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# Regulating continent growth and composition by chemical weathering

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Continents ride high above the ocean floor because they are underlain by thick, low-density, Si-rich, and Mg-poor crust. However, the parental magmas of continents were basaltic, which means they must have lost Mg relative to Si during their maturation into continents. Igneous differentiation followed by lower crustal delamination and chemical weathering followed by subduction recycling are possible solutions, but the relative magnitudes of each process have never been quantitatively constrained because of the lack of appropriate data. Here, we show that the relative contributions of these processes can be obtained by simultaneous examination of Mg and Li (an analog for Mg) on the regional and global scales in arcs, delaminated lower crust, and river waters. At least 20% of Mg is lost from continents by weathering, which translates into >20% of continental mass lost by weathering (40% by delamination). Chemical weathering leaves behind a more Si-rich and Mg-poor crust, which is less dense and hence decreases the probability of crustal recycling by subduction. Net continental growth is thus modulated by chemical weathering and likely influenced by secular changes in weathering mechanisms.

geochemistry | igneous | lithium | continent | crust

he most obvious feature of Earth's surface is that it is characterized by bimodal topography: continents ride high and ocean basins ride low. This is because continents are buoyed up by thick, low-density felsic (Si-rich and Mg-poor) lithologies, such as granodiorites and granites, whereas ocean basins are underlain by thinner- and higher-density mafic (Si-poor and Mg-rich) crust, for example, basalt. The presence of felsic continents on Earth is enigmatic. The continental crust houses a significant fraction of the Earth's budget of highly incompatible trace elements, whereas the mantle is depleted in these same elements (1). This complementary trace element relationship between the continents and the mantle establishes a geochemical link between continents and the mantle (1). Yet on every rocky planet in our solar system, melts derived from planetary interiors are basaltic because planetary interiors are high in Mg and low in Si and therefore always generate mafic magmas. Earth is no exception because primary magmas from midocean ridges, hotspots, and arcs are basaltic. Parental magmas of continental crust most likely were also basaltic. Thus, to explain the present felsic composition of continental crust, Mg-rich and Si-poor components must have later been preferentially extracted from the basaltic parent and recycled back into the mantle (2-4)(Fig. 1A).

Many hypotheses have been suggested to resolve the felsic nature of continents (Fig. 1*A*). One popular hypothesis is that basaltic crust undergoes igneous intracrustal differentiation during arc magmatism or continent–continent collisions (3–6): partial melting or fractional crystallization leaves behind a mafic lower crust, which because of its high density, founders into the mantle so that what remains of the crust becomes felsic. In another hypothesis, differentiation occurs by nonigneous processes. Interactions between the upper crust and the Earth's hydrosphere and atmosphere result in chemical weathering, where Mg is preferentially leached out of the crust compared with Si, because Si-rich minerals (alkali feldspars and quartz) are more resistant to chemical and physical weathering than mafic minerals (olivine, pyroxene, amphibole, and plagioclase) (7–10) (Fig. 1B). Then, because the dissolved Mg is eventually sequestered in oceanic crust during widespread hydrothermal alteration, Mg is effectively recycled back into the mantle by subduction (9, 11, 12). Although these hypotheses have been investigated by many, as far as we know, the relative contributions of these two contrasting styles of differentiation in crustal evolution have not been adequately quantified, that is, we still do not know how much original (juvenile) continental material is recycled back into the mantle by delamination and how much is recycled by subduction of weathering-related components. Quantification of these processes requires knowledge of the compositions and amounts of these "missing" mafic components, but because they are missing, they are inconveniently hidden and generally inaccessible.

This article represents an attempt to quantify the missing weathering component and forms part two of a series of articles on the origin and evolution of the continental crust. Part one (13) described the tectonic and igneous aspects of crust formation and differentiation by using a case study of Mesozoic continental arcs in western North America. This study builds on that case study (13) by investigating the role of weathering by using new elemental tracers.

#### Island Arcs to Continental Arcs and Continent Formation: Case Study in the North American Cordillera

Although the mechanisms of continent formation certainly evolved over the course of Earth's history, the overall arc trace-element signature (enrichment in fluid-mobile elements) of continental crust (13–15) and the geologic evidence for island arc accretion and continental arc magmatism as far back as the Archean (16, 17), suggest that arc magmatism (in various forms) has been an important driver of continent formation over much of Earth's history. As just one example of continent formation, we turn to Cordilleran batholiths associated with Mesozoic (mostly Cretaceous) continental arc magmatism in North America (13) (Fig. 1*C*). The Cordilleran batholiths, which include the Sierra Nevada and Peninsular Ranges batholiths, exemplify how continents grow outward by basaltic island arc accretion but are compositionally refined into EVOLUTION

