Lithium in >4.0 Ga Jack Hills zircons

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Abstract

In situ Li analyses of 4348 to 3362 Ma detrital zircons from the Jack Hills, Western Australia by SIMS reveal that the Li abundances (typically 10 to 60 ppm) are commonly over 10,000 times higher than in zircons crystallized from mantle-derived magmas and in mantle-derived zircon megacrysts (typically <2 ppb). The Jack Hills zircons also have fractionated Li isotope ratios (δ^7Li = -19 to +13 ‰) about five times more variable than those recorded in primitive ocean floor basalts (2 to 8 ‰), but similar to continental crust and its weathering products.

The high Li concentrations indicate that primitive magmas were not the source of Jack Hills zircons and the fractionated values of δ^7Li suggest that highly weathered regolith was sampled by these early Archean magmas. The high Li concentration and extremely low δ^7Li were observed in zircons as old as 4300 Ma. Thus, Li compositions of Jack Hills zircons support the existence of chemically differentiated and extensively weathered crust by at least 4300 Ma.

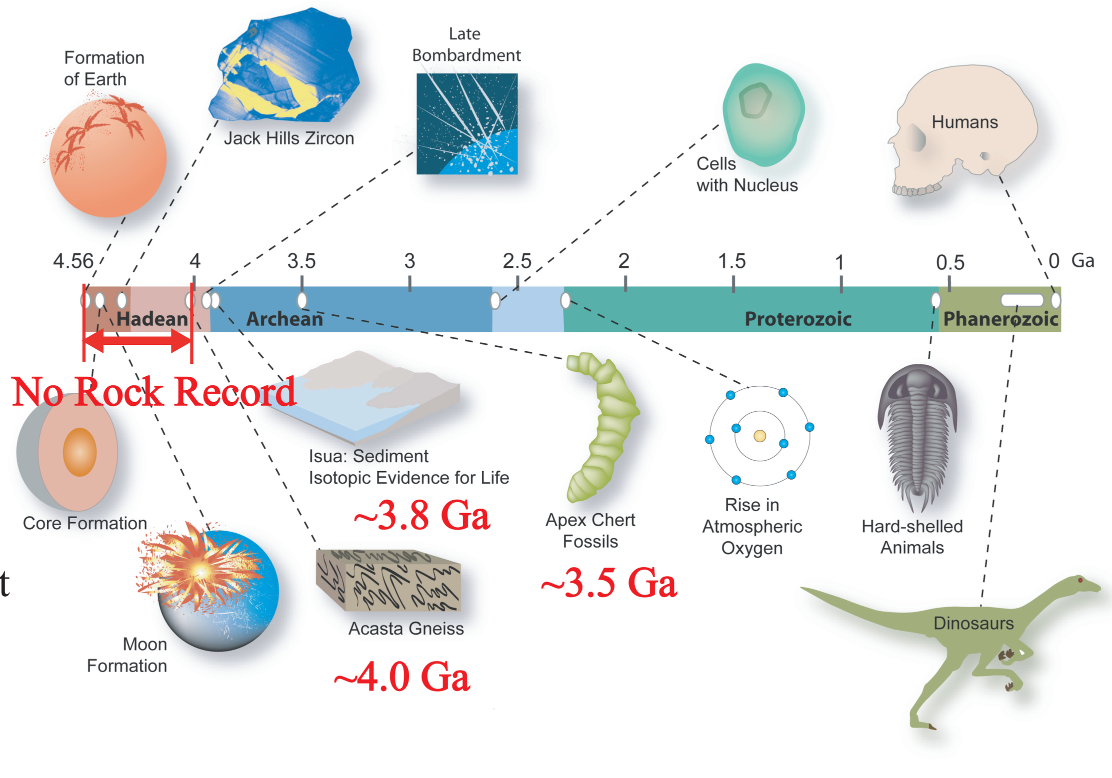
1. Introduction

Why zircon?

There is no rock sample older than ~4.0 Ga.

However, differentiated crust and ocean may have formed before 4.0 Ga [ref.1].

