CONSTRAINING CRUSTAL SILICA ON ANCIENT EARTH

PREPRINT, COMPILED MAY 5, 2020

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ABSTRACT

Accurately quantifying the composition of continental crust on Hadean and Archean Earth is critical to our understanding of the physiography, tectonics, and climate of our planet at the dawn of life. One longstanding paradigm involves the growth of a relatively mafic planetary crust over the first 1-2 billion years of Earth history, implying a lack of modern plate tectonics, a paucity of subaerial crust, and consequently lacking an efficient mechanism to regulate climate. Others have proposed a more uniformitarian view in which Archean and Hadean continents were only slightly more mafic than at present. Apart from well-known complications in assessing early crustal composition introduced by crustal preservation and sampling biases, emerging effects such as the secular cooling of Earth's mantle and the dramatic, biologically-driven oxidation of Earth's atmosphere have not been fully investigated. We examine the limits imposed by these constraints on published models and find that several existing studies are not robust against these complications. We find that the data are most parsimoniously explained by a model with nearly constant crustal SiO_2, in which Earth's early crust may be considered more mafic in relative to modern compatible element abundances, but not silica.

ALONE among the planets of our solar system, Earth possesses two compositionally and morphologically distinct types of planetary crust — a basaltic variety underlying the oceans, and a higher-silica variety comprising the continents. Of these two, the oceanic crust is more analogous in composition to the primordial crusts of other silicate planets, while the felsic continental crust is the anomaly [1, 2, 3, 4]. In this context, It has long been suggested that this unique continental crust mutually *requires*, and is *required for* the long-term stability of liquid water oceans — in a scheme where tectonic transport of water to the mantle by oceanic crust enables the production of felsic magmas by altering solidus temperature, viscosity, and phase relationships during magmatic differentiation [3], and in turn, buoyant, felsic crust stabilizes liquid water oceans by increasing the area of exposed subaerial crust, and strengthening the silicate weathering feedback [5, 6].

At the same time, there is a hard limit to the maximum age of Earth's first continental crust, since energetic planetary accretion culminating in the moon-forming impact prior to 4.51 Ga [7, 8] likely left in its wake a primordial magma ocean [9]. In the complete lack of any consensus on the subsequent formation and growth of Earth's continental crust [10, 11], two competing conceptual endmember models have emerged. In the first, what Moorbath [12] characterized as the "majority view" of continental crust growth, Earth features predominantly mafic crust, no plate tectonics, and (presumably) a less well regulated climate until sometime in the mid-Archean [e.g., 13, 14, 15, 16, 17, 18]. The second more uniformitarian view posits felsic continental crust, plate tectonics, and relatively equable climate since the Hadean and perhaps during [19, 10]. Consequently, the question of Earth's ancient crustal composition is deeply connected with our understanding of the inferred physiography, tectonics, and climate of our planet at the dawn of life.

Our ability to determine the past composition of Earth's continental crust, however, is limited by the very same processes that make our planet habitable: erosion by the wind, rain, and ice of an active hydrosphere; the slow return of ancient felsic crust to the mantle by sediment subduction and subduction-erosion; the assimilation and metamorphism accompanying the birth of new crust from mantle derived magma [e.g., 20]. In comparison to quiescent worlds like Mars [21] or our Moon [22], most of Earth's crust is geologically young [23]. While this first-order challenge is well known, recent estimates of the composition of Earth's Archean crust have nonetheless reached widely divergent results, from mafic [15, 16, 17, 18] to felsic [24, 25, 26].

We suggest that this set of divergent results may be explained primarily by two factors which have been less universally understood than the first-order problems of preservation and sampling bias: (1) the secular cooling of Earth's mantle and (2) the radically changing oxidation state of Earth's atmosphere and hydrosphere, driven primarily by oxygenic photosynthesis.

Secular mantle cooling is widely expected as a consequence of Earth's ongoing loss of heat, today estimated to be about 42 TW [27], compounded by exponentially declining radiogenic heat production [28, 29, 30]. The primary observable consequence is the declining melt fraction in mantle magmas, as has long been noted in the context of the declining abundance of komatiites (magnesian magmas produced by high-degree melting of mantle peridotite) since the Archean [31, 32, 33]. This declining melt fraction results in changing major element systematics of mantle-derived basalts, notably including decreasing MgO [34, 35]. The rather straightforward generalization of this phenomenon to compatible and incompatible trace elements is discussed at some length by Keller and Schoene [36, 37]; in brief, compatible element concentrations decrease while incompatible element concentrations increase in preserved continental basalts over the past 4 Gyr.

