Potassic, high-silica Hadean crust

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Understanding Hadean (>4 Ga) Earth requires knowledge of its crust. The composition of the crust and volatiles migrating through it directly influence the makeup of the atmosphere, the composition of seawater, and nutrient availability. Despite its importance, there is little known and less agreed upon regarding the nature of the Hadean crust. By analyzing the $^{87}Sr/^{86}Sr$ ratio of apatite inclusions in Archean zircons from Nuvvuagittuq, Canada, we show that its protolith had formed a high (>1) Rb/Sr ratio reservoir by at least 4.2 Ga. This result implies that the early crust had a broad range of igneous rocks, extending from mafic to highly silicic compositions.

early Earth | Nuvvuagittuq | zircons | habitability | hadean

Understanding the formation and evolution of the continental crust provides crucial insights into early terrestrial habitability and, possibly, the origin of life itself. Despite the importance of knowing the composition of the Hadean (>4 Ga) continental crust, there is remarkably little agreement regarding its nature. For example, the geochemistry and inclusions in Hadean zircons can be seen to support the existence of felsic crust (1) and possibly even life (2) or a solely mafic crust that formed as the result of a terrestrial magma ocean (3). Resolving this controversy, by establishing when felsic magmatism first occurred on Earth, would help to constrain everything from how life first arose to what role meteorite impacts played in the Hadean (4, 5) to when plate tectonics first operated (6).

Evidence for felsic crust in the Hadean comes from both hafnium isotopes of and inclusions in zircons from the Jack Hills, Western Australia (1). However, the interpretation of hafnium isotopes in ancient zircons has been challenged, on the basis that a zircon from a mafic reservoir could be misinterpreted as originating from a felsic source if ancient lead loss occurred (3). Ancient lead loss causes the age of a given zircon to be underestimated, making the inferred $^{176}Hf/^{177}Hf$ ratio more primitive than it should be, ultimately leading to an underestimated protolith Lu/Hf ratio. This potential source of bias led to the proposal that the "least disturbed" Hadean zircons array about a hafnium isotope evolution line corresponding to a fixed Lu/Hf ratio of ∼0.14 for the reservoir from which they crystallized (3), which appears to imply a mafic source. However, the Lu/Hf ratio is not a simple, monotonic function of SiO_2 content—mafic reservoirs significantly overlap those of felsic ones (Fig. 1)—because zircon, which takes up a substantial fraction of available hafnium, is a cumulate phase in high-silica magmas. For example, melt inclusions in Bishop Tuff rhyolite, a rock with ∼77 wt % SiO_2, can have Lu/Hf ratios of 0.14 (7). Thus, even if one accepts the argument that the least disturbed Hadean zircons fall on a reservoir evolution line with a Lu/Hf ratio of ∼0.14 (3), then Hadean zircon Lu-Hf data are consistent with both a basaltic and a rhyolitic crust.

In a recently developed approach to inferring the composition of the Hadean crust, we analyzed the strontium isotopic compositions of apatites included in ancient zircons to infer the Rb/Sr ratio of the source reservoir, which is highly correlated with SiO_2 (Fig. 1). Strontium isotopes can be used to infer the source Rb/Sr ratio because ^{87}Rb decays to ^{87}Sr. Therefore, a higher Rb/Sr ratio leads to a higher $^{87}Sr/^{86}Sr$ ratio. Since higher Rb/Sr ratios are associated with higher SiO_2, ancient lead loss in the zircons would bias our inferences toward mafic reservoirs. This happens because ancient lead loss means that zircon is actually older than the measured age, which leaves more time for ^{87}Rb to decay. A lower Rb/Sr ratio would then be inferred from the $^{87}Sr/^{86}Sr$ ratio, implying a more mafic composition. The Rb/Sr system has the opposite behavior to the Lu/Hf system in the case of ancient lead loss. Apatite is a calcium phosphate mineral that incorporates significant strontium while essentially excluding rubidium (8). The measured $^{87}Sr/^{86}Sr$ ratio in apatite provides an accurate measure of the $^{87}Sr/^{86}Sr$ at the time the source magma crystallized (9, 10), obviating the need for extrapolations back to the initial $^{87}Sr/^{86}Sr$ ratios. Additionally, apatite inclusions are thought to be preferentially destroyed (11, 12) by later metamorphism and fluid flow, thereby creating voids for secondary inclusions (e.g., xenotime). Thus, preserved apatite inclusions are almost certainly primary (*SI Appendix*, Section 1). This conclusion is supported by the observation that apatite inclusions are found in isolation from cracks and not as crack-filling phases (13). Other phases (e.g., xenotime) are common as crack-filling phases and are therefore more likely secondary (13). Apatite inclusions in the Jack Hills zircons are found in portions of the zircon with a magmatic zoning pattern in cathodoluminescence, rather than in altered regions (13). Finally, Creaser and Gray (14) showed that apatite accurately preserves the initial $^{87}Sr/^{86}Sr$ ratio in hydrothermally altered granites, which is reasonable given the generally low strontium diffusion rates in apatite (15). Therefore, even if the zircon was infiltrated by metamorphic fluids