Zircons of >4.0 Ga are the only samples to investigate the Earth's surface environment before 4.0 Ga.



Why lithium?

(1) Li is moderately incompatible:
Li would be concentrated in zircons from the evolved magma.

(2) Li isotopic fractionation is less than 5 ‰ at magmatic temperature [ref. 2]:
Zircon preserves the Li isotopic ratio of its parent magma.

(3) Li isotopes largely fractionate when minerals react with water at low temperature [ref. 3]:
Fractionated Li isotopes would be observed if precursors of zircons reacted with water.

2. Analytical Technique

(Instrument)
Wisc-SIMS (CAMECA ims-1280)
Primary: 13 keV O^- (0.7 to 3 nA, ~15 μm in dia.)
Secondary: 10 keV acceleration, MRP = 2,200
$^6Li^+$ & $^7Li^+$ were detected by two EMs.

(Standard)
Xinjiang zircon (NMNH #146260)
δ^7Li = +7.9 +/- 2.1 ‰ (2SD)
[Li] = 6.4 +/- 1.9 ppm (2SD)
NIST SRM 612 glass [ref. 4, 5]
δ^7Li = +31.2 ‰ [Li] = 41.5 ppm

References

[1] Cavosie et al. (2007) in Developments in Precambrian Geology, 15, Elsevier, pp. 91-111. [2] Halama et al. (2007) EPSL, 254, 77-89. [3] Wunder et al. (2006) Contrib. Mineral. Petrol., 151, 112-120. [4] Pearce et al. (1996) Geostand. Newsl., 21, 115-145. [5] Kasemann et al. (2005) Anal. Chem., 77, 5251-5257. [6] Finch et al. (2001) Am. Mineral., 86, 681-689. [7] Cavosie et al. (2006) GCA, 70, 5601-5616. [8] Cavosie et al. (2005) EPSL, 235, 663-681.