The second factor, the progressive oxygenation of Earth's atmosphere and hydrosphere, is mediated primarily by biological factors: oxygenic photosynthesis. For much of Earth's

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early history, before 2450 Ma, atmospheric oxygen is thought to have been less than 10^{-5} of the modern partial pressure, as indicated by mass independent sulfur isotope fractionation driven by atmospheric photochemical reactions that occur only in the absence of oxygen [38, 39]. The path of subsequent oxygenation is less clear, but is thought to have reached comparatively modern, breathable levels no later than 400 Ma [40, 41, 42]. The effects of this oxygenation on the geochemistry and phase relations of exposed crust and sediment have been widely considered in other contexts [e.g. 43, 44], yet many estimates of Archean crustal composition persist in relying on redox-sensitive trace element ratios in terrigenous sediments [e.g. 16, 17, 18].

SECULAR VARIATION AS A FUNCTION OF SILICA CONTENT

To further explore the difficulties posed by secular cooling for some previous estimates of Archean crustal composition, we employ the dataset and weighted bootstrap resampling approach of Keller and Schoene [36, 37]. This *weighted* bootstrap resampling approach attempts to reduce sampling bias by assigning to each sample a resampling probability that is inversely related to spatiotemporal sample density [36, 37]. However, more critical to the results than any improvement in evenness is simply the ability to accurately represent each measured value (be it age, silica, K_2O, etc.) as a *distribution* rather than a single value. We accomplish this numerically, by adding Gaussian noise with appropriate variance to each sample in each resampling step — but an analogous result can be equally obtained by Gaussian kernel methods as in Ptáček et al. [26]. As in Keller and Schoene [36, 37], the dataset includes data previously compiled by EarthChem [48] (including contributions from NAVDAT and GEOROC), Condie and O'Neill [49], and Moyen [50].

Since many studies rely upon trace element ratios as proxies to infer major element concentration of the Archean crust [15, 16, 17, 18], it is critical to understand the relationship between such ratios and SiO_2 if we wish to infer Archean crustal silica content in this way. To quantify such relationships, and any potential variation therein over time, we calculate the mean (for single elements), median (for ratios) and the 95% credible interval thereof for several elements and ratios binned as a function of SiO_2, for four age intervals 0-1 Ga, 1-2 Ga, 2-3 Ga, and 3-4 Ga.

As seen in Figure 1, the relationship between major and trace element concentrations with SiO_2 has not been constant through time. For instance, MgO abundance has consistently decreased as a function of time at constant SiO_2 (Figure 1A), with the most significant changes occurring at low silica. Conversely, K_2O content has dramatically increased as a function of time for preserved continental igneous rocks of every SiO_2 from basalt to granite (Figure 1B). Similarly dramatic variation through time *at constant silica* is observed in a range of signif-