Significance

To understand early Earth's habitability, we need to know when the continental crust first formed. However, due to the combined actions of plate tectonics and erosion, most of the evidence of the early crust has been destroyed. To shed light on this debate, we analyzed the strontium isotopic composition of apatite inclusions in zircons from Nuvvuagittuq, Canada, where independent evidence suggests a crust-forming event prior to 4.2 Ga, possibly as early as 4.4 Ga. Our results show that this early crust had a high Rb/Sr ratio and therefore a high silica content. This suggests that the early Earth was capable of forming continental crust within <350 million y of solar system formation.

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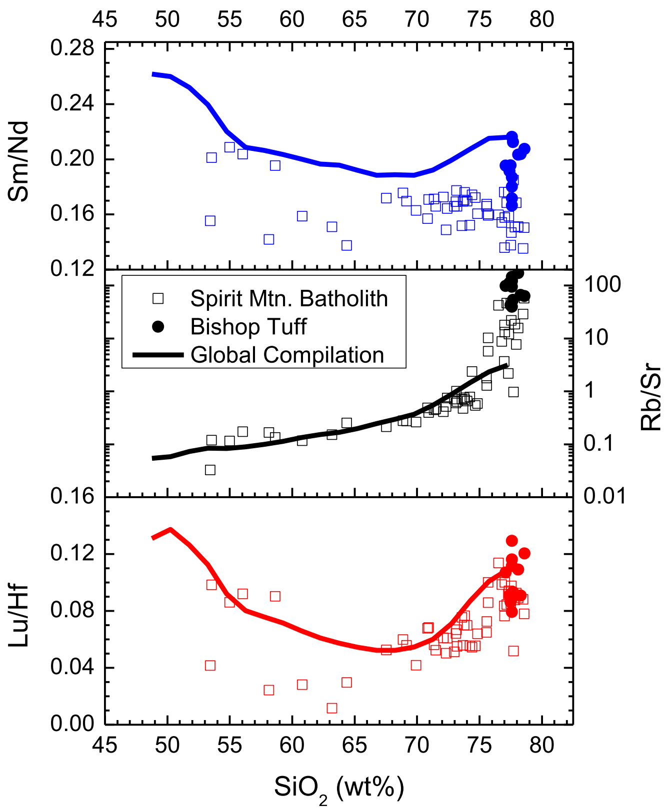

Fig. 1. The Sm/Nd (*Top*), Rb/Sr (*Middle*), and Lu/Hf (*Bottom*) ratios as a function of SiO_2 content for a compilation of Phanerozoic rocks (35), the Spirit Mountain Batholith (36), and the Bishop Tuff (7) show that Sm/Nd and Lu/Hf ratios are not monotonic functions of SiO_2 content, and, thus, high-silica magmas can appear similar to mafic ones. In contrast, Rb/Sr ratios are a monotonic function of SiO_2 content. The Spirit Mountain Batholith was included, because it is a well-sampled pluton that ranges from 52 wt% to 78 wt% SiO_2 and shows broadly the same trends as the global rock compilation, especially in Rb/Sr and Lu/Hf ratios. The Bishop Tuff was included to show an extreme case of high-silica magmatism.

that did not dissolve the apatite inclusion, the measured $^{87}Sr/^{86}Sr$ ratio should remain undisturbed. Further discussion of the robustness of Sr isotopes in apatite inclusions is provided in *SI Appendix*, Section 1.