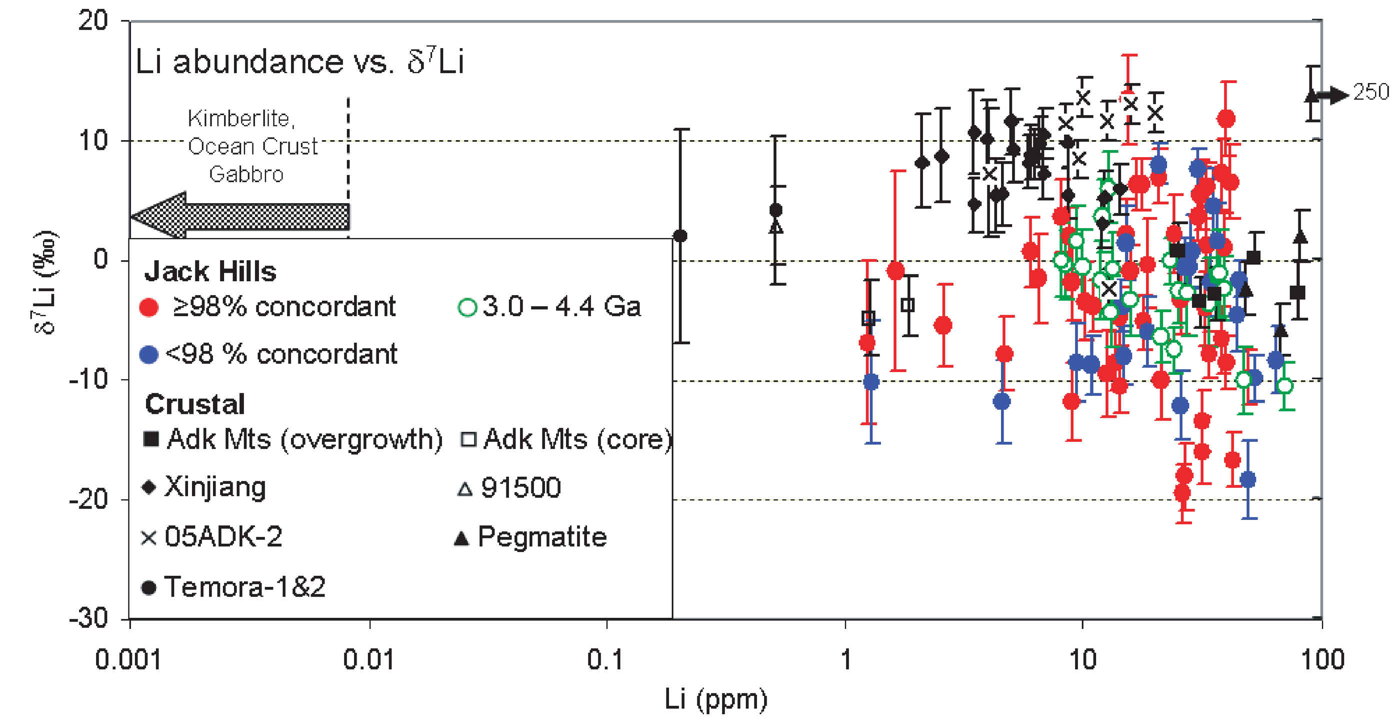
3. Results

Samples:

Jack Hills zircons:
55 grains (4348 to 3362 Ma)

Mantle derived zircons:
Kimberlite,
Ocean floor gabbro

Continental crustal zircons:
Adirondack Mts (migmatite),
91500 (unknown),
Temora-1, -2 (gabbroic diorite),
05ADK-2 (felsic pegmatite intrusion),
Li-rich granitic pegmatites

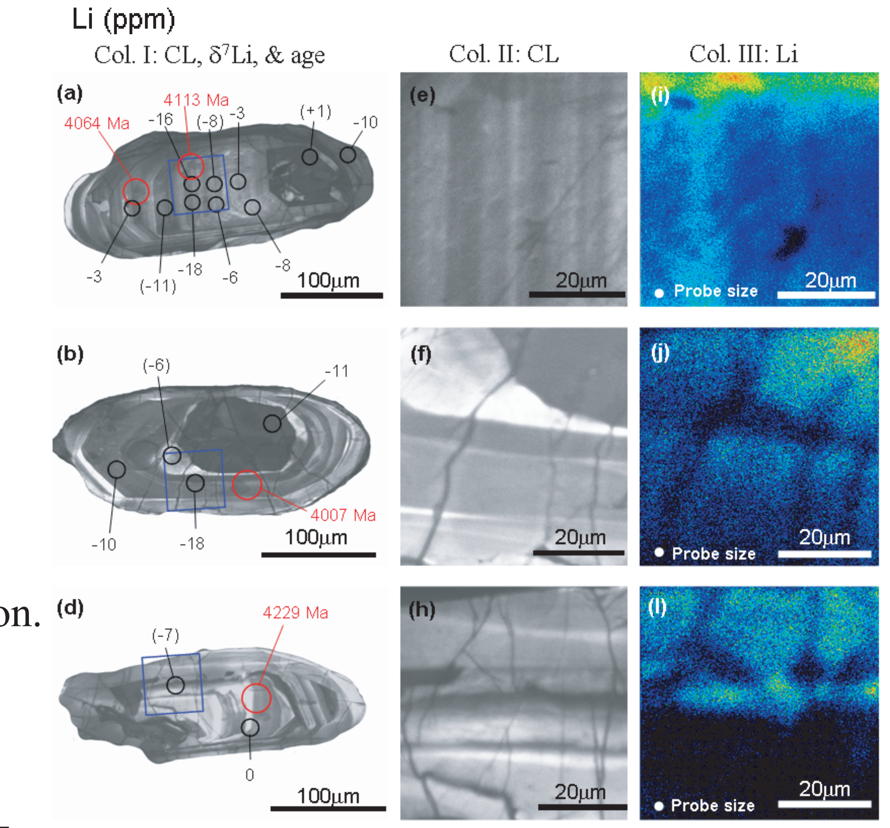


CL-Li correlation in Jack HIlls zircons

Li mapping:
- Li concentration correlates with CL bands.
- No localized Li hot spot.