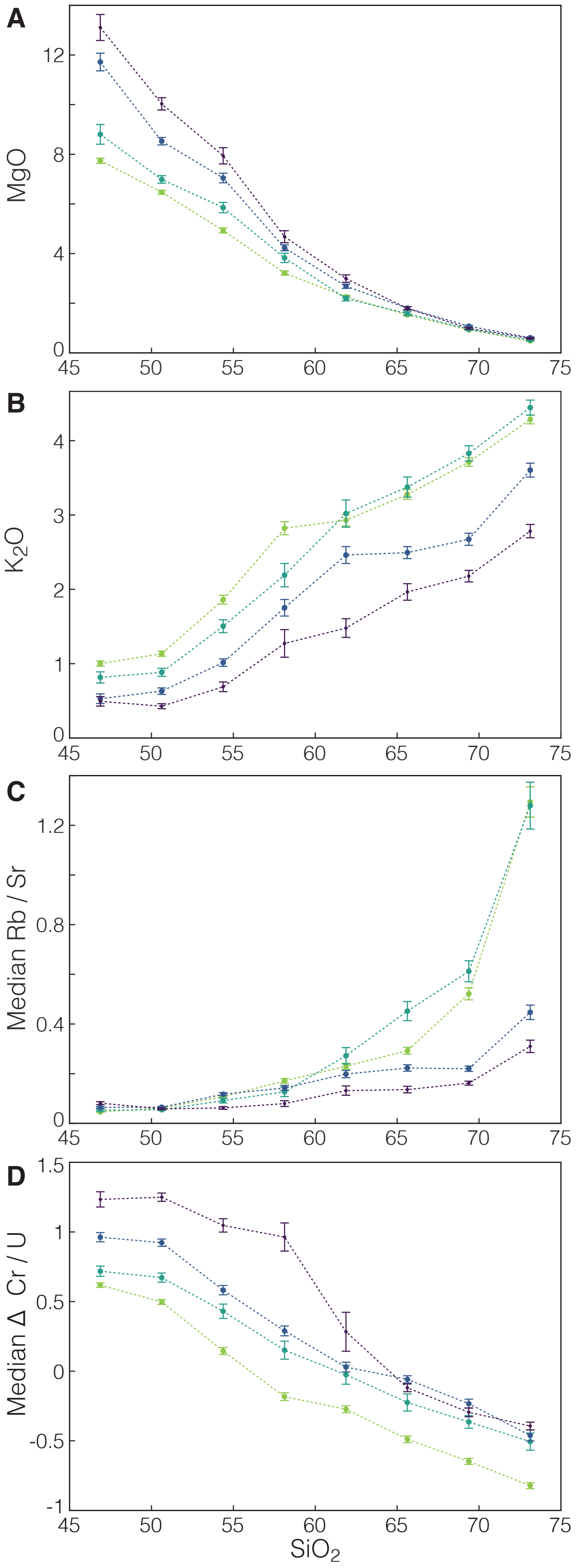

Figure 1: Variations in MgO, K_2O, Rb/Sr and Cr/U as a function of SiO_2 for four Gyr-long time intervals between 0 and 4 Ga, plotted as the mean (MgO, K_2O), median (Rb/Sr, Cr/U) along with the 95% credible interval thereof, determined using the dataset and weighted bootstrap resampling approach of Keller and Schoene [36, 37].

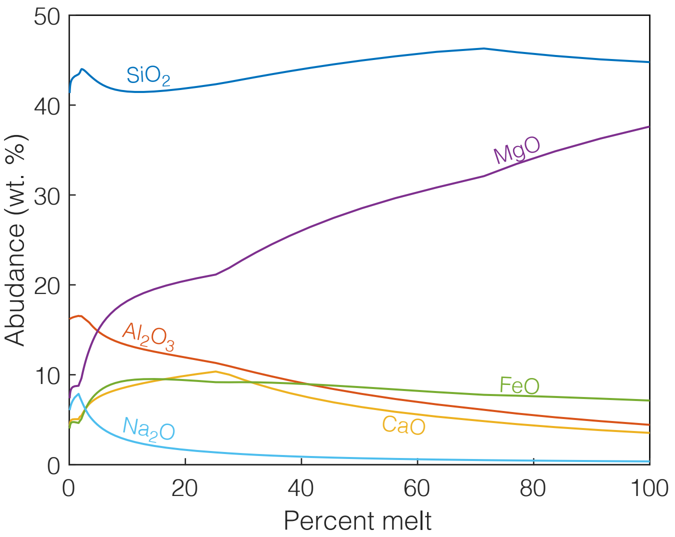

Figure 2: Modeled melt composition, as a function of percent melt, that would result from mantle melting calculated using pMELTS-mode alphaMELTS simulations [45, 46] and the pyrolite composition of McDonough and Sun [47] at 2 GPa and 0.15 wt.% H_2O.

icant trace element ratios. In particular, as illustrated in Figure 1C, Rb/Sr ratios were dramatically lower at a given SiO_2 in the Archean, especially at the felsic end of the spectrum. Similarly large variations are observed in Cr/U, this time with higher values in the Archean (Figure 1D) as shown here in the Δ(Cr/U) notation ($\Delta(Cr/U) = \log(Cr/U)/\log(Cr/U)_{PAAS}$ where PAAS is Post-Archean Australian Shale) of Smit and Mezger [17]. Notably, such trends are not always monotonic as a function of time; on the contrary, while both broadly increase over time, K_2O is slightly higher and Rb/Sr markedly higher circa 1-2 Ga than 0-1Ga for granodioritic and granitic compositions.

This result – varying compatible and incompatible element concentrations at constant silica – may seem counterintuitive if we approach the problem with an assumption that partial melting and fractional crystallization are diametrically opposed, i.e., if we qualitatively consider higher degree melts to be "more mafic" and lower degree melts "more felsic." In reality, such a description would be highly inaccurate. In contrast to calc-alkaline differentiation driven by hydrous fractional crystallization, which rapidly drives magmas to higher silica, the extent of mantle melting has remarkably little influence on magma SiO_2 at all. Instead, as illustrated in Figure for the case of isobaric equilibrium melting of McDonough and Sun [47] pyrolite primitive mantle at 2 GPa and 0.15 wt.% H_2O, magma SiO_2 only fluctuates by only a few weight percent for melting extents between ~5 and 100%.

If not accounted for, such effects significantly undermine the accuracy of trace element proxies for Archean crustal silica. To further illustrate this point we consider, as a conceptual framework, a constant crustal silica reference model — or more specifically, a reference model based on a null hypothesis that Archean crust featured the same relative proportions of mafic, felsic, and intermediate compositions as observed in the modern crust.

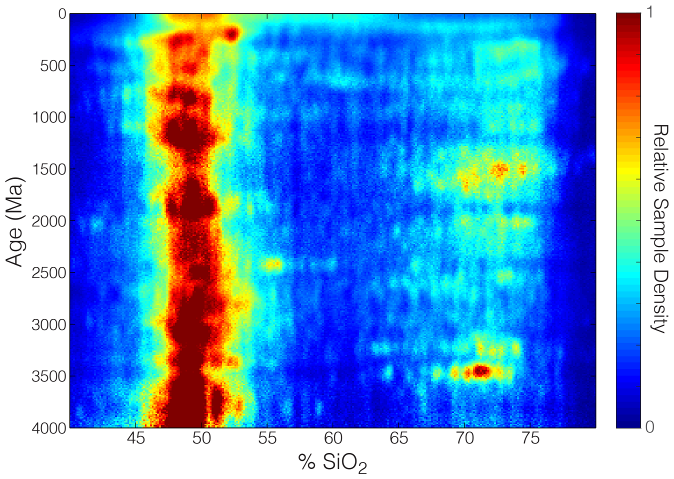

Figure 3: Igneous whole-rock sample abundance as a function of age and SiO_2, calculated and visualized as a 2-D histogram by Keller [51] and reproduced here with permission; hotter colors represent greater sample abundance.

