Use of Zircon U-Pb Ages And Bulk Trace Element and Nd-Hf Isotope Compositions to Determine Soil Provenance in a Limestone Terrane, Middle TN, USA

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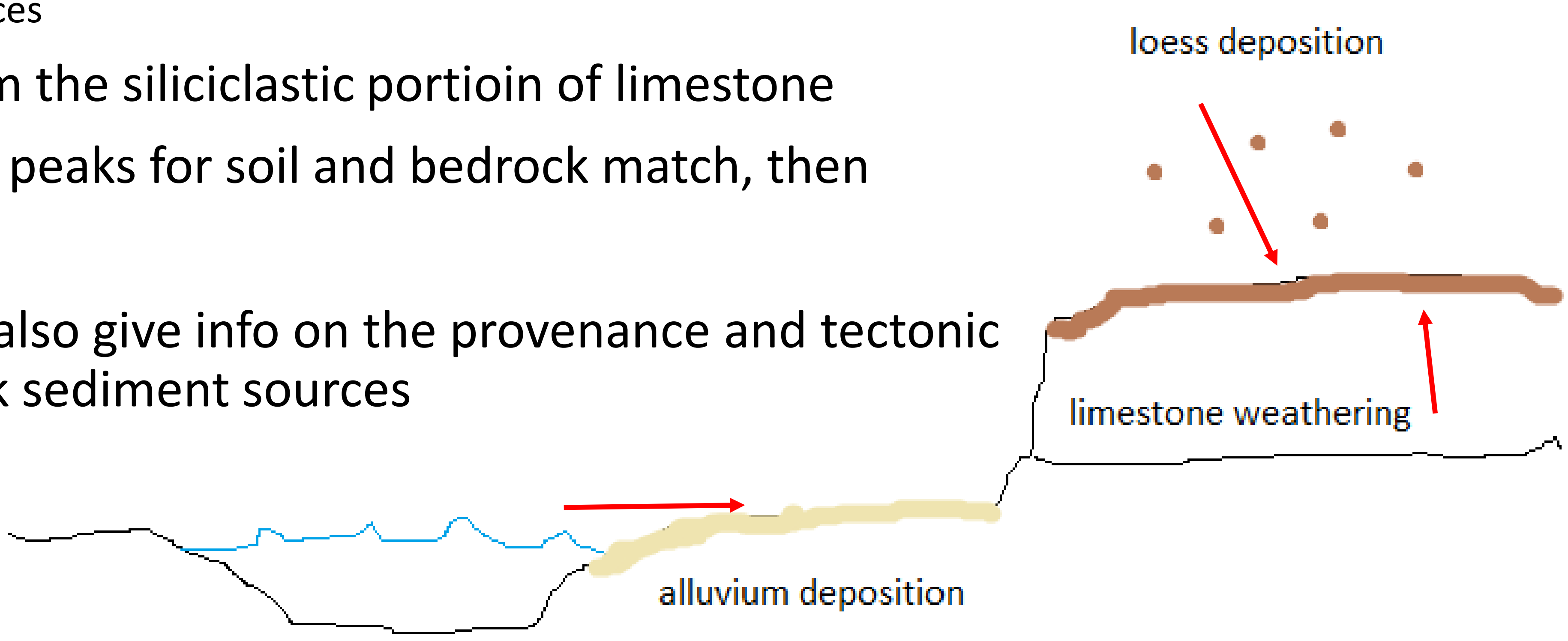
How did soil form in middle TN?

- In-situ chemical weathering of limestone?
- Input of exotic material such as alluvium or loess?
- Identify the source (provenance) of soil-forming material by studying samples of
  - undisturbed soil (high, flat, non-agricultural areas)
  - potential soil sources
- Obtain zircon from the siliciclastic portioin of limestone
- If zircon U-Pb age peaks for soil and bedrock match, then

soil formed in-situ

- Zircon U-Pb ages also give info on the provenance and tectonic setting of bedrock sediment sources



Why zircon U-Pb dating?