Multiple Li isotope analyses:
- δ^7Li in single growth bands is identical within analytical precision.
- No correlation between δ^7Li and distance from the grain edge.

No evidence for post-crystallization Li exchange

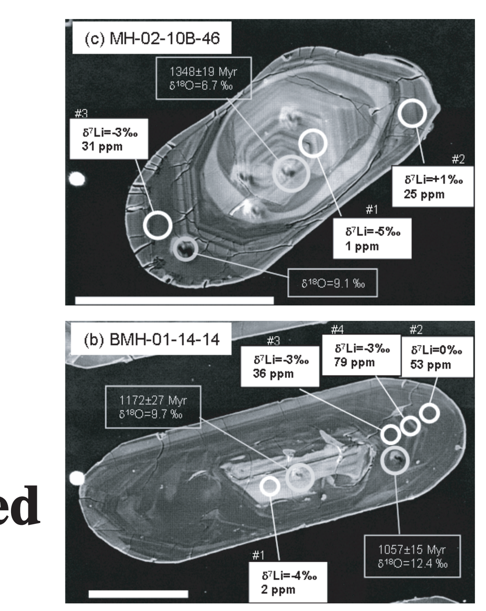


Adirondack Mts migmatite zircons

MH-02-10B-46: Upper amphibolite facies
BMH-01-14-14: Granulite facies

- Detrital igneous core and metamorphic overgrowth from pelitic migmatites have distinct Li abundances.
- Zonation and absence of low δ^7Li argue against diffusion exchange.

The primary Li compositions are preserved after high-grade metamorphism.



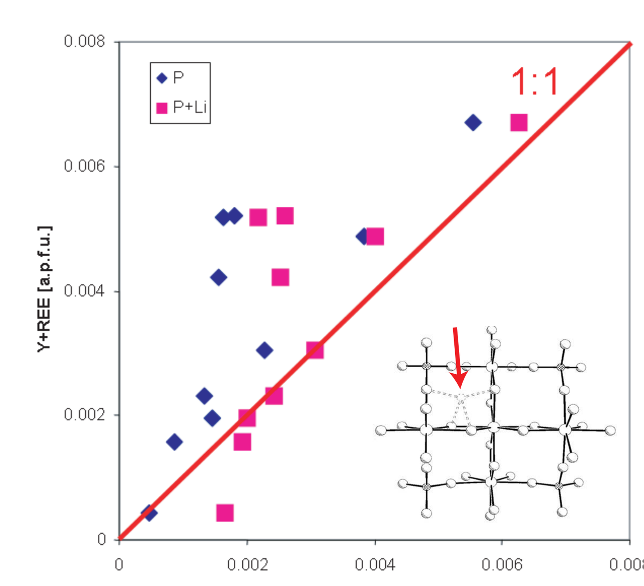
(Scale Bars: 50 μm)

Li substitution in zircons

(1) Xenotime substitution:
$(Y, REE)^{3+} + P^{5+} = Zr^{4+} + Si^{4+}$
(2) Li interstitial substitution [ref. 6]:
$Li^{1+}_{(interstitial)} + (Y, REE)^{3+} = Zr^{4+}$

(1) only: (REE + Y)/P = 1.84. [ref. 7]
(1) + (2): (REE + Y)/(P + Li) = 1.23.

Li in zircon may be linked to charge-balanced trivalent cations.