At present, the abundance of continental igneous rocks a function of SiO_2 in many settings displays a pronounced bimodality sometimes referred to as the "Daly gap" — the larger-scale version of two phenomena with this name [52, 53, 54, 55]. Of these two compositional modes, the mafic mode includes a high proportion of basalts, while the felsic mode is dominated by granites, due to the well-known eruptibility contrast of mafic and felsic magmas in the context of hydrous stalling [56, 55]. Consequently, this gap is frequently muted or absent in settings such as active arcs too young to have a well-exposed plutonic record, but readily appears in accreted arcs [51]; otherwise, as shown by Keller [51], this marked compositional biomodality persists throughout the entirety of the preserved continental igneous record (Figure 3).

Consequently, while there are slight variations in the positions of the two modes, and numerous temporal gaps potentially attributable to limited sampling, there is some reason to expect that the underlying process producing this bimodal distribution has been active throughout the preserved rock record. Our null hypothesis of constant crustal silica is in this context equivalent to a hypothetical scenario where the this histogram of silica content were fully constant through time. However, it may be noted that this scenario, as illustrated by Figure 3 in fact involves surprisingly little deviation from the observed proportions in each 1-Gyr time bin.

The results, for a range of major and minor elements are shown in Figure 4; the variations over time for each element in this figure may be considered the minimum level of change over time which must be exceeded in order to reject a null hypothesis of constant crustal silica. Such trends may be calculated for any element or ratio of interest using code available at github.com/brenhinkeller/StatGeochem.jl. To first order, incompatible element concentrations increase through time while compatible element concentrations decrease through time *even at constant silica* as a first-order effect of secular mantle cooling which, as we have shown, has relatively little impact on