- Elemental and isotopic composition and mineralogy not reliable provenance indicators
  - Transport of loess and river alluvium can change composition and mineralogy of deposit
  - Chemical weathering during soil formation changes composition and mineralogy
- Zircon age spectra less likely to be affected by transport or chemical weathering
- Only two previous studies of soil provenance using zircon U-Pb dating; the first was:

Brimhall, G.H., Lewis, C.J., Compston, W., Williams, I.S., Reinfrank, R.F., 1993. Darwinian zircons as provenance tracers of dust-size exotic components in laterites: mass balance and SHRIMP ion microprobe results, in Soil Micromorphology: Studies in Management and Genesis. Elsevier, pp. 65–81. http://dx.doi.org/10.1016/S0166-2481(08)70398-2

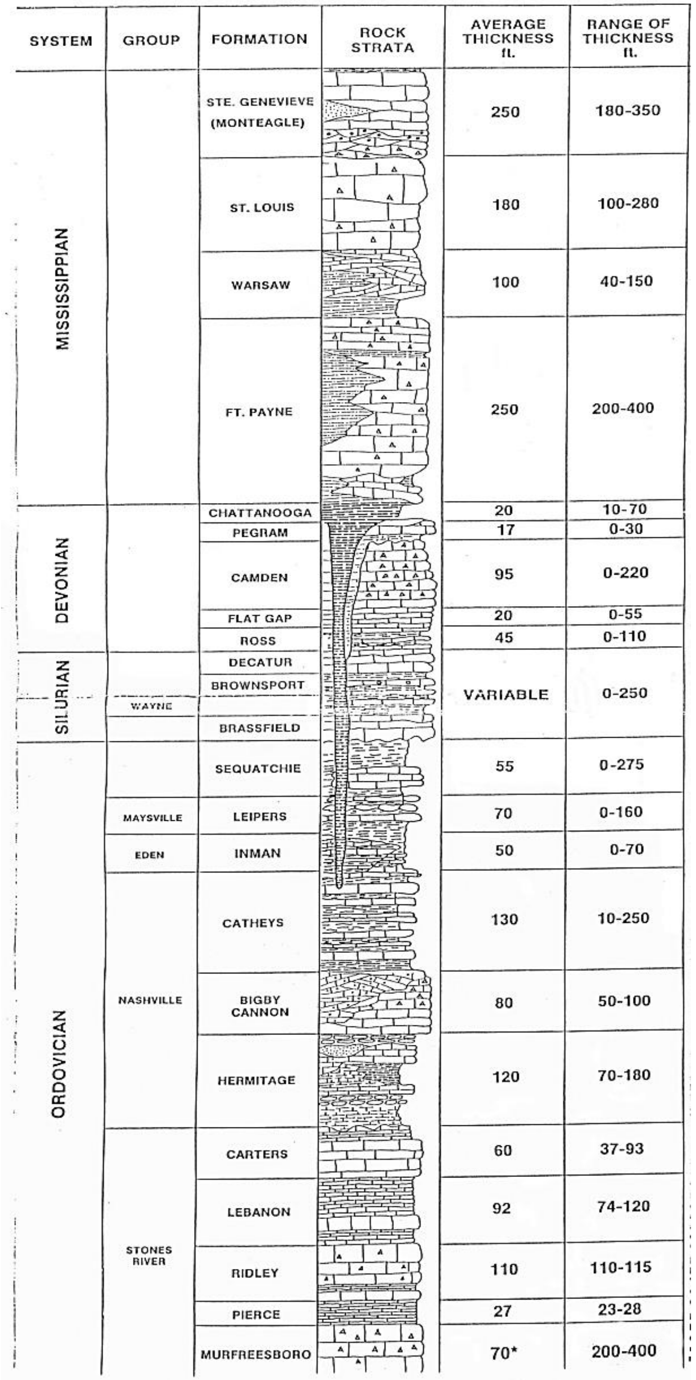