While apatite inclusions in zircon could provide an important record of time-integrated Rb/Sr ratios for the Archean and Hadean, as inferred from the measured $^{87}Sr/^{86}Sr$ ratios, this record has not previously been exploited due to their generally small (<10 μm in diameter) size. However, the advent of high spatial resolution resonance ionization mass spectrometry (RIMS) (16) permits analysis of strontium isotopes with adequate precision in such tiny inclusions (see *Materials and Methods*).

To study early crustal Rb/Sr ratios, we analyzed apatite inclusions in Archean zircons from the Nuvvuagittuq supracrustal belt (NSB) in northern Quebec, Canada (17, 18), using the Chicago Instrument for Laser Ionization (CHILI) (16). The NSB is of particular interest because its rocks are argued to be the oldest pieces of the Earth's crust, dating back to 4.28 Ga (18). However, the age of these rocks is controversial. Cates and Mojzsis (19) established a minimum age for the NSB of ∼3.75 Ga while O'Neil et al. (18) initially argued that these rocks are as old as 4.28 Ga, based on a claimed ^{146}Sm-^{142}Nd isochron. However, the ^{147}Sm-^{143}Nd system in the same rocks is disturbed, invalidating any interpretation of the apparent ^{146}Sm-^{142}Nd data array as an isochron. Subsequent geochronology showed the age to be ∼3.8 Ga, based on U-Pb dating of zircon (17). While the age of these rocks remains in dispute, there is general agreement that the mantle reservoir from which they formed experienced profound fractionation at ∼4.4 Ga (17–20), based on the revised ^{146}Sm half-life (21). We note though that the 4.4-Ga age is an upper limit and ages as low as 4.2 Ga can still produce sufficiently large ^{142}Nd anomalies (22). Finally, O'Neil and Carlson (22) argued only that the Hadean age for the NSB is a signature of a fractionation event producing mafic crust, on the basis of Sm/Nd ratios inferred from $^{142}Nd/^{144}Nd$ ratios, not that any physical samples are older than 3.8 Ga. Therefore, the only clues we have about the >4.2-Ga fractionation event come from inherited isotopic signatures; the NSB geology, which is Archean aged, is irrelevant for this study as it is ∼600 My younger than the 4.4-Ga event.

Our results show that apatites included in 10 3.6- to 3.8-Ga zircons (for zircons with multiple apatite inclusions we averaged the measured $^{87}Sr/^{86}Sr$ ratios) have $^{87}Sr/^{86}Sr$ ratios that range from 0.70 to 0.75 (Fig. 2 and Dataset S1). These zircons are drawn from two NSB rocks: NSB11 is a green fuchsitic quartzite unit ∼20 cm wide, found within amphibolite units and similar to units Aqf of Cates and Mojzsis (19) and N09-28 of Darling et al. (23). Unit NSB14 is a gray, fine- to medium-grained tonalite–trondhjemite–granodiorite (TTG) orthogneiss similar to units Ag of Cates and Mojzsis (19), ∼50 cm wide and intruding amphibolite units. Unit NSB11 is a clastic sediment (cf. ref. 23) containing detrital zircon mainly ca. 3.78 Ga of unidentified sources, while unit NSB14 is part of the suite of 3.75-Ga TTGs intruding the NSB (17). Zircons from both NSB11 and NSB14 contain apatite inclusions with elevated $^{87}Sr/^{86}Sr$ ratios. The extent of scatter in our dataset is expected, as some of the zircons are detrital. If our analyses had sampled a reservoir with a uniform $^{87}Sr/^{86}Sr \sim 0.699$ (e.g., primitive mantle), we would expect our analyses to be symmetrically distributed around that value. The probability of all 10 samples ending up on one side of the early mantle value due to chance is low (0.5^{10} or $P < 0.001$). Moreover, the observed values consistently fall on the high, interpretable side, not the low, impossible side. From Fig. 2, it is apparent that a 4.4-Ga reservoir with a Rb/Sr ratio of ∼1.7 is consistent with our highest measured $^{87}Sr/^{86}Sr$ ratios. We evaluate three possible high-Rb/Sr reservoirs to explain our data: (*i*) altered basaltic crust, (*ii*) a terrestrial analog to lunar KREEP (3), and (*iii*) a high-silica crust.