4. Discussion

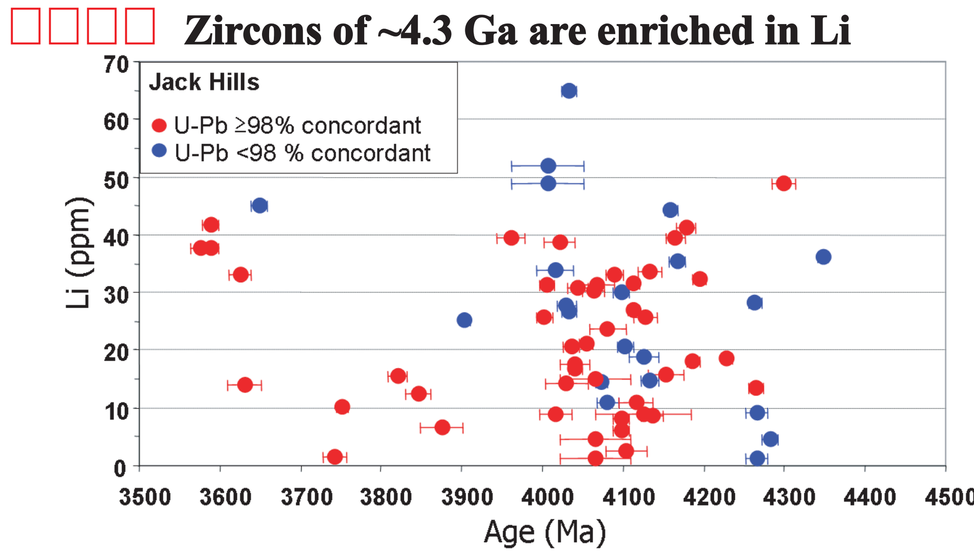
Li abundance in Jack Hills zircons

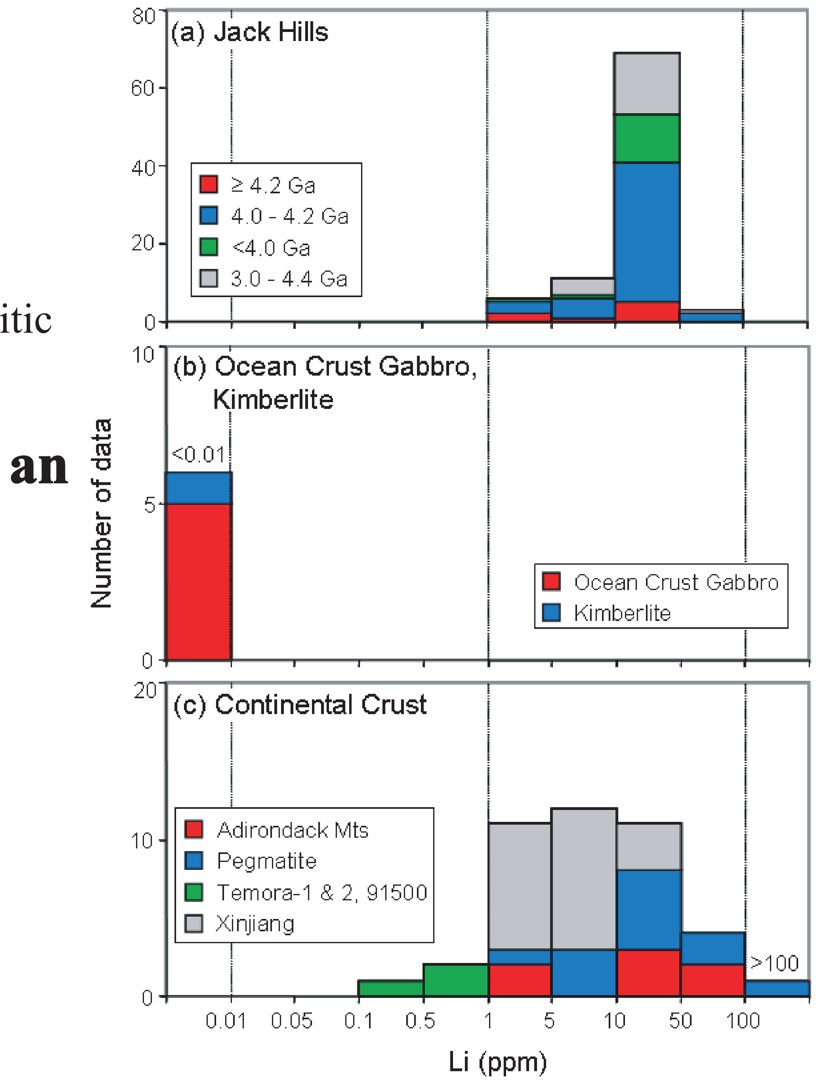
Li rich (typically >10 ppm)

- Distinct from Ocean crust and Kimberlite.zircons.
- Comparable to zircons from granitic pegmatite and pelitic migmatite.

