Titanium isotopic evidence for felsic crust and plate tectonics 3.5 billion years ago

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Earth exhibits a dichotomy in elevation and chemical composition between the continents and ocean floor. Reconstructing when this dichotomy arose is important for understanding when plate tectonics started and how the supply of nutrients to the oceans changed through time. We measured the titanium isotopic composition of shales to constrain the chemical composition of the continental crust exposed to weathering and found that shales of all ages have a uniform isotopic composition. This can only be explained if the emerged crust was predominantly felsic (silica-rich) since 3.5 billion years ago, requiring an early initiation of plate tectonics. We also observed a change in the abundance of biologically important nutrients and nickel across the Archean-Proterozoic boundary, which might have helped trigger the rise in atmospheric oxygen.

Modern oceanic crust, produced by mantle melting, is basaltic in composition and is continuously recycled into the mantle at subduction zones. Earth’s earliest crust was also presumably mafic but eventually evolved into two distinct components: an oceanic crust composed of mafic minerals (dark-colored; rich in magnesium and iron) and a continental crust bearing felsic minerals (light-colored; rich in silicon and aluminum). Constraining when a felsic crust first developed and how its chemical composition changed through time are important questions because the composition of the crust influences the composition of the atmosphere, controls the flux of biologically important nutrients to the ocean, and is related to the initiation of plate tectonics (1–4). This issue has been, however, the subject of much controversy (4–12), reflecting the difficulty in interpreting Earth’s earliest rock record. To reconstruct the chemical composition of the continental crust through time, many studies have relied on chemical analyses of fine-grained, terrigenous sediments (shales) (9, 10). Shales are the product of physical and chemical weathering of the part of the crust that is above sea level and exposed to the atmosphere (hereafter referred to as “emerged crust”). Using the chemical composition of shales as a proxy for the emerged crust is challenging because their composition can be modified by weathering, grain size sorting during transport, and sediment diagenesis (5). As a result, aspects of the shale composition observed today—such as their silica (SiO2) content—might no longer reflect those of their source rocks.

We developed a proxy for reconstructing the chemical composition of the emerged crust based on analyses of the titanium (Ti) isotopic composition of shales. This proxy is based on the observation that in igneous rocks, the 49Ti/48Ti ratio (expressed as δ49Ti; the deviation in parts per thousand of the 49Ti/48Ti ratio relative to the Orignis Laboratory Ti reference material) correlates with the SiO2 concentration (Fig. 1 and table S1). This is most likely the result of preferential incorporation of light Ti isotopes into Fe-Ti oxides during fractional crystallization (13). Mid-ocean ridge, island arc, and ocean island basalts, as well as komatites, have within error the same 49Ti value as the bulk silicate Earth (6.05 ± 0.05 per mil [%]; 95% confidence interval (CI)) (13, 14). More evolved rocks of Phanerozoic and Archean ages have heavier 49Ti values that reach +0.6% at a SiO2 concentration of 75 weight % (wt %) (Fig. 1). Therefore, by measuring the 49Ti value of shales, the SiO2 content of their source rocks can be estimated, providing constraints on the proportion of mafic and felsic rocks in the emerged continental crust. This system overcomes several important shortcomings of previous studies: (i) Ti is highly insoluble in terrestrial surface environments (15), so its isotopic composition is immune to processes involving water-rock interactions such as weathering and diagenesis. (ii) On Earth, Ti is present under a single oxidation state (Ti4+), so its chemical behavior is not affected by fluctuating redox conditions in the atmosphere and oceans. (iii) Ti is biologically inert and was thus not affected by the large-scale biogeochemical reorganizations that affected terrestrial surface environments. (iv) During weathering, Ti is incorporated into clay and silt fractions (16, 17), so that Ti in shales is minimally affected by grain size sorting during riverine and oceanic transport (18).

We measured the 49Ti values of 48 individual shale samples (table S2), as well as 30 composite samples, which are mixtures of several shale samples with similar ages and locations (table S3) (19). At any given age, some scatter is noticeable in the 49Ti value, indicating that local source rocks influenced the Ti isotopic composition of the shale. A similar feature has also been observed in the neodymium (Nd) isotopic composition of shales (20). Nevertheless, the average 49Ti value of shales is almost constant over the past 3.5 billion years, exhibiting only a subtle shift toward heavier values from the Archean to the present (Fig. 2). The average shale 49Ti value is always heavier than that of basalts and komatites (Fig. 2), indicating that felsic rocks were the major constituent of the emerged crust throughout the past 3.5 billion years.

