}} = -0.35 \pm 0.04\%$), but smaller fractionation factors are expected at a lower oxidation state in komatiite melts. Olivine $\delta^{56}\text{Fe}$ values tightly clustered at $0 \pm 0.1\%$ (Fig. 2) likely reflect magma composition, minor iron isotope fractionation during olivine crystallization (23, 27), and postdepositional alteration (24). Because iron isotope values of Fe-Ni sulfides are fractionated toward both positive and negative values, it seems unlikely that magmatic processes alone are responsible for this range. Iron oxide minerals in banded iron formations typically have strongly positive to slightly negative iron isotope values, whereas iron sulfides in Archean black shales and VMS deposits of various ages systematically show negative iron isotope values (25, 28). We therefore infer that the iron isotope composition of komatiite-hosted Fe-Ni sulfides reflects a mixture of locally assimilated crustal materials with heterogeneous iron isotope compositions and mantle-derived metals with iron isotope values close to $0\%$.

Multiple sulfur and iron isotope signatures of Fe-Ni sulfides indicate assimilation of sulfur-rich crustal lithologies with a large range of $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ values into sulfur-poor komatiitic magma with $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ values close to $0\%$. Consequently, whereas the sulfur isotope composition of Fe-Ni sulfides was dominated by crustal sources, their iron isotope composition was buffered by komatiite melt. The only notable exception in our data set to an unambiguous sulfur-rich crustal sulfur source for Fe-Ni sulfide deposits is the basal komatiite-hosted massive Fe-Ni sulfide ore of the Kambalda deposit, which does not show non–mass-dependent fractionation of sulfur isotopes and has unfractuated to moderately negative iron isotope values. These data can be explained by either a magmatic sulfur source (29) or assimilation of multiple crustal sulfur sources and mixing with mantle-derived sulfur in a dynamic lava channel during transport (30), leading to dilution of weak non–mass-dependent sulfur isotope signal and equilibrium iron isotope fractionation between pyrrhotite and silicate magma (26). In this case, when non–mass-dependent fractionation in magmatic sulfides is lacking or small, sulfur isotopes neither prove nor disprove assimilation of Archean wall-rock sulfides.

Our data suggest that most Neoarchean komatiites achieved sulfide saturation by assimilating wall-rock crustal sulfur. Most Archean deeper-water sediments were sulfur-poor due to low sulfate contents in the Archean anoxic oceans (11) except for those deposited during the short-lived mantle plume breakout events when extensive subaerial and submarine volcanism delivered larger amounts of sulfur compounds to the atmosphere and oceans (2, 3, 31).

Even these sulfidic black shales were largely restricted to shallow margins in basins far from komatiite plumbing systems (33). The ~2.7-Ga mineralized komatiites correspond to a peak in the global abundance of VMS deposits (2). The sulfur in the latter deposits is a mixture of mantle-derived sulfur with $\Delta^{33}\text{S} \approx 0$ leached at depth from the underlying volcanic rocks with a minor, but significant, component derived by thermochemical reduction of seawater sulfate with negative $\Delta^{33}\text{S}$ values that was produced by atmospheric photochemical reactions (15, 18). Consequently, VMS deposits within or near active volcanic plumbing systems would have been an abundant and easily accessible sulfur source in ~2.7-Ga submarine environments (Fig. 3).

Recent studies of mineralized komatiites at Mount Keith, Western Australia, indicate magma emplacement in a proximal felsic volcanic environment, with both felsic and komatiitic magmas most likely using the same plumbing system (32). Formation of basal massive Fe-Ni sulfide deposits in komatiites such as Mount Keith therefore likely involved cannibalization of VMS deposits during magma emplacement along preexisting plumbing systems in submarine felsic volcanic successions or in lava channels (3). However, our results also indicate that there is no single unique process to achieve sulfide saturation in komatiite magmas. Whereas Agnew-Wiluna and, possibly, Alexo deposits used sulfur from volcalnogenic massive sulfide deposits, Dundonald and Kambalda deposits likely derived sulfur from wall-rock sediments. The style and size of Fe-Ni sulfide deposits are therefore largely determined by the sulfur source in country rock. Consequently, emplacement of hot komatiite magmas during a peak in magmatic activity in submarine volcanic are environments and in mantle plume breakpoints appears to be the key to formation of komatiite-hosted Fe-Ni sulfide deposits in Archean greenstone belts at a time when the oceans and sediments were sulfur-poor.

References and Notes
8. $\delta^{34}\text{S}$ and $\delta^{56}\text{Fe}$ values are conventional $\delta$ notations with respect to VCDT (Vienna Canyon Diablo Troilite) defined as $\delta^{34}\text{S} = 1000\left(\frac{^{34}\text{S}}{^{32}\text{S}}/^{34}\text{S}_{\text{VCDT}}\right)-1000$, where $x = 33$ and 34, respectively. $\Delta^{33}\text{S}$ value ($\Delta^{33}\text{S} = \delta^{33}\text{S} - 0.515\delta^{34}\text{S}$) is a measure of non–mass-dependent fractionation of 5 isotopes, is based on $\Delta^{33}\text{S}$ and $\delta^{56}\text{Fe}$ values defined as $\Delta^{33}\text{S} = 1000\left(\frac{^{33}\text{S}}{^{32}\text{S}}/^{34}\text{S}_{\text{VCDT}}\right)-1$, where $x = 33$ and 34, respectively.
Geophysical Detection of Relict Metasomatism from an Archean (~3.5 Ga) Subduction Zone

Chin-Wu Chen,1 Stéphane Rondenay,1 Rob L. Evans,2 David B. Snyder3

When plate tectonics started on Earth has been uncertain, and its role in the assembly of early continents is not well understood. By synthesizing coincident seismic and electrical profiles, we show that subduction processes formed the Archean Slave craton in Canada. The spatial overlap between a seismic discontinuity and a conductive anomaly at ~100 kilometers depth, in conjunction with the occurrence of mantle xenoliths rich in secondary minerals representative of a metasomatic front, supports cratonic assembly by subduction and accretion of lithospheric fragments. Although evidence of cratonic assembly is rarely preserved, these results suggest that plate tectonics was operating as early as Paleoarchean times, ~3.5 billion years ago (Ga).

Archean cratons form the core of many of Earth’s continents. By virtue of their longevity, they offer important clues about plate tectonic processes during early geologic times. A question of particular interest is whether subduction is the main mechanism of cratonic assembly and, if so, when this process began to operate. Answers to these questions may be found in the lithosphere of the Archean Slave craton, which is located in the northwestern Canadian Shield (Fig. 1) and represents the oldest known fragment of the North American continent (1). The Slave craton has been studied extensively to reveal processes of cratonic assembly by subduction and accretion of lithospheric fragments. Although evidence of cratonic assembly is rarely preserved, these results suggest that plate tectonics was operating as early as Paleoarchean times, ~3.5 billion years ago (Ga).

When plate tectonics started on Earth has been uncertain, and its role in the assembly of early continents is not well understood. By synthesizing coincident seismic and electrical profiles, we show that subduction processes formed the Archean Slave craton in Canada. The spatial overlap between a seismic discontinuity and a conductive anomaly at ~100 kilometers depth, in conjunction with the occurrence of mantle xenoliths rich in secondary minerals representative of a metasomatic front, supports cratonic assembly by subduction and accretion of lithospheric fragments. Although evidence of cratonic assembly is rarely preserved, these results suggest that plate tectonics was operating as early as Paleoarchean times, ~3.5 billion years ago (Ga).

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