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Fig. 1. Models for crust formation. (A) Mass of parental juvenile arc basalt (MARC) differentiates into three components: mafic lower crust followed by delamination (Mpic), weathering losses by dissolution and eventual subduction (MDIS), and the bulk continental crust (MBCC). (B) Diagram illustrating how Mg and Li are leached out of continents during weathering (soil formation), transported to the ocean in dissolved form, and then sequestered into oceanic crust during hydrothermal alteration. Subduction of oceanic lithosphere recycles Li and Mg into the mantle. Nb and SiO<sub>2</sub> are retained in refractory or resistant minerals and thus are deposited on continental shelves and remain with continents. Future arc magmas partly assimilates the Nb-rich and SiO<sub>2</sub>-rich edge of continents, resulting in the gradual increase of Si in continents with time. (C) Map of Cordilleran batholiths discussed in the text.

felsic crust during continental arc magmatism, which represents the final stage of crust formation [tectonic and petrogenetic details are described elsewhere (13)]. What makes the Cordilleran batholiths ideal in the context of this article is that, here, we have a rare opportunity to document both igneous and weathering differentiation. For example, the thicker lithosphere associated with the continental arc stage should cause juvenile basaltic arc magmas to undergo deep-level fractionation of mafic garnet pyroxenites in the form of cumulates or restites (13, 18, 19). In almost all other areas of the continents, these mafic lower crustal lithologies no longer exist (presumably because they have already foundered), but in the Cordilleran batholiths, mafic garnet pyroxenites still occur as xenoliths in late Miocene eruptive centers associated with presentday extension. These xenoliths provide a snapshot of the mafic lower crust before foundering and thus reveal the original "igneous stratigraphy" of the continental arc (18-20). Finally, there is considerable isotopic evidence (18O/16O, 143Nd/144Nd, and 87Sr/ <sup>86</sup>Sr) in the Cretaceous plutonic rocks (e.g., in the Peninsular Ranges batholith) for interaction of juvenile arc magmas with preexisting crust (Paleozoic) in the form of metamorphic or sedimentary rocks (13, 21-23). These prebatholithic basement rocks clearly passed through the "rock cycle" sometime before onset of arc magmatism, which means that they have been subjected to chemical modification by weathering processes. Quantifying the effect of chemical weathering on crustal composition is the aim of this study, but the above-mentioned isotopic systems, although sensitive to the presence of ancient continental crust, provide limited information on major element fractionations associated with chemical weathering.

#### **Regional and Global Paradox in Li/Nb Systematics**

The relative magnitudes of igneous and weathering differentiation on the compositional evolution of the crust can be better quantified by elemental mass balance. However, any given elemental balance is still underconstrained. For example, assuming that the original Mg associated with a juvenile island arc basalt eventually partitions into three "reservoirs" [a delaminated lower crust (DLC) of igneous origin, a recycled solute component associated with weathering and subduction, and finally the remaining felsic continental crust], there are two unknowns for any given mass balance constraint. To add an additional constraint, we simultaneously examine Li and Mg. Although Li is a trace element and has no direct relevance to the major element composition of the continental crust, Li and Mg track each other during chemical weathering as evidenced by the fact that dissolved Li and Mg in river waters are highly correlated (24, 25). As we will show in the following, the correlation of Li and Mg during chemical weathering provides an extra constraint that permits our system of mass balance equations to be solved.

An important feature of Li in igneous processes is that it is preferentially released from the mantle during hydrous melting, such as in subduction zones (26, 27). Arc magmas thus tend to be enriched in Li. A good index of fluid contributions to melting is the Li/Nb ratio. Nb is highly fluid-immobile during hydrous mantle melting, so hydrous melts should have high Li/Nb ratios. Although Li/Y and Li/Yb ratios have also been used as indicators of fluid components (27), their ratios are complicated by Y and Yb fractionation during deep-level igneous differentiation where garnet is involved in petrogenesis. In contrast, Li and Nb can be shown to behave incompatibly during igneous differentiation [see supporting information (SI) Appendix], so that the Li/Nb ratio of a magma should change little unless the magma assimilates country rock with different Li/Nb. In other words, Li/Nb should represent a conservative tracer of mixing between parental magmas and contaminants.

We measured the Li and Nb contents of plutonic rocks in the eastern Peninsular Ranges batholith, which are associated with the late Cretaceous stage of North American Cordilleran arc magmatism (Fig. 2A and B) (see SI Appendix). In Fig. 2A, Li/Nb is plotted against initial <sup>87</sup>Sr/86Sr [e.g., back-calculated to the crystallization age of the pluton (21)]. This ratio reflects the accumulated ingrowth of <sup>87</sup>Sr by radioactive decay of <sup>87</sup>Rb: high (radiogenic) values of this ratio indicate long ingrowth times and high time-integrated Rb/Sr ratios. Thus, the observed range of Sr isotopic ratios to high values reflects contamination of juvenile arc basalts (low <sup>87</sup>Sr/<sup>86</sup>Sr) by preexisting upper continental crust as represented by ancient sedimentary or metamorphic basement (which, because of their old age and more evolved compositions, are characterized by high <sup>87</sup>Sr/<sup>86</sup>Sr). If continents are thought to dominantly derive from arcs as discussed earlier, Li/Nb of the plutons should stay approximately constant or possibly increase with increasing crustal contamination and hence increasing <sup>87</sup>Sr/86Sr. Instead, a negative correlation is seen. This paradoxically implies that the preexisting crustal basement through which the juvenile basaltic arc magmas intruded had low Li/Nb ratios.