The chemical composition of shales is the result of the erosion of diverse rock types present in the crust. Some of these rocks have very different Ti concentrations (for example, ~0.95 and ~0.25 wt % TiO2 for typical basalts and granites, respectively), so that shale 49Ti values are more heavily influenced by basaltic than granitic input. We have developed a mixing model to translate the 49Ti values of shales into an estimate of the crustal composition, assuming that the emerged continental crust is composed of three end-member rock types. These correspond to mafic (M; SiO2 = 45 to 52 wt %, MgO <18 wt %), felsic (F; SiO2 = 63 to 80 wt %), and komatiitic (K; Archean komatites with MgO >18 wt %) rocks. A complication to this mixing model is that magma compositions changed through time, reflecting the secular cooling of Earth and the transfer of incompatible elements into Earth’s crust (20–22). Furthermore, ultramafic komatiitic magmas were common in the Archean, whereas they almost disappeared after ~2.4 billion years ago (23, 24). The chemical compositions of the end-members relevant to Earth’s early history therefore differ slightly from those of their more recent counterparts. Hence, following (20), we assume that the transition from Archean-type to modern-type mafic and felsic end-members occurred gradually across the Archean-Proterozoic boundary (tables S4 and S5) (25).

A three-component mixture cannot be resolved by relying solely on the 49Ti value of shales. In particular, the 49Ti values of komatites are identical to those of mafic rocks, but their Ti concentrations resemble felsic rocks. Because komatites are strongly enriched in nickel (Ni) relative to cobalt (Co) (Ni/Co = 16) compared with either mafic or felsic rocks (Ni/Co = 2 to 3), the Ni/Co ratio is a sensitive indicator of the contribution of the komatiite component to terrigenous sediments (fig. S1) (9). Thus, the combination of 49Ti values and Ni/Co ratios allows us to calculate the contributions of mafic, felsic, and komatiitic...
higher Ni/Co ratio of Archean sediments reflects the contribution of komatiites to terrigenous sediments. and square kernel of 0.15-billion-year width. The gray band is the 95% CI of the moving average. The x–SiO2 (igneous rocks define identi-
trondhjemite-granodiorites (yellow symbols, tonalite-
komatiitic components in a given shale are noted
and SiO2 concentration in Fig. 1. Correlation between

trend in Ni/Co versus chromium/scandium (Cr/Sc) ratios (fig. S2 and tables S6 and S7) (18). After filtering, we found a decrease in the Ni/Co ratios of terrigenous sediments from 3.5 to 2.25 Ga that then remained constant at the value found in modern sediments (Fig. 2B). This trend is consistent with the independently observed decrease in komatiite abundance at the end of the Archean (23, 24).

The mixing model shows that heavy δ49Ti values in shales of all ages can only be explained if felsic lithologies dominated the emerged crust since at least 3.5 Ga (Fig. 3). Although the proportion of mafic rock remained constant at ~30 ± 8 wt % throughout Earth’s history, the amount of felsic rock increased from 58 ± 9 to 72 ± 8 wt %, with the major shift occurring gradually from 3.5 to 2.25 Ga (Fig. 3 and table S8). This increase coincided with the sharp decrease in komatiite abundance from 15 ± 5 wt % at 3.5 Ga to <1 wt % at 2.25 Ga. These abundances are operative estimates because the mixing calculation does not distinguish between igneous rocks and supracrustal terrigenous sediments. In particular, we calculated that komatiites represented 15 ± 5 wt % of emerged rocks at 3.5 Ga, whereas only a few greenstone belts contain such a high proportion (23). These 3.5-billion-year-old shales possibly received the contribution from older supracrustal detrital sediments deposited when komatiites were more prevalent in the upper crust. Knowing the relative proportions of komatiitic, mafic, and felsic rocks, we can use the estimated end-member compositions to calculate the average composition of the emerged crust as a function of age (Fig. 3 and table S8). For example, the average SiO2 concentration increased from 61 to 65 (±2) wt % from 3.5 Ga to the present, corresponding to an andesitic to dacitic composition (Fig. 3).

We tested the sensitivity of our model to changes in the definitions of the end-members and in assumptions on how the igneous end-members evolved through time (18). The reconstructed chemical compositions and rock proportions are similar in all considered scenarios (figs. S3, S4, and S5), demonstrating the robustness of our results. We also compared our calculated composition of
the modern emerged crust (table S8) with an independent estimate of the upper continental crust (26). For the vast majority of elements, both estimates agree within error (fig. S6). Our calculated modern-day proportion of mafic to felsic rock (fig 3) is likewise in agreement with recent estimates based on the areal extent of modern rocks (18, 25). Thus, detritus from mafic and ultramafic rocks are not strongly overrepresented in shales, even though they are less resistant to chemical weathering. Our mixing models can also explain previously documented variations in the thorium/scandium (Th/Sc) and lanthanum/scandium (La/Sc) ratios of shales (fig. S7), which were interpreted to reflect a shift in the composition of the crust from more mafic to more felsic (5). These shifts instead reflect changes in the composition of mafic and felsic magmas, which became progressively enriched in incompatible elements (Th and La) because of the lower degrees of partial melting that accompanied the cooling of Earth (20) and larger degrees of intracrustal differentiation (fig. S8 and table S4).