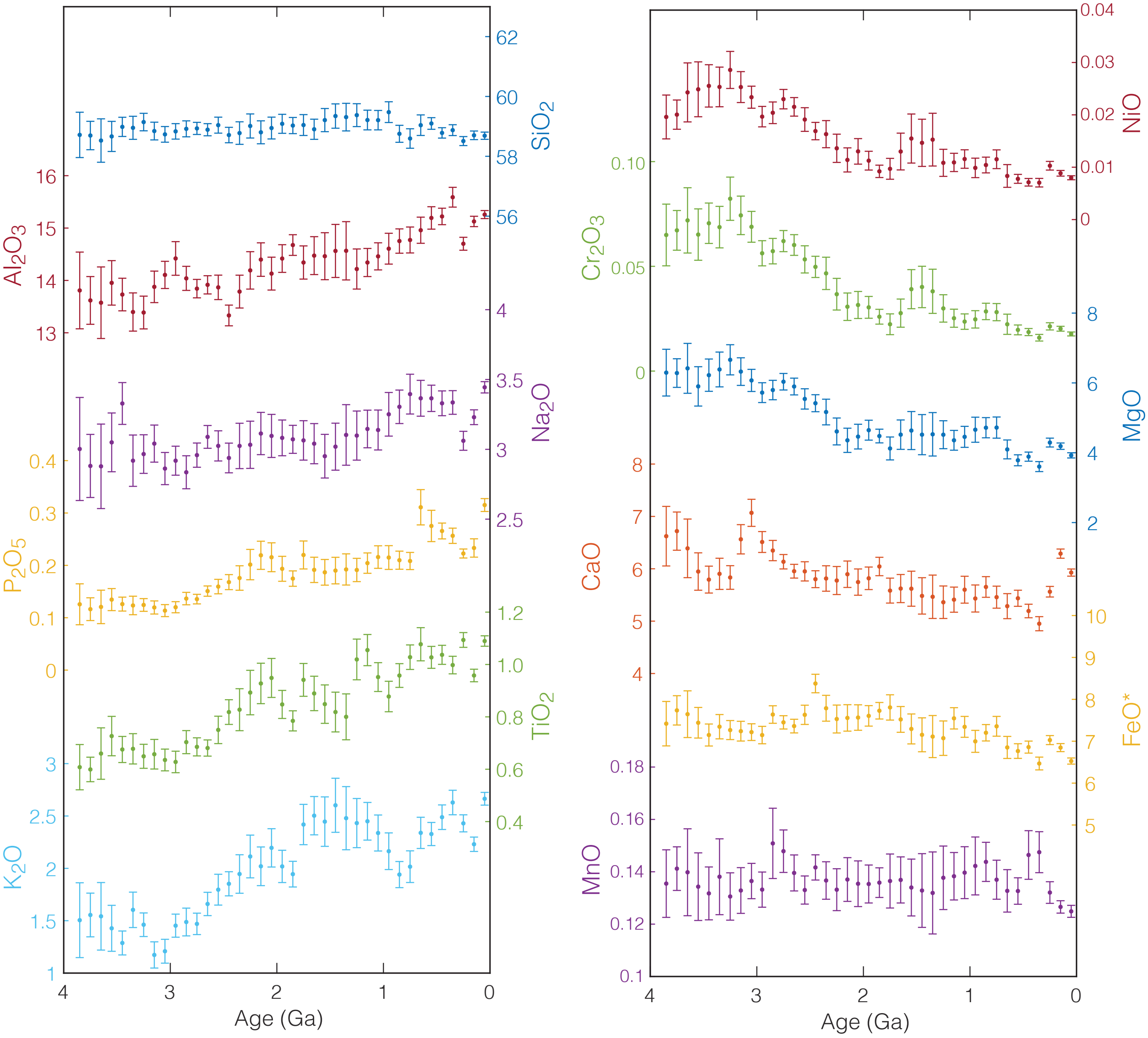

Figure 4: Major and minor element concentrations for our constant-silica reference model, built to illustrate a null hypothesis the proportion of mafic, intermediate, and felsic magmas has remained constant over time. To first order, incompatible element concentrations increase through time while compatible element concentrations decrease through time *even at constant silica* as a first-order effect of secular mantle cooling which, as we have shown, has relatively little impact on the silica content of mantle derived magmas despite its well-established influence on major element such as MgO as well as compatible and incompatible trace elements [36, 37].

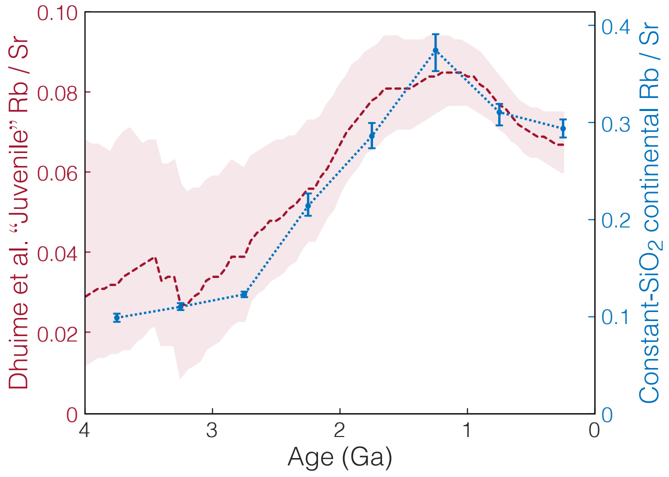

Figure 5: Estimated "juvenile" Rb/Sr ratios of Dhuime et al. [15] (left axis) compared our estimate of crustal Rb/Sr ratio for a "constant-silica" crust (right axis) with proportions of mafic, intermediate, and felsic rocks matching those observed at present. While the model-age dependent method of Dhuime et al. [15] results in extremely low "juvenile" Rb/Sr ratios roughly a quarter of that observed in average crust, the trend observed by Dhuime et al. [15] matches ours, indicating that the level of increase in Rb/Sr over time can be explained solely by secular cooling without any change in crustal SiO$_2$.

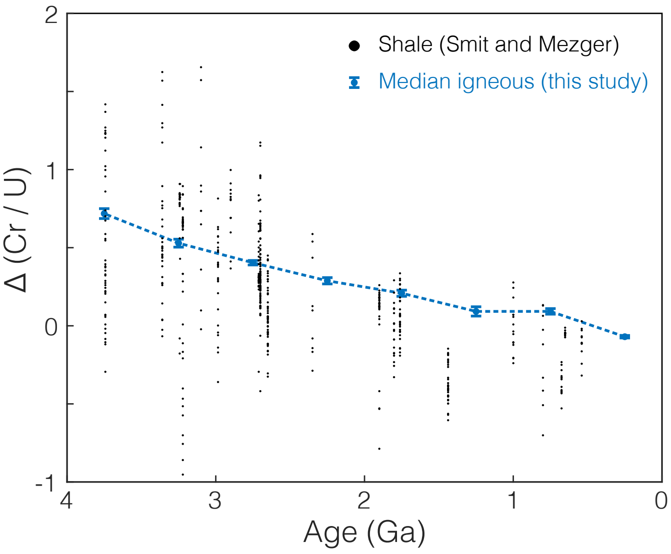

Figure 6: Variation in Δ(Cr/U) over time as calculated for our constant-silica reference model, compared to the shale data of Smit and Mezger [17]. The quantity Δ(Cr/U) is defined by Smit and Mezger [17] as $\log(Cr/U)/\log(Cr/U)_{PAAS}$, where PAAS refers to the standard "Post-Archean Austrailian Shale."

the silica content of mantle derived magmas despite its well-established influence on major element such as MgO as well as compatible and incompatible trace elements [36, 37].