This paradox is not just confined to our regional study. Fig. 2C shows that, as expected, the majority of arc magmas (from the



**Fig. 2.** Lithium systematics. (*A*) Li/Nb versus <sup>87</sup>Sr/<sup>86</sup>Sr for plutonic rocks from the eastern Peninsular Ranges batholith. (*B*) Li/Nb versus Nb for Peninsular Ranges batholith plutons. MORB, midocean ridge basalt (31); DM (31); BSE, bulk silicate Earth (28). Bulk (BCC), upper (UCC), and lower continental crust (LCC) estimates are from ref. 29. Mixing trajectories are shown for BCC-DM and MORB-DM mixing. (*C*) Global compilation of arc Li/Nb versus Nb from the GEOROC database. (*D*) Li/Nb and Nb of young alluvial sediments (35) and Franciscan greenschists (chlorite-clay protolith), the latter a potential Li and Mg sink for weathered Li and Mg.

GEOROC database) have higher Li/Nb ratios than midocean ridge basalts (MORBs; RidgePetDB database) and bulk silicate Earth (BSE) (28). However, global bulk continental crust (BCC) (29, 30) estimates have very low Li/Nb ratios, seemingly contradicting the idea that continents derive from arcs (Fig. 2 *B* and *C*). Adding to this apparent contradiction is the fact that the depleted mantle (DM), that is, the source for MORBs, has a high Li/Nb ratio (31). If continents derive from arcs and if the upper mantle is presumed to be the depleted complement in terms of incompatible trace elements, high Li/Nb ratios for the upper mantle, yet the opposite is seen.

#### **Chemical Weathering Is Required**

These contradictions potentially can be resolved as follows. One possibility is that arc magmatism is not the dominant mechanism for making continents. Intraplate magmas have low Li/Nb ratios because of their very high Nb concentrations, so a larger intraplate component to continents could explain the low Li/Nb ratios (3). Adding an intraplate component, however, does not explain the low Li/Nb ratios in our Peninsular Ranges case study because there is no geologic evidence for intraplate contributions to the continental arc or basement rocks in the study area (32, 33). Another possibility is that the high Li/Nb ratio of upper mantle could be caused by generation and storage of MORB-type oceanic crust over time and have nothing to do with continental crust extraction. However, mixing trajectories between MORB-crust and DM do not pass through BSE because the Li/Nb ratio of MORB is only slightly lower than that of BSE (Fig. 2D). The BSE instead falls on the mixing line between DM and BCC as shown in Fig. 2 C and D [any effects of Nb retention in the Earth's core (34) are already implicitly accounted for by the BSE model chosen (28)].

A simple alternative explanation for the low Li/Nb ratios of continents is that crustal basement rocks were compositionally modified by chemical weathering before being assimilated by juvenile arc basalts (Fig. 1A). Soil chronosequence studies have shown that deep weathering results in preferential leaching of soluble Li and retention of insoluble Nb (24). As a result, deeply weathered soil residues progressively develop low Li/Nb ratios. These low Li/Nb soil residues are then physically eroded from the continents and transported as suspended load in rivers. For example, alluvial sediments are characterized by low Li/Nb ratios (35) (Fig. 2D). Most of the suspended load, consisting of refractory oxides, quartz grains, and accessory minerals, settle out quickly and are thus deposited in deltas along the continental shelf or slope. Most of the Nb, which is housed in refractory minerals, stays on the continents, whereas soluble Li is transported out into the open ocean and thus leaves the continents. Numerous studies have suggested that seawater Li is eventually sequestered in Mg-rich clays within hydrothermally altered zones in the oceanic crust and would therefore be subducted back into the mantle (36). For subduction to represent a net output of Li from the surface environment, the Li bound up in the altered oceanic crust must not be completely remobilized and returned to the continents in arcs. We note that Franciscan greenschists (see SI Appendix), whose protoliths are likely Mg-rich illite and chlorite alteration zones in oceanic crust, have high Li/Nb ratios and could represent a sink for Li that ultimately survives subduction recycling (Fig. 2D). In short, the combination of chemical weathering and physical erosion results in continental crust becoming progressively more enriched in Nb and depleted in Li through time

#### The Amount of Mass Lost from Continents by Weathering

To summarize, the preceding regional and global Li/Nb systematics indicate that chemical weathering plays an important role in controlling the Li content of continents [this is also suggested by the Li and O isotopic composition of granites and average upper continental crust (30, 37, 38)]. The strong coupling of Mg to Li during weathering (25), however, naturally implies that weathering