Chemical alteration can increase the rubidium content of basalt; however, this requires a source of rubidium, which would likely not exist if the planet was then without an evolved (i.e., high-silica) crust. Indeed, the rubidium source for alteration of oceanic crust is weathering of the continental crust (24). That is to say, hydrothermal alteration of basalt will not increase the basalt's Rb/Sr ratio in the absence of continental crust. While KREEP, an incompatible-element–enriched layer on the Moon, does have a higher Rb/Sr ratio than the bulk Moon (25), it is not sufficiently enriched to explain the high average $^{87}Sr/^{86}Sr$ ratios. The first two explanations, therefore, are inconsistent with the results (see *SI Appendix*, Section 2 for further discussion of these scenarios). However, it is well known that high-silica rocks are characterized by high Rb/Sr ratios (Fig. 1); early felsic magmatism would therefore explain our results.

Our results suggest a significantly more felsic reservoir for the >4.2-Ga fractionation event, recorded in NSB rocks, than previously thought (18, 20). This is perhaps not surprising, as the methods used previously cannot distinguish between high-silica and mafic reservoirs (Fig. 1). That is to say, the Sm-Nd (18), Lu-Hf (20), and Rb-Sr (this study) isotopic data are all consistent only with a >4.2-Ga high-silica reservoir; the Sm-Nd and Lu-Hf systems were simply overinterpreted in previous studies. It is only through the analyses of strontium isotopes that we are able to uniquely ascertain the SiO_2 content of the NSB source reservoir.

Indeed, our data are consistent with a proposed scenario in which the younger TTG series rocks surrounding the NSB formed by partial melting of 3.8-Ga mafic rocks (22). However,

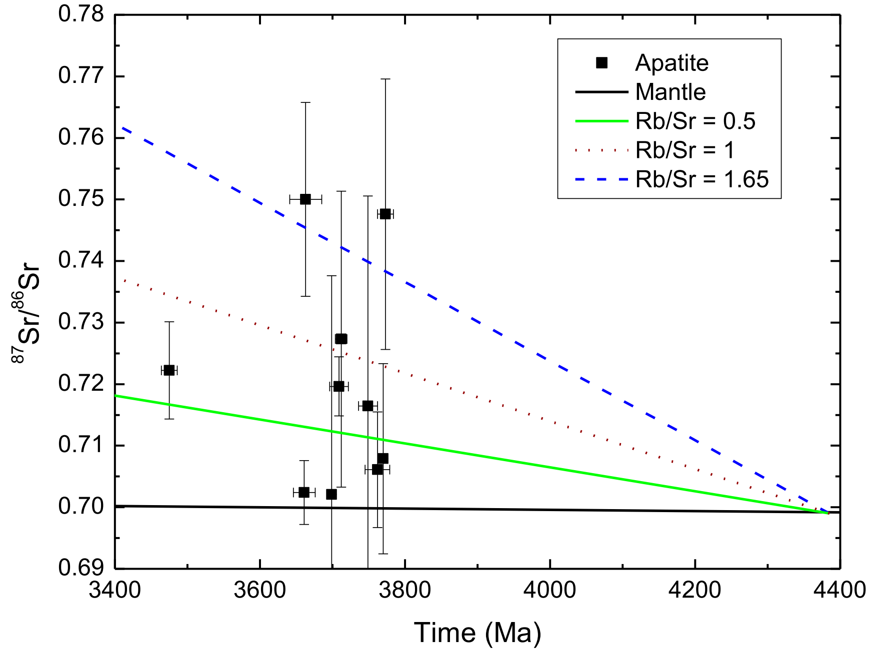

Fig. 2. Measured $^{87}Sr/^{86}Sr$ ratios from our 10 apatite inclusions. The green, brown, and blue lines show the evolution of ∼4.4-Ga reservoirs with Rb/Sr ratios of 0.5, 1.0, and 1.65, respectively. These Rb/Sr ratios are significantly higher than those in mafic rocks and suggest a felsic crust formed by ∼4.4 Ga. Uncertainties are 1σ.

our data suggest that the 3.8-Ga mafic rocks inherited an isotopic signature from the >4.2-Ga high-silica reservoir, rather than from a Hadean mafic crust. This anomaly is then preserved through partial melting. This implies that the O'Neil and Carlson (22) model cannot provide a general explanation for the origin of continental crust, as the NSB has included a high SiO_2 component since at least 4.2 Ga, possibly back to 4.4 Ga.