For some trace element ratios, accounting for this variation in trace element abundances *at constant silica* causes previous models to entirely fail to reject the null hypothesis. For example, Dhuime et al. [15] use a compilation of ^{87}Sr/^{86}Sr ratios, Rb/Sr ratios, Sm/Nd model ages, and crystallization ages for igneous rocks to infer the "juvenile" Rb/Sr ratio of an assumed protolith by calculating how much ingrowth of radiogenic ^{87}Sr is required in the time between assumed extraction from the mantle (Sm/Nd model age) and crystallization of the observed sample to produce the observed Sr isotope ratio. They then use modern relationships between Rb/Sr ratio, SiO$_2$, and crustal thickness to argue that Earth's continental crust transitioned from thin and mafic to thick and felsic starting around ~3 Ga. However, as seen in Figure 1C, the relationship between Rb/Sr and silica has been far from constant over time. In Figure 5, we compare the estimated "juvenile" Rb/Sr ratios of Dhuime et al. [15] with our estimate of crustal Rb/Sr ratio in the null hypothesis case of constant crustal silica. While the model-age dependent method of Dhuime et al. [15] infers "juvenile" Rb/Sr ratios roughly a quarter of that observed in average crust, the trend matches our null hypothesis reference model within uncertainty, indicating that their variations in Rb/Sr over time can be explained solely by changing Rb/Sr at constant silica over time.

Intriguingly, while the overall trend is to increasing Rb/Sr over time (consistent with the generally greater incompatibility of Rb), both records show declining average Rb/Sr ratio over the last ~Gyr after reaching zenith circa 1.4 Ga, despite ongoing secular cooling. We suggest that this peak may be associated with the remarkable high-K, high-Rb A-type granitoid event circa 1.4 Ga, first noted by Anderson and Bender [57]. The degree to which this reflects a true global signal rather than a North-American bias is less clear, but it is nonetheless remarkable how reproducible this phenomenon is across two greatly contrasting methodologies — both our direct whole-rock estimate and the isotopic approach of Dhuime et al. [15]

In other cases, such as the variations in Cr/U inferred from terrigenous sediment compositions by Smit and Mezger [17], secular variation in the relationship between the trace element proxy and silica only acts to reduce the magnitude – but not entirely eliminate – inferred changes in SiO$_2$. For instance, as seen in 6, the decrease in median igneous Δ(Cr/U) for the constant-silica reference model appears to underestimate the decrease in Δ(Cr/U) that would be inferred if the shale compositions of Smit and Mezger [17] are assumed to accurately reflect those of their igneous and metamorphic protoliths.

Finally, we may note that some other isotopic approaches, such as the titanium isotope method of Greber et al. [24], should be comparatively less sensitive to complications introduced by secular mantle cooling and its associated variations in mantle melting extent. A second order complication might be introduced in this case if secular cooling resulted in a change in the ratio of plume to arc magmas incorporated into continental crust over time Deng et al. [58]. However, such secular variation in the ratio of flux to decompression melting appears to be strongly excluded in continentental basalts preserved in the continental crust from at least 3.8 Ga to the present [37], which reflect a consistent dominance of calc-alkaline differentiation over the entire interval.