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Table	1.	Com	positions	of	reservo	oirs

Element	DLC	BCC	ARC	Rivers
SiO <sub>2</sub> , wt %	50	61	50	
MgO, wt %	15	4.7	10	
Li, ppm	7	16	15	
Nb, ppm	0.5-3.8	8	0.4	
Mg/Li, ppm/ppm	13,000	1,800	4,000	2,000

also plays a role in decreasing the Mg content of continents, but how big is this role? We can address this by considering a simple mass balance. We assume that, averaged over time, continents are ultimately derived from juvenile arc basalts (ARC). For the sake of simplicity, we then assume that the ARC is balanced by the sum of its derivative reservoirs, DLC, a dissolved and subducted component (DIS), and the remaining BCC, such that  $X_{BCC} + X_{DLC} + X_{DIS} = 1$ , where  $X_i$  represents the mass fraction of each reservoir relative to the parental juvenile arc mass (note that this mass balance ignores the detailed timing and mechanisms of generating these reservoirs).

Expressions for the net fraction of Li and Mg lost by dissolution (and subsequent subduction) can be formulated after rearranging simple mass balance equations for Li and Mg:

$$f_{\rm DIS}^{\rm Li} = 1 - X_{\rm BCC} \left( \frac{C_{\rm BCC}^{\rm Li} + C_{\rm DLC}^{\rm Li}Q_{\rm DLC/BCC}}{C_{\rm ARC^{\rm Li}}} \right)$$
$$f_{\rm DIS}^{\rm Mg} = 1 - X_{\rm BCC} \left( \frac{C_{\rm BCC}^{\rm Mg} + C_{\rm DLC}^{\rm Mg}Q_{\rm DLC/BCC}}{C_{\rm ARC}^{\rm Mg}} \right), \qquad [1]$$

where  $X_{BCC}$  and  $X_{DLC}$  represent the mass fractions of BCC and DLC relative to parental juvenile arc basalt, *C* represents concentration, and *Q* represents the mass ratio of DLC to BCC ( $Q_{DLC/BCC} = X_{DLC}/X_{BCC}$ ). Recent xenolith and seismic studies of the Sierra Nevada batholith constrain the vertical distribution of mafic garnet

pyroxenites and felsic continental crust in the Sierran Nevadan batholith and suggest that  $Q_{DLC/BCC}$  is  $\approx 1$  for the study area (13, 18, 20). The Mg and Li concentrations in the juvenile arc, DLC, and BCC have also been estimated from combined xenolith and pluton studies of the Sierran and Peninsular Range batholiths or have been tabulated elsewhere (Table 1 and refs. 13, 18, and 29). This leaves three unknowns,  $f_{DIS}^{Li}$ ,  $f_{MS}^{Mg}$ , and  $X_{BCC}$ , and two equations. However, one more constraint is provided by the empirically observed coupling of Mg and Li during chemical weathering. That is,  $f_{DIS}^{Mg}/f_{DIS}^{Li} = (C_{riv}^{Mg}/C_{riv}^{Li})(C_{ARC}^{Li}/C_{ARC}^{Mg})$ , where  $C_{riv}^{Mg}/C_{riv}^{Li}$  is the empirical concentration ratio of dissolved Mg to Li in river waters. Because  $f_{DIS}^{Mg}/f_{DIS}^{Li}$  represents the ratio of the two mass balance equations above, our system of equations is now solvable.

above, our system of equations is now solvable. Fig. 3 shows  $f_{\text{DIS}}^{\text{Li}}$ ,  $f_{\text{DIS}}^{\text{Mg}}$ , and  $f_{\text{DIS}}^{\text{Mg}}/f_{\text{DIS}}^{\text{Li}}$  plotted against  $k = 1 - X_{\text{BCC}}$ , which is the proportion of parental ARC that is removed by delamination and chemical weathering. Taking  $C_{\text{riv}}^{\text{Mg}}/C_{\text{riv}}^{\text{Li}}$  as  $2 \times 10^3$  ppm/ppm (25, 39) and  $C_{\text{ARC}}^{\text{Mg}}/C_{\text{Lir}}^{\text{Li}}$  as  $4 \times 10^3$  ppm/ppm (Table 1; see *SI Appendix*) yields  $f_{\text{DIS}}^{\text{Mg}}/f_{\text{Li}}^{\text{Li}} \approx 0.5$ , which then gives  $k \approx 0.6$  (Fig. 3A), that is, 60% by mass of parental island arc basalt is recycled by weathering/subduction and delamination to make a continent. Thus, 40% and 20% of Li and Mg, respectively, are removed from continents by dissolution (whereas 20% of Li and 60% of Mg is lost by igneous differentiation and delamination; Fig. 3 B and C). Although this loss of Mg by weathering is less than that by delamination, a 20% loss is significant.

