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 87Sr/86Sr ratio of apatite inclusions in Archean zircons from Nuvvuagittuq, Canada, we show that its protolith had 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.

U nderstanding 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 felsic inclusions of and inclusions in zircons from the Jack Hills, Western Australia (1). However, the interpretation of felsic 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 176Hf/177Hf ratio more primitive than it should be, ultimately leading to an underestimated protolith Lu/Hf ratio. This source of bias is led to the proposal that the “least disturbed” Hadean zircons array about a felsic 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 SiO2 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 % SiO2, 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 ofapatites included in ancient zircons to infer the Rb/Sr ratio of the source reservoir, which is highly correlated with SiO2 (Fig. 1). Strontium isotopes can be used to infer the source Rb/Sr ratio because 87Rb decays to 87Sr. Therefore, a higher Rb/Sr ratio leads to a higher 87 Sr/86Sr ratio. Since higher Rb/Sr ratios are associated with higher SiO2, 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 87Rb to decay. A lower Rb/Sr ratio would then be inferred from the 87Sr/86Sr 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 87Sr/86Sr ratio in apatite provides an accurate measure of the 87Sr/86Sr at the time the source magma crystallized (9, 10), obviating the need for extrapolations back to the initial 87Sr/86Sr 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 mafic zoning pattern in cathodoluminescence, rather than in altered regions (13). Finally, Creaser and Gray (14) showed that apatite accurately preserves the initial 87Sr/86Sr 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...
that did not dissolve the apatite inclusion, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, this record has not previously been exploited due to their generally small (10 $\mu$m) size. However, the advent of high spatial resolution 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 thought 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 $^{143}\text{Sm}^{144}\text{Nd}$ isochron. However, the $^{143}\text{Sm}^{144}\text{Nd}$ system in the same rocks is disturbed, invalidating any interpretation of the apparent $^{143}\text{Sm}^{144}\text{Nd}$ data array as an isochron. Subsequent geochronology showed the age to be $\sim$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 $\sim$4.4 Ga (17–20), based on the revised $^{146}\text{Sm}$-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 $^{143}\text{Nd}$ 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 $^{143}\text{Nd}^{144}\text{Nd}$ 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 $\sim$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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) have $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $\sim$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), $\sim$50 cm wide and intruding amphibolite units. Unit NSB11 is a clastic sediment (cf. ref. 23) containing detrital zircons mainly ca. 3.75 Ga of unaltered 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.699$ (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 $\sim$1.7 is consistent with our highest measured $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 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, 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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.

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 ims1270 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 ims1290 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.7122 ± 0.0015 (1σ), which agrees within uncertainty with the known value of 0.711798 ± 0.000013 (1σ) (33) (SI Appendix, Fig. 51).

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 $^{87}\text{Sr}$ in the zircon decaying to $^{87}\text{Sr}$ 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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