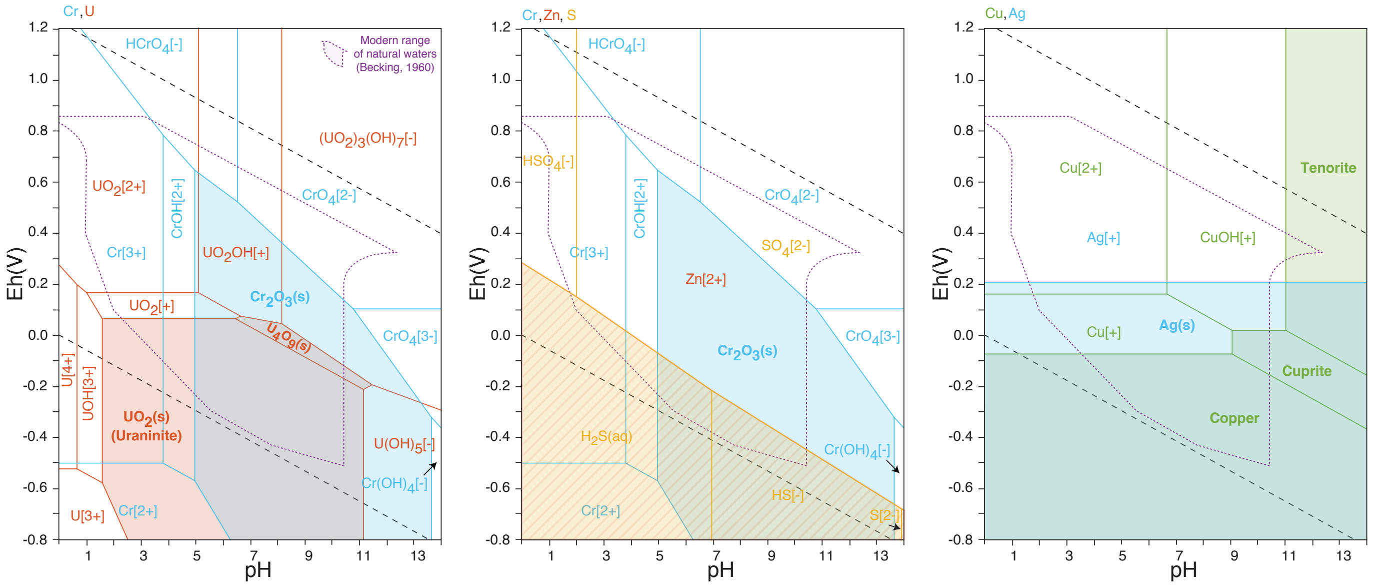

Figure 7: Eh-pH (Pourbaix) diagrams for a range of trace and minor element pairs, based on the LLNL/GWB dataset 0.3245r46 as compiled by Takeno [59] for a solute concentration of 10^{-10} M at 298.15 K and 10^5 Pa. The natural Eh-pH range of modern near-surface waters from Becking et al. [60] is shown for context; the upper limit thereof would be markedly reduced for Archean surface- and ground-water due to lower atmospheric pO_2. The stability limits of insoluble phases (bold) are shaded. In (B), while Zn alone is soluble at all Eh-pH conditions, we additionally shade the stability range of sulfide, which if co-occuring with certain otherwise soluble metals such as Zn^{2+} would allow the formation of insoluble precipitates such as (in this case) sphalerite. Illustrated element pairs are especially subject to aqueous fractionation under any conditions where one is soluble and the other is not.

ATMOSPHERIC OXYGENATION AND TRACE ELEMENT RATIOS IN TERRIGENOUS SEDIMENTS

In an attempt to avoid preservation bias, many estimates of the composition of the Archean crust are based on the com[61]position of terrigenous sediments, rather than directly upon the concentration of Archean igneous rocks [16, 17, 18, 24, 25, 26]. While such an approach has advantages, it also brings risks. Many elements, especially those with low ionic charge-to-size ratios in their favored oxidation states, are soluble or partially soluble in aqueous fluids. This includes such elements as Ni and Co, as used to estimate crustal silica by [e.g., 16]. Worse, other are only selectively soluble as a function of redox state and/or pH, raising the spectre of selective fractionation.

Such concerns are especially relevant given that proposed transitions in crustal silica [e.g., 16, 17, 18] frequently coincide with the Great Oxidation event, when Earth's atmosphere first became partially oxygenated. While perhaps best placed at 2450 Ma on the basis of mass-independent sulfur isotope fractionation [38, 39], the a process of gradual oxidation may have spanned a considerable interval, with debated "whiffs" proposed as early as 3 Ga [62], and a hypothesized "overshoot" as late as 2 Ga [63]. However, the impacts of this transition on the use of trace element proxies in terrigenous sediments has been considered only perfunctorily, if at all, in previous studies [16, 17, 18]. To illustrate the extent of this problem, we show in Figure 7 a range of Eh-pH (Pourbaix) diagrams [59] for several element pairs that have been previously employed to estimate crustal silica. Herein, we observe that, even considering only the system O-H-x, relevant minor and trace elements display marked variation in solubility at different Eh-pH conditions within the modern natural aqueous range [60] — soluble at some conditions but unavoidably precipitating as oxides or native metals at others.

For instance, while Smit and Mezger [17] acknowledge that both Cr and U are redox-sensitive elements, they imply that this is a matter of only limited concern since both Cr and U are both immobile when reduced, and so "fractionation of Cr/U may be expected only in cases where Cr and U are not equally oxidized." However, as seen in Figure 7A, the stability limits of the insoluble oxidized forms of U (UO_2; uraninite) and Cr (Cr_2O_3, in the system O-H-Cr) are markedly distinct, with Cr remaining insoluble at substantially higher Eh; this difference would be only exacerbated in a natural system with Fe to stabilize the Fe-Cr oxide mineral chromite. In the Archean, where detrital uraninite is (along with pyrite) one of the classic indicators for low atmospheric pO_2 [61, 64], it may be safe to assume that both U and Cr are relatively fluid-immobile, and that shale Cr/U ratios accurately represent the protolith from which they were eroded. The same is manifestly not true in the post-Archean, when detrital chromite is still widespread [e.g., **? ?**], but detrital uraninite is absent [61, 64] and uranium is thus subject to preferential dissolution and leaching in terrigenous sediments. Consequently, we may predict from first principles that terrigenous sedimentary Cr/U should accurately reflect the protolith from which it is derived in the Archean, but undershoot is exactly congruent with the relationship between our constant-silica reference model and the shale data of Smit and