Of the 60% loss of original juvenile crustal material, we find that  $\approx 20\%$  is lost by weathering and 40% by delamination (because the ratio of delaminated crust to remaining crust was estimated to be  $\approx 1$ ), leaving only 40% behind for continental crust (Fig. 3D). This weathering loss is equivalent to an effective integrated exhumation of  $\approx 18$  km ( $\approx 0.6$  GPa; assuming a present crustal thickness of 35 km). This number is well within reason: exposures of metamorphic rocks in the interiors of continents often show that  $\approx 1-1.5$  GPa ( $\approx 30-45$  km) of overburden has been removed (40). The higher exhumation depths recorded in metamorphic rocks compared with the calculated effective exhumation simply shows that approximately half of the material stripped (eroded or dissolved) from the



Fig. 3. Mass balance calculations. (A) The ratio of fractional loss of Mg to Li by chemical weathering  $(f_{DIS})$  is plotted versus fraction of crust recycled  $k = 1 - X_{BCC}$ . Horizontal gray line is the estimate of this ratio as determined from the correlation of Mg and Li in riverine and groundwaters ( $\approx 2 \times 10^3$  ppm/ppm) and normalized to the Mg/Li ratio of ARCs ( $\approx$ 4  $\times$  10<sup>3</sup> ppm/ ppm); see *SI Appendix* for details. Intersection with line gives estimate of k. (B) Fractional distribution of Li in DLC, weathering loss (DIS), and BCC. Vertical line represents k determined in A. Intersection with curves here indicate inferred distribution of Li. (C) This is the same as B except Mg is plotted. (D) Fractional masses are plotted versus k. X<sub>DIS</sub> represents mass lost from continents by weathering and subduction. X<sub>DLC</sub> and X<sub>BCC</sub> represent mass lost by delamination and mass retained to make BCC. The ratio  $Q = X_{DLC}/X_{BCC}$  was assumed to be 1 to match observations from continental arc studies (18). Values for Li and Mg for each component are given in Table 1.

surface of continents returns to the continents (perhaps in subduction zones), whereas the other half is recycled into the mantle.

In summary, our analysis here shows that the weathering flux out of continents is not only significant by mass but also important in influencing crustal composition. Our approach does not explicitly tell us how major elements other than Mg are affected by weathering, but we can speculate. Ca and Mg are housed in mafic minerals (plagioclase, olivine, pyroxene, biotite, and hornblende); both Ca and Mg weather faster than felsic minerals (quartz and alkali feldspar), thus Ca is expected to be preferentially leached out like Mg. Most of the Ca is likely to be deposited as carbonates on continental margins, and because carbonate sediments are not accounted for in most crustal models, an apparent loss of Ca would be recorded. Likewise, if Ca is deposited as pelagic carbonates and subducted, some of this calcium might be recycled into the mantle. As for Al and Si, these elements are hosted in the more chemically and physically resistant felsic minerals and would therefore be expected to be selectively retained in soil residues. In other words, chemical weathering leaves behind Al- and Si-rich soil residues, and hence more felsic continents.

#### Weathering Modulates Continental Growth

We now reconsider factors that enhance continent formation. If what keeps continents from being recycled is their buoyancy, and if their buoyancy is partly the result of their felsic compositions, it can be inferred that chemical weathering promotes net continent formation by decreasing the fraction k (probability) of crust recycled by subduction. Expressed in another way, continents made up of basaltic crust would be indistinguishable from oceanic crust in terms of density and would have a higher probability of being subducted eventually. We can define the net growth rate of continental crust (kg/Myr) as

$$\frac{dM_{\rm BCC}}{dt} = J_{\rm ARC} - (J_{\rm DLC} + J_{\rm DIS}) = J_{\rm ARC}(1-k), \qquad [2]$$

where  $J_i$  represents the mass flow rates for juvenile arc formation, delamination, and weathering, and the definition of k remains unchanged. As a thought experiment, we allow k to decrease exponentially with SiO<sub>2</sub> content of the continental crust to simulate the effect of increasing buoyancy (which decreases the probability of subduction) with SiO<sub>2</sub> content. Thus,  $k = k_o \exp(-(C_{BCC}^{SiO_2} - C_{ARC}^{SiO_2})/c_k)$ , where  $k_o$  is the recycling factor for basaltic crust (assumed to be close to 1 so a value of 0.9 is chosen), and  $C_i^{SiO_2}$  is the concentration in wt. % of SiO<sub>2</sub> in BCC or ARC. The decay constant  $c_k$  is taken to be  $\approx 30$  wt. %, which is the difference in SiO<sub>2</sub> content between primary basalt (45–50 wt %) and the most silicic end members in continental crust, rhyolite and granite (75–80 wt %). The SiO<sub>2</sub> content of BCC,  $C_{BCC}^{SiO_2}$  can then be tracked by simultaneously calculating the change in mass of SiO<sub>2</sub> with time:

$$\frac{dm_{\rm BCC}^{\rm SiO_2}}{dt} = J_{\rm ARC} (C_{\rm ARC}^{\rm SiO_2} - kC_{\rm out}^{\rm SiO_2}), \qquad [3]$$

where  $C_{\text{out}}^{\text{siO}_2}$  represents the average SiO<sub>2</sub> concentration of the mass (DLC + DIS) removed from the parental ARC to generate BCC. Like *k*, we expect  $C_{\text{out}}^{\text{siO}_2}$  to also decay with increasing  $C_{\text{BCC}}^{\text{SiO}_2}$ , so a similar expression is adopted:  $C_{\text{out}}^{\text{siO}_2} = C_{\text{out}}^{\text{siO}_2}$  (o)  $\exp(-(C_{\text{BCC}}^{\text{SiO}_2} - C_{\text{ARC}}^{\text{siO}_2})/c_k)$ .  $C_{\text{out}}^{\text{siO}_2}$  is assumed to be the average SiO<sub>2</sub> concentration of the initial material removed from the continents (49 wt %) and  $c_k$  is assumed to be identical to the  $c_k$  described earlier (35 wt %).

Fig. 4 shows the effect of chemical weathering on continent formation. We arbitrarily assumed juvenile arc production  $J_{ARC}$  decreased exponentially with time with a mean life of 2 Gy. The exact functional relationship of  $J_{ARC}(t)$  is irrelevant because we are not interested here in this forcing function but are instead interested in the superimposed effect of weathering on recycling rates and



**Fig. 4.** Models. Shown are the results of a model of net crustal growth, where an exponentially decaying juvenile crust production function is assumed and the recycling rate is assumed to decrease exponentially with increasing SiO<sub>2</sub> content of continents (BCC). Black curve ("minor weathering") represents the case in which recycling factor *k* is assumed to be constant at 0.9 to approximate the high probability of basaltic crust in being recycled. Red curve ("weathering") shows the case in which this condition is relaxed and *k* is allowed to decrease with increasing SiO<sub>2</sub>. (A) Net crustal growth rate is plotted versus time forward. (B) Cumulative net crustal growth normalized to mass of initial crustal nucleus (assumed to be  $1.5 \times 10^{21}$  kg or 10% of the present-day mass of continental crust). (C) Effective SiO<sub>2</sub> concentration in BCC and the sum of DLC and weathering losses (DIS). (*D*) Crustal recycling factor *k* as a function of time.

hence net crustal growth. The black curves represent the case of a basaltic crust, where a constant recycling fraction of  $k = k_o = 0.9$  is assumed. The red curves depict the case in which k decreases because the SiO<sub>2</sub> content of BCC is gradually increasing. Fig. 4 C and D shows that our SiO<sub>2</sub> contents and k values are reasonable, the latter overlapping with that constrained by Mg and Li systematics in Fig. 3A. Our simple modeling results support the idea that weathering substantially enhances the net growth of continents by rendering them less prone to subduction (Fig. 4 A and B).

#### **Implications and Further Work**

One detail not addressed by our study is the exact timing and sequence of events needed to achieve a felsic crust. Juvenile island arc basalt assimilates preexisting basement rocks that have previously passed through the weathering process, but how much time is required for weathering is not constrained from our study. Detailed regional studies would go far in clarifying this process. Our hypothesis also makes specific predictions about the composition of the Earth's mantle and crust through time. Progressive crustal formation should lead to a secular increase in the Li/Nb ratio of the mantle. This should be compensated by a secular decrease in Li/Nb and increase in SiO<sub>2</sub> content of the crust.

Our work also does not fully address the effects of weathering on other major elements (besides Mg and Si) in the crust because this is far beyond the scope of the present article. The behaviors of Fe, Na, and K could be much more complicated than that of Li and Mg. For example, the aqueous behavior of Fe is redox-sensitive. One might speculate that before  $\approx 2.3$  Gy ago when oxygen levels in the atmosphere were considerably lower, some ferrous iron may have been transported out into the ocean and deposited as banded iron formations, some of which may have been subducted, thereby representing a net loss of Fe from the continents. In the more

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oxidized environment since  $\approx 2.3$  Gy ago, Fe is expected to be immobilized as ferric iron and is relatively insoluble. In any case, we note that the average Fe content of continental crust (bulk and upper crust) (29) is only slightly depleted relative to basalt, so depletion of Fe by weathering is proportionately less than that of Mg. As for Na and K, important issues that we have not considered are how the mineralogy of clays has changed with time and how this might affect the fluxes and sinks of these elements.