Given the high SiO_2 contents of rocks that have Rb/Sr ratio >1 (Fig. 1), the >4.2-Ga reservoir was likely of a per- or metaluminous rhyolite composition. To further narrow the compositional range, we note that if our high Rb/Sr reservoir formed in a similar manner to the peraluminous leucogranites, elevated $^{18}O/^{16}O$ ratios not seen in our zircons would be present. The $^{18}O/^{16}O$ ratios measured in our zircons are indistinguishable from the mantle value (26). A metaluminous magma that evolved to felsic compositions through fractional crystallization (27) is therefore the most likely source. It is not possible with our data to specify the origin of the metaluminous magma.

Regardless of the specific nature of the ∼4.4-Ga reservoir, our results, and those of the previous Hf and Nd isotopic analyses, appear to require that a high-silica crustal reservoir was present during the Hadean. Thus, contrary to previous work (1, 3, 28), we suggest that ancient zircons that evolved along a $^{176}Lu/^{177}Hf \sim 0.02$ array are evidence for a high-silica reservoir (Fig. 1) and that the least radiogenic hafnium isotopes recorded the existence of a 65- to 70-wt % SiO_2 reservoir (1). Testing this hypothesis will require analyses of strontium isotopes in apatite inclusions in Hadean zircons. Additionally, since this high Rb/Sr reservoir survived from at least 4.2 Ga, although most likely 4.4 Ga, to 3.8 Ga, impact fluxes must have been lower than those recently proposed (4), suggesting the early Earth was more habitable than previously thought. Finally, we speculate that since cells have a high K/Na ratio (29), continental crust may provide a more likely setting than mafic crust for early life on Earth. Our results therefore push back the possibility of terrestrial habitability to at least 4.2 Ga.

Materials and Methods

Zircons were separated from a sample of orthogneiss (NSB14) and a fuchsite-rich quartz unit (NSB11b and NSB11a) (17, 19). U-Pb dating of the zircons was performed using the UCLA CAMECA *ims*1270 secondary ion mass spectrometer, using standard procedures (30). Because a Pb-Pb age of a discordant zircon is a lower limit on the crystallization age, our inferred Rb/Sr ratios are biased to be too low rather than too high. Additionally, because detecting ancient Pb loss by secondary ion mass spectrometry (SIMS) is difficult due to the flat nature of concordia, we do not use the U-Pb information and interpret only the Pb-Pb ages as the minimum age of the zircon. This is in contrast to the Lu/Hf system, where precise knowledge of concordance is vital for an accurate ingrowth correction; we do not perform an ingrowth correction because of the low Rb/Sr ratios in apatites. Three zircons were dated in a different analytical session, and, thus, only Pb-Pb ages are available. The inclusion search was conducted using energy-dispersive X-ray detectors on the University of Chicago TESCAN LYRA3 focused ion beam/scanning electron microscope following the procedure of Bell et al. (13). Oxygen isotopes were analyzed for five zircons on the UCLA CAMECA *ims*1290 SIMS using standard procedures (31). Strontium isotopes were analyzed on CHILI following the procedures described by Stephan et al. (16) and using the resonance ionization scheme of Liu et al. (32).

RIMS is a technique in which atoms are liberated from the sample surface and then resonantly ionized using tunable lasers, before being analyzed in a time-of-flight mass spectrometer. The advantages to this technique are that it is element specific and has very high sensitivity. We used CHILI (16), which has a 351-nm desorption laser with ∼0.8 μm spatial resolution for sample removal and has achieved precisions of ∼2‰ (as determined in this study). When using Durango apatite as a standard for Madagascar apatite, our measured $^{87}Sr/^{86}Sr$ ratio is 0.7123 ± 0.0015 (1σ), which agrees within uncertainty with the known value of 0.711798 ± 0.000013 (1σ) (33) (*SI Appendix*, Fig. S1).

The uncertainty propagation includes the contribution from counting statistics, standard reproducibility, and background subtraction. Uncertainties on the reported isotopic ratios of the apatite inclusions are dominated by counting statistics.

Since our apatites are included in zircon, we attempted to measure the strontium concentration in the host zircon, but we did not detect any strontium ions. This precludes the possibility of ^{87}Rb in the zircon decaying to ^{87}Sr and therefore biasing our result. In other words, zircon does not contain any significant rubidium. These findings are not surprising in light of the low zircon/melt partition coefficients expected for rubidium and strontium, based on their atomic sizes and charges (34).

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