Most of Jack Hills zircons crystallized in an evolved magma.

Zircons of ~4.3 Ga are enriched in Li





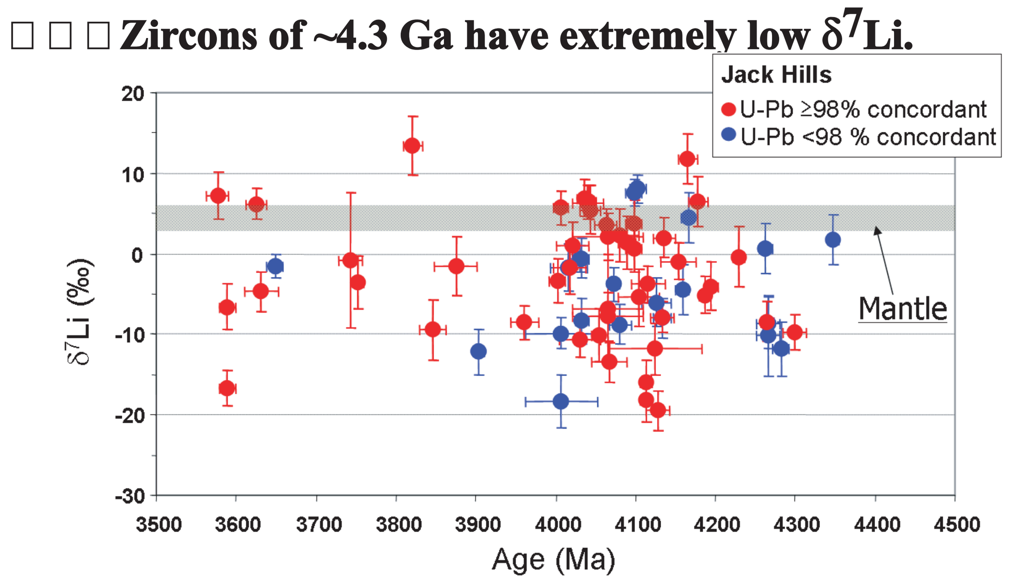
Li isotope in Jack Hills zircons

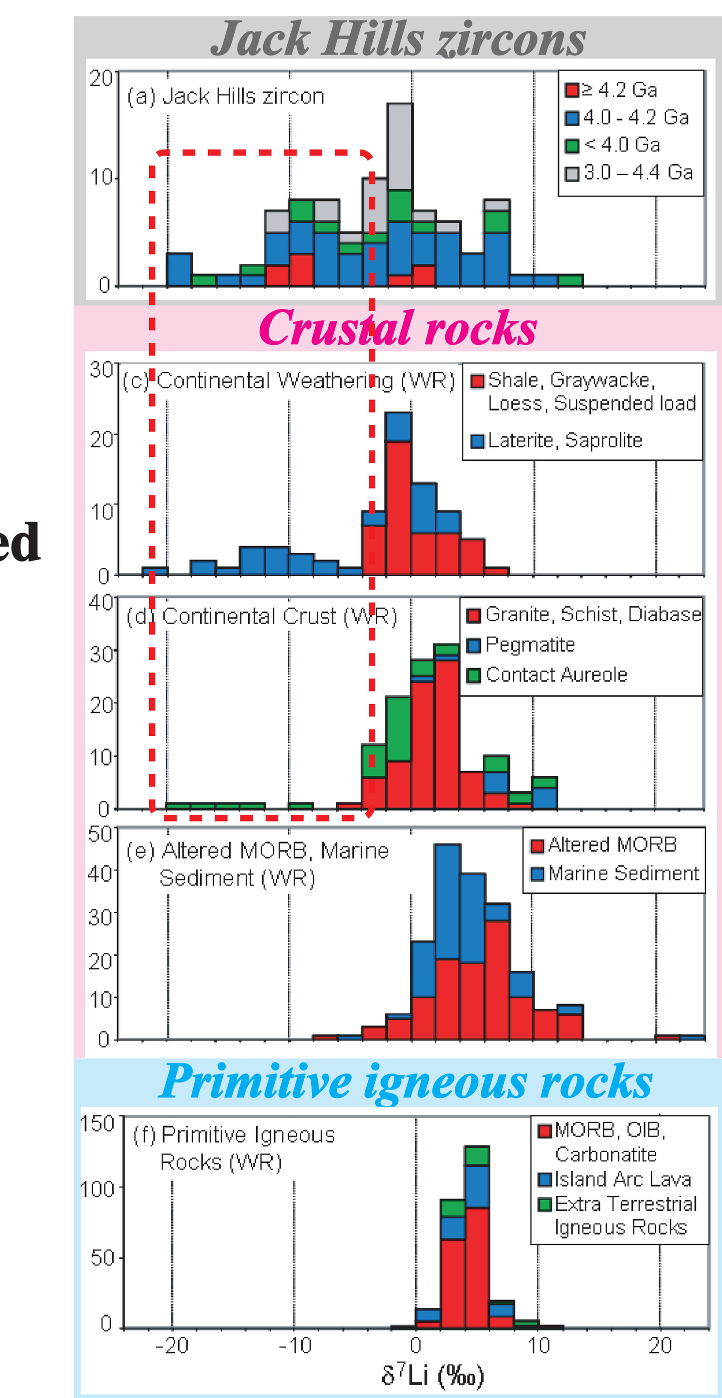
Large variation in δ^7Li
Extremely low δ^7Li (< -10 ‰)

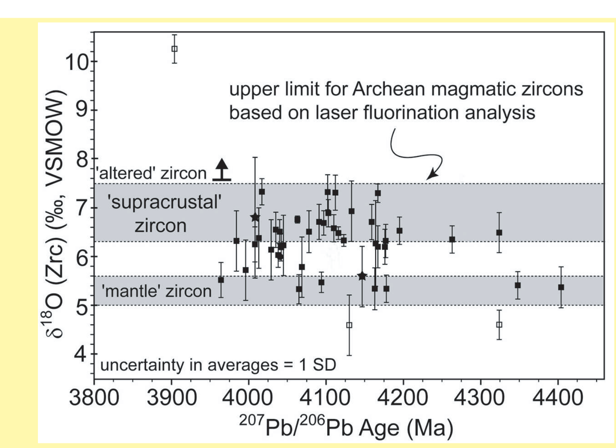
- Distinct from primitive magma (e.g. MORB, OIB).
- Extremely low δ^7Li is observed in weathered component in contirental crust.

Evidence for magmatic recycling of weathered crust formed at low temperature.

Zircons of ~4.3 Ga have extremely low δ^7Li.







The supracrustal δ^{18}O is observed in Jack Hills zircons as early as 4.3 Ga [e.g. ref. 8]. The Li data is consistent with the O isotope data.

5. Conclusions

(1) Correlation between Li composition and the pattern of magmatic growth-zoning of Jack Hills zircons suggests Li chemical diffusion in zircon is slow and zircons preserve primary igneous Li composition and information for the origin of their parental magma.
(2) High Li concentration in Jack Hills zircons suggests they crystallized from an evolved magma or magma contaminated with surface material as early as 4.3 Ga.
(3) The highly variable δ^7Li can be explained as the result of aqueous alteration at the surface of the Earth. Especially, extremely low δ^7Li implies the magmatic recycling of weathered crust as old as 4.3 Ga.
(4) Thus, Li composition of Jack Hills zircons supports the existence of chemically differentiated and extensively weathered crust by at least 4.3 Ga.
(5) Parhaps rocks >4.0 Ga were weathered and only zircons remain.