Several implications follow from our conclusions. Previous investigators have speculated that continents require granites and granites require water, and therefore, the existence of continents may imply the presence of a hydrologic cycle (41, 42). Our results are in agreement but go further in showing that the link with the hydrologic cycle is not just by subduction of hydrated oceanic lithosphere and the generation of hydrous arc magmas, but also through a net chemical modification of the continents by weathering. It is well known that chemical weathering is catalyzed by life (42, 43): energy from the sun is transferred to the crust by photosynthetic absorption by plants or photoautotrophic bacteria. This energy is used to generate organic acids, break apart rocks during root growth (in the case of vascular plants), or generate inorganic carbonic acid from root or microbial respiration, all of which expedite chemical weathering by increasing the reactivity of the

- 1. Hofmann AW (1988) Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust. Earth Planet Sci Lett 90:297–314
- 2 Albarède F (1998) The growth of continental crust. *Tectonophysics* 296:1–14. Rudnick RL (1995) Making continental crust. *Nature* 378:571–578.
- 3.
- 4. Hawkesworth C, Kemp AIS (2006) Evolution of the continental crust. Nature 443:811-817
- 5. Kay RW, Kay SM (1988) Crustal recycling and the Aleutian arc. Geochim Cosmochim Acta 52:1351–1359
- 6. Kelemen PB (1995) Genesis of high Mg# andesites and the continental crust. Contrib Mineral Petrol 120:1–19.
- Holland HD (1984) The Chemical Evolution of the Atmosphere and Oceans (Princeton 7. Univ Press, Princeton, NJ).
- Albarede F, Michael A (1986) Transfer of continental Mg, S, O and U to the mantle through hydrothermal alteration of the oceanic-crust. *Chem Geol* 57:1–15. 9. Retallack, G. J (2001) Soils of the Past: An Introduction to Paleopedology (Blackwell,
- Malden, MA). 10. Edmond JM, et al. (1979) Ridge crest hydrothermal activity and the balances of the
- major and minor elements in the ocean: The Galapagos data. Earth Planet Sci Lett 46:1-18. 11. Retallack GJ (2003) Soils and global change in the carbon cycle over geological time.
- Treatise Geochem 5:1-28.
- Arvidson RE, Mackenzie FT, Guidry M (2006) MAGic: A Phanerozoic model for the geochemical cycling of major rock-forming components. Am J Sci 306:135–190.
- 13. Lee C-TA, Morton DM, Kistler RW, Baird AK (2007) Petrology and tectonics of Phanerozoic continent formation: from island arcs to accretion and continental arc magmatism. Earth Planet Sci Lett 263:370-387.
- Plank T (2005) Constraints from thorium/lanthanum on sediment recycling at subduction zones and the evolution of continents. *J Petrol* 46:921–944. Polat A, Kerrich R (2006) Reading the geochemical fingerprints of Archean hot sub-
- 15. duction volcanic rocks: evidence for accretion and crustal recycling in a mobile tectonic regime. AGU Monograph 164:189–213. 16. Chamberlain KR, Frost CD, Frost BR (2003) Early Archean to Mesoproterozoic evolution
- of the Wyoming province: Archean origins to modern lithospheric architecture. Can J Earth Sci 40:1357-1374.
- Hoffman PF (1989) Precambrian geology and tectonic history of North America. The 17. Geology of North America-An Overview, eds Bally AW, Palmer AR (Geological Society of America, Boulder, CO), Vol A, pp 447–511.
- 18. Lee C-TA, Cheng X, Horodyskyj U (2006) The development and refinement of continental arcs by primary basaltic magmatism, garnet pyroxenite accumulation, basaltic recharge and delamination: Insights from the Sierra Nevada, California. Contrib Mineral Petrol. 10.1007/s00410-005-0056-1.
- 19. Ducea MN, Saleeby JB (1998) The age and origin of a thick mafic-ultramafic keel from beneath the Sierra Nevada batholith. Contrib Mineral Petrol 133:169–185. 20.
- Ducea MN (2002) Constraints on the bulk composition and root foundering rates of continental arcs: A California arc perspective. J Geophys Res, 10.1029/2001JB000643.
- Kistler RW, Wooden JL, Morton DM (2003) Isotopes and ages in the northern Peninsular Ranges batholith, southern California. U.S. Geological Survey Open-File Report 03-489, p 45.
- Kistler RW (1990) Two different lithosphere types in the Sierra Nevada, California. The Nature and Origin of Cordilleran Magmatism, ed Anderson JL (Geological Society of America, Boulder, CO), Geol. Soc. Am. Memoir, Vol 174, pp 271–281.
- Ague JJ, Brimhall GH (1988) Regional variations in bulk chemistry, mineralogy, and the compositions of mafic and accessory minerals in the batholiths of California. Geol Soc Am Bull 100:891–911.
- Huh,Y, Chan L-H, Chadwick OA (2004) Behavior of lithium and its isotopes during weathering of Hawaiian basalt. Geochem Geophys Geosys, doi:10.1029/ 2004GC000729.
- 25. Huh Y, Chan LH, Zhang L, Edmond JM (1998) Lithium and its isotopes in major world rivers: Implications for weathering and the oceanic budget. Geochim Cosmochim Acta 62:2039-2051.

rock substrate (42-45). Could the growth of continents have been indirectly modulated by the evolution of life (42, 43)? For example, terrestrial weathering could have been dominated by cyanobacteria in the Archean and Proterozoic [some of which could have also used  $Fe^{2+}$  as an energy source (46)], lichen and fungi in the late Proterozoic and Cambrian, vascular land plants beginning in the Devonian, and Angiosperms beginning in the Cretaceous; these life forms have different effects on the styles and rates of chemical weathering (43, 47) and might be expected to influence the composition of the crust and mantle in different ways.