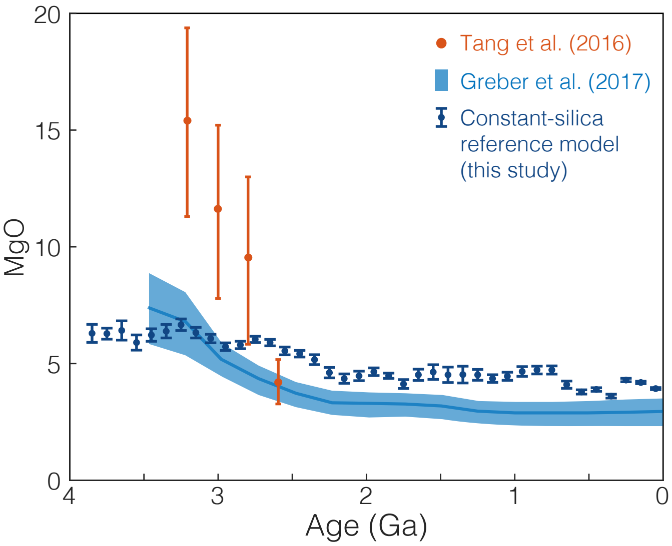

Figure 8: The MgO content of our constant-silica reference model in alongside the estimates of Greber et al. [24] and Tang et al. [16].

Mezger [17], where post-Archean shales exhibit lower Δ(Cr/U) than the reference model.

Equivalent difficulties apply to other sedimentary trace element proxies for crustal silica, including the Cr/Zn ratio of Tang et al. [16] (Figure 7B) and the Cu/Ag ratio of Chen et al. [18] (7C), both of which are liable to fractionate due to weathering at different Eh-pH conditions. The situation becomes only more concerning when a fuller range of elements is considered beyond the O-H-x system. For instance, while Zn alone is soluble at all Eh-pH conditions, its solubility in natural low-Eh conditions would depend heavily on the availability of sulfide, which if present would allow the formation of insoluble metal sulfide precipitates; in this case, sphalerite. Continuing this line of thought, quantifying the redox-dependence of an element ratio such as Ni/Co would require us to evaluate, at a minimum, the relative stability ranges of Ni and Co sulfides and sulfosalts such as millerite, cattierite, linnaeite, gersdorffite, skutterudite *et cetera*. Further, such complications do not end with simple precipitation of pure endmembers; a full analysis would include their sorption to other mineral surfaces (especially of clays), the mineralogy of which may in turn change as a function of O_2. Such effects appear to present a parsimonious explanation for the extraordinarily rapid rate of change inferred from such ratios by Tang et al. [16] across the GOE, and the contrast thereof with the relatively gradual decrease suggested by Greber et al. [24] and our reference model.

In brief, the use of potentially fluid-mobile trace element ratios in terrigenous sediment to infer crustal silica should be strongly abjured. Full mass-balance models that include a wide range of elements with different redox sensitivities should be more robust to such effects [e.g., 25, 26], especially if care is taken to avoid contamination of the sedimentary signal by alteration and diagenesis [e.g., 26], but extreme caution is nonetheless advised in any attempt to infer the composition of primary igneous crust that involves the fluid-mobile trace or minor elements of siliciclastic detritus..

Conclusions

The geochemical community has long favored a view that early terrestrial crust was broadly mafic, in part owing to misconceptions regarding both feldspar buoyancy on a hydrous magmatic substrate and the deep stabilization of restitic garnet, which retards crystallization of aluminous phases from derived melts [13, 14, 15] c.f. [22**?**]. It follows from this conceptual framework that the simplest evolution to the present felsic crust occurred either in a monotonic fashion or during a discontinuity related to the discrete onset of subduction [e.g., 15].

The composition of the continental crust has clearly changed over Earth history. For example, there is evidence for a progressive depletion in compatible elements (e.g., Cr) and enrichment in incompatible elements (e.g., Rb). However, the early Earth mantle was almost certainly hotter than today, resulting in higher degrees of mantle partial melting and, as a result, incompatible element abundances were almost certainly lower than today [36, 37]. By not taking this effect into account, we show using a reference model characterized by constant proportions of mafic, intermediate, and felsic rocks (i.e., constant SiO_2) that incorrect inferences regarding secular changes to the composition of continental crust [15] can result. Further errors are introduced when fluid-mobile and redox-sensitive trace element ratios in terrigenous sediments are used to indirectly estimate the composition of the continental crust [e.g., 16, 17, 18]. Notably, our analysis of a constant-silica reference model leads to similar conclusions as several other recent reevaluations [24, 25, 26]. This observation, especially in the context of recent results suggesting a consistent dominance of arc-style flux melting throughout the preserved rock record [37] presents a challenge to the longstanding paradigm of early mafic crust, warranting further examination.

Code and Data Availablility

All underlying data and computational source code is available at github.com/brenhinkeller/StatGeochem.jl

Acknowledgements

Many of the concepts herein were originally developed over the course of discussion and collaboration with Patrick Boehnke, who declined to participate as an author of the present manuscript after transitioning to the private sector.

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