The Ti isotopic record of shales, combined with Ni/Co data, requires that felsic lithologies were the most abundant component of the emerged crust since at least 3.5 Ga. Our results contrast with other studies (8, 9) that suggest that the upper continental crust was predominantly mafic during the Archean Eon and evolved toward a more felsic composition between 3 and 2 Ga. These studies inferred the interpreted low proportion of felsic rocks in the Early Archean as evidence that subduction-driven plate tectonics was not initiated before ~3.0 Ga. Following the same line of reasoning, we conclude that plate tectonics with subduction of oceanic crust was already in operation at 3.5 Ga and possibly even earlier. Because melting of an anhydrous basaltic source is expected to generate only low amounts of felsic magmas (27), an emerged crust containing almost twice as much felsic as mafic rock cannot be produced without a continuous supply of water to the melting region. Recycling of hydrated oceanic crust or oceanic plateaus at subduction zones provides such a supply in a plate tectonics regime. Felsic crust can also be generated without plate tectonics by the melting of hydrated basalts at the base of a thickened crust (28). The lower part of the crust is, however, generally dry (4). In Iceland, interaction of a mantle plume with the Mid-Atlantic ridge produces a thick crust and high geothermal gradient comparable with those inferred for the Archean (29, 30), but its crust is mainly mafic and contains only 11% of felsic rock (38). Thus, melting at the base of a thickened mafic crust is unlikely to produce the observed high felsic-to-mafic rock ratio 3.5 Ga.

The nature of the emerged crust influenced Earth’s atmospheric composition (1) and ocean chemistry (25). It also controlled the availability of biologically important nutrients in the oceans. The decrease in the abundance of komatiites between 3.5 and 2.25 Ga caused a decrease in the average Ni content of the emerged crust from 313 ± 74 μg/g in the Archean to 43 ± 10 μg/g in the post-Archean (Fig. 4). Ni is a metal cofactor in enzymes involved in microbial methanogenesis (3). The high Ni abundance in the emerged crust during the Archean and associated high flux of Ni to the oceans might have helped sustain a higher abundance of biogenic CH4 in the water column and atmosphere at that time (3). We also found a 50% increase in the concentration of P (from 0.10 to 0.15 wt % P2O5) across the Archean-Proterozoic boundary, mainly driven by the higher average P2O5 concentration of post-Archean mafic rocks (0.19 wt %) compared with Archean mafic rocks (0.11 wt %) (fig. S8). P is one of the main limiting nutrients for biological productivity in the modern ocean (32). The surface area of continents exposed to weathering may have increased across the Archean-Proterozoic boundary (1, 2), which would have further bolstered the export of P to the oceans (2). It is thus likely that biological productivity was stimulated by an increase in the supply of P at the Archean-Proterozoic transition, which might have paved the way for the expansion of oxygenic photosynthesis and the rise in atmospheric O2 that occurred ~2.45 Ga (33).

**REFERENCES AND NOTES**

18. Materials and methods and supplementary text are available as supplementary materials.

ACKNOWLEDGMENTS
This work was supported by grants from the Swiss National Science Foundation (grant P2BEP2_158983) to N.D.G.; NSF (grant CSEDI EAR1502591 and Petrology and Geochemistry grant EAR1444951) and NASA (grants LARS NNX17AE86G, EW NNX17AE87G, and SSW NNX15A125G) to N.D.; and NSF (grant EAR-05-45484), NASA (Astrobiology Institute Award NNA04CC09A), and the Natural Sciences and Engineering Research Council of Canada Discovery and Accelerator program to A.B. Comments on an earlier version of the manuscript by N. Arndt, M.-A. Millet, D. Rowley, R. Rudnick, and M. Tang are greatly appreciated. We also thank four reviewers for their constructive comments that improved the quality of the manuscript. We gratefully acknowledge N. Aubet, P. Fralick, G. Jackson, B. Krapež, A. Kuznetsov, A. Maslov, S. Master, P. Medvedev, T. Nagler, C. Noce, L. Ostes, F. Ossa-Ossa, F. Pecota, T. Pettke, V. Podkovyrov, R. Rainbird, B. Rasmussen, R. Ruhanen, M.J. Severson, W. Su, D. Thomson, P. Thurston, and D. Winston for advice and access to sample collections. All data used in the paper are either tabulated in the supplementary material, published in the cited references, or archived in the PetDB Database (www.earthchem.org/petdb). N.D.G. and N.D. conceived the study. A.B., I.N.B., and A.H. selected and provided the samples. N.D.G. processed the samples and measured their Ti isotopic compositions. N.D.G., M.P.P., and N.D. compiled literature data and implemented the three-component mixing model. All authors contributed to writing and editing the manuscript.

SUPPLEMENTARY MATERIALS
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25 May 2017; accepted 23 August 2017
10.1126/science.aan8086
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Science 357 (6357), 1271-1274.
DOI: 10.1126/science.aan8086

An early call for plate tectonics
The composition of continental crust far back in Earth's history gives us insight into when plate tectonics ramped up and has influenced ocean chemistry. Greber et al. looked at titanium isotopes in shales, which form from eroded continental crustal sediments, to estimate the composition 3.5 billion years ago, closer to the origins of Earth. They found a silica-rich composition, which indicates that plate tectonics was happening deep in our distant past. Other changes in crustal composition might be linked to changing ocean chemistry and major events such as the oxygenation of our atmosphere.

Science, this issue p. 1271