Finally, although we did not consider here what controls juvenile crust production (the crustal growth forcing function), it is likely that this variable is also coupled to net continental growth. Large expanses of continents have an insulating effect on heat loss from the interior of our planet, which implies that the thermal evolution of the Earth and its vigor of convection may be indirectly coupled to continental growth (48). If so, what is the role of chemical weathering in the thermal evolution of Earth?

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- 26. Ryan JG, Langmuir CH (1987) The systematics of lithium abundances in young volcanicrocks. Geochim Cosmochim Acta 51:1727-1741.
- 27. Leeman WP (1996) Boron and other fluid-mobile elements in volcanic arc lavas: Implications for subduction processes. Subduction Top to Bottom, eds Bebout GE, Scholl D, Kirby S, Platt JP (American Geophysical Union, Washington, DC), American Geophysical Union Monograph 96, pp 269-276.
- 28. McDonough WF, Sun S-S (1995) The composition of the Earth. Chem Geol 120:223-253.
- 29. Rudnick RL, Gao S (2003) Composition of the continental crust. Treatise Geochem 3:1-64.
- 30. Teng F-Z, et al. (2004) Lithium isotopic composition and concentration of the upper continental crust. Geochim Cosmochim Acta 68:4167-4178.
- 31. Workman RK, Hart SR (2005) Major and trace element composition of the depleted MORB mantle (DMM). Earth Planet Sci Lett 231:53-72.
- 32. Morton DM, Matti JC (2001) Geologic map of the Lakeview 7.5' quadrangle, Riverside County, California. U.S. Geological Survey Open-File Report 2001-174, p 26. 33. Todd VR, Erskine BG, Morton DM (1988) Metamorphic and tectonic evolution of the
- Penisular Ranges batholith. Metamorphism and Crustal Evolution of the Western United States, ed Ernst WG (Prentice-Hall, Englewood Cliffs, NJ), Rubey Vol VII, pp 894-937.
- 34. Wade J, Wood BJ (2001) The Earth's "missing" niobium may be in the core. Nature 409.75-78
- 35. Kamber BS, Greig A, Collerson KD (2005) A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. Geochim Cosmochim Acta 69:1041-1058.
- 36. Chan L-H, Edmond JM, Thompson G, Gillis KM (1992) Lithium isotope composition of submarine basalts - implications for the lithium cycle in the oceans. Earth Planet Sci Lett 108.151-160
- 37. Teng F-Z, McDonough WF, Rudnick RL, Walker RJ, Sirbescu, M-LC (2006) Lithium isotopic systematics of granites and pegmatites from the Black Hills, South Dakota. Am Mineral 91:1488-1498
- 38. Kemp AIS, et al. (2007) Magmatic and crustal differentiation history of granitic rocks from Hf-O isotopes in zircon. Science 315:980-983.
- 39. Aiuppa A, et al. (2000) Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). Geochim Cosmochim Acta 64:1827-1841.
- 40. Brown M (2007) Metamorphic conditions in orogenic belts: A record of secular change. Int Geol Rev 49:193-234.
- Campbell IH, Taylor SR (1983) No water, no granites—No oceans, no continents. Geophys Res Lett 10:1061–1064.
- 42. Rosing MT, Bird DK, Sleep NH, Glassley W, Albarede F (2006) The rise of continents-An essay on the geologic consequences of photosynthesis. Palaeogeogr Palaeoclimatol Palaeoecol 232:99-113.
- 43. Berner RA (1997) The rise of plants and their effect on weathering and atmospheric CO2. Science 276:544-546.
- 44. Drever JI (1994) The effect of land plants on weathering rates of silicate minerals. Geochim Cosmochim Acta 58:2325-2332.
- 45. Sleep NH, Bird DK (2007) Niches of the pre-photosynthetic biosphere and geologic preservation of Earth's earliest ecology. Geobiology 5:101-117.
- 46. Kappler A, Newman DK (2004) Formation of Fe(III)-minerals by Fe(II)-oxidizing photoautotrophic bacteria. Geochim Cosmochim Acta 68:1217-1226.
- 47. Banfield JF, Barker WW, Welch SA, Taunton A (1999) Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. Proc Natl Acad Sci USA 96:3404-3411.
- 48. Lenardic A, Moresi L-N, Jellinek AM, Manga M (2005) Continental insulation, mantle cooling, and the surface area of oceans and continents. Earth Planet Sci Lett 234:317-333.