Middle Tennessee Geology

Site 1: Fort Payne Formation

Site 2

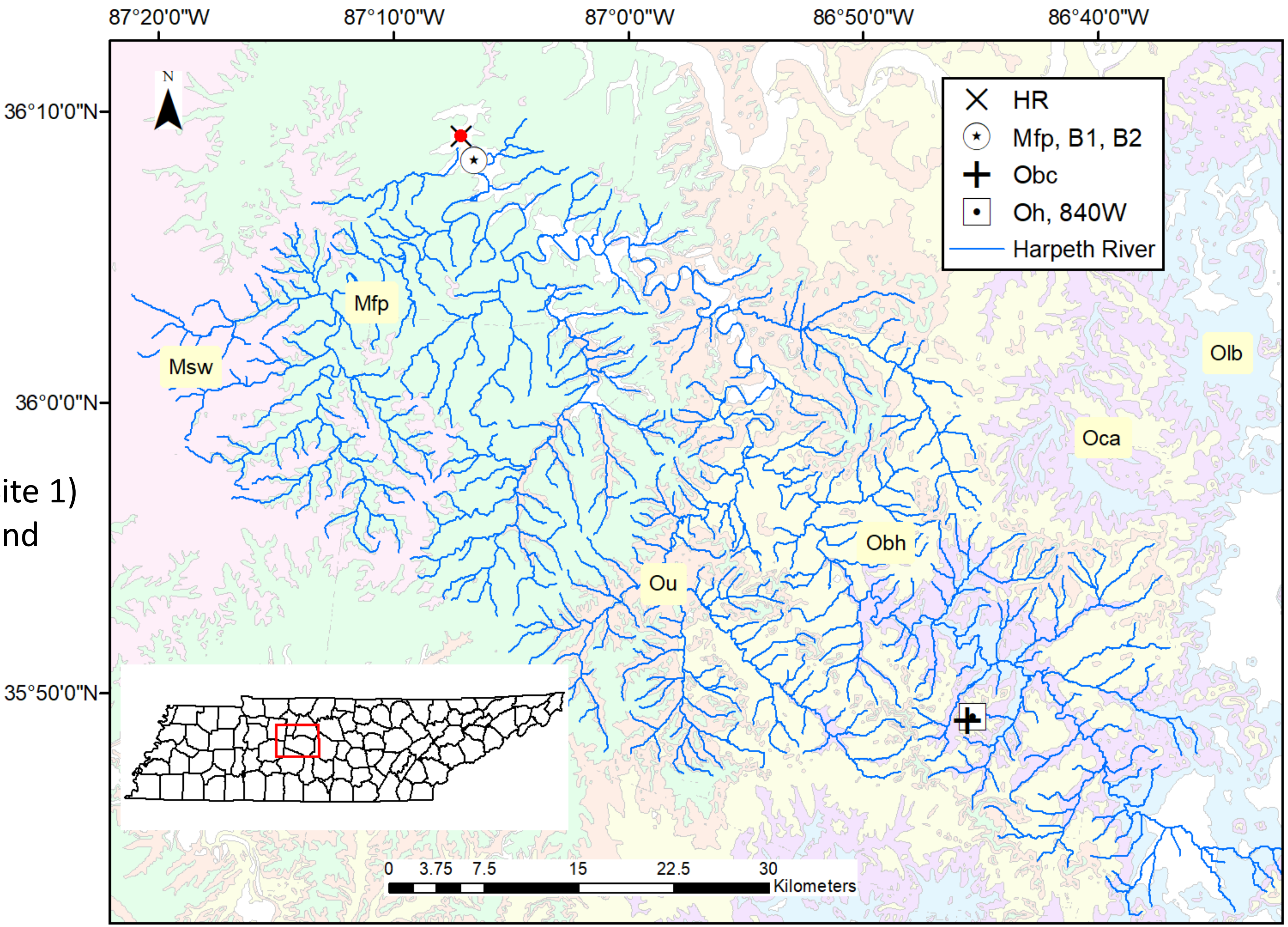
Bigby-Cannon Limestone

Hermitage Formation

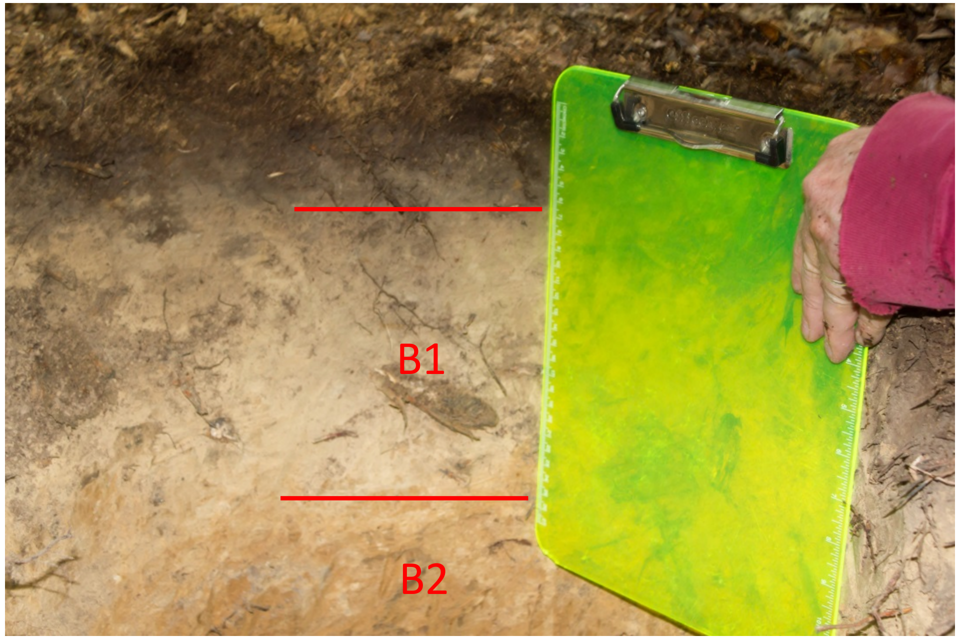


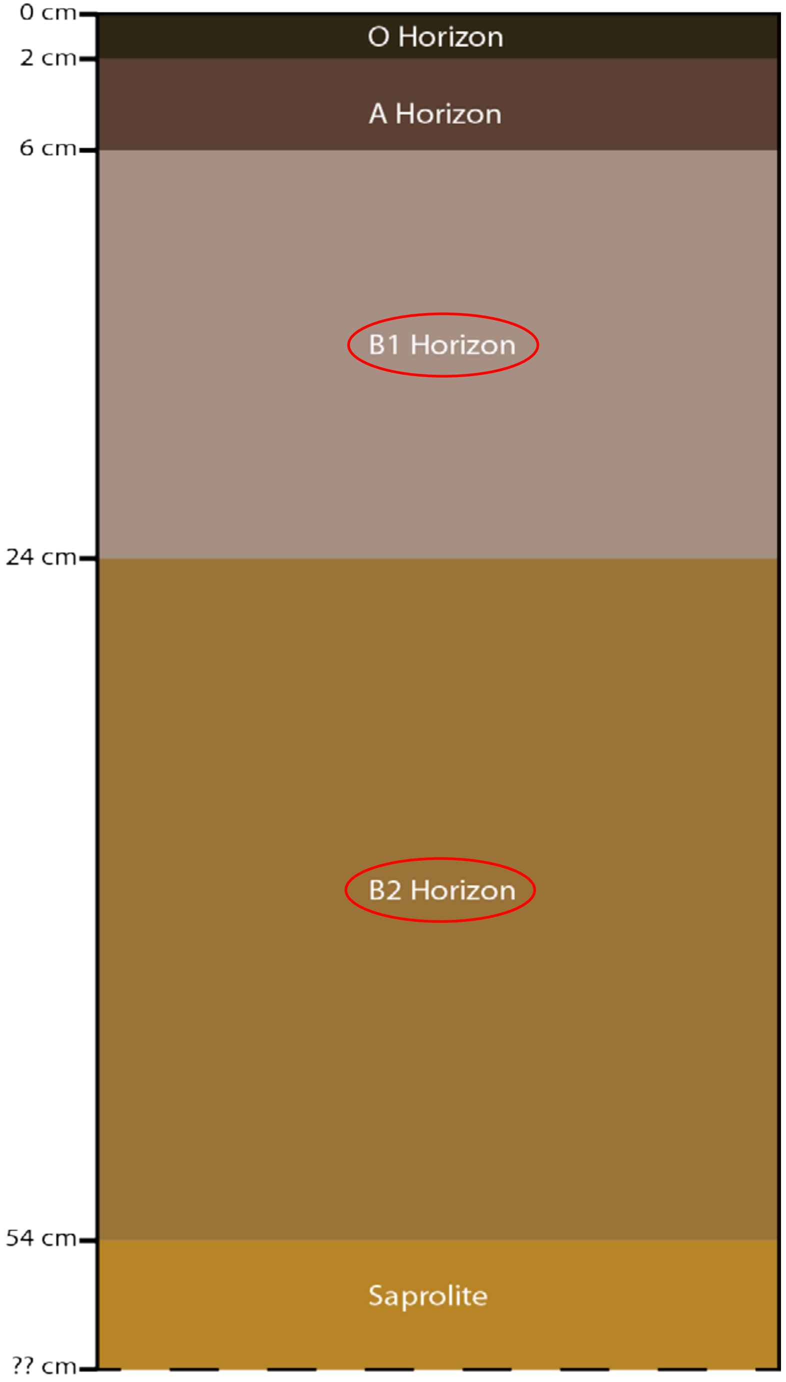
Sample Locations

- Mfp = Mississippian Fort Payne (Site 1)
- Obh = Ordovician Bigby Cannon and Hermitage limestones (site 2)



Field Site 1: Harpeth River Terrace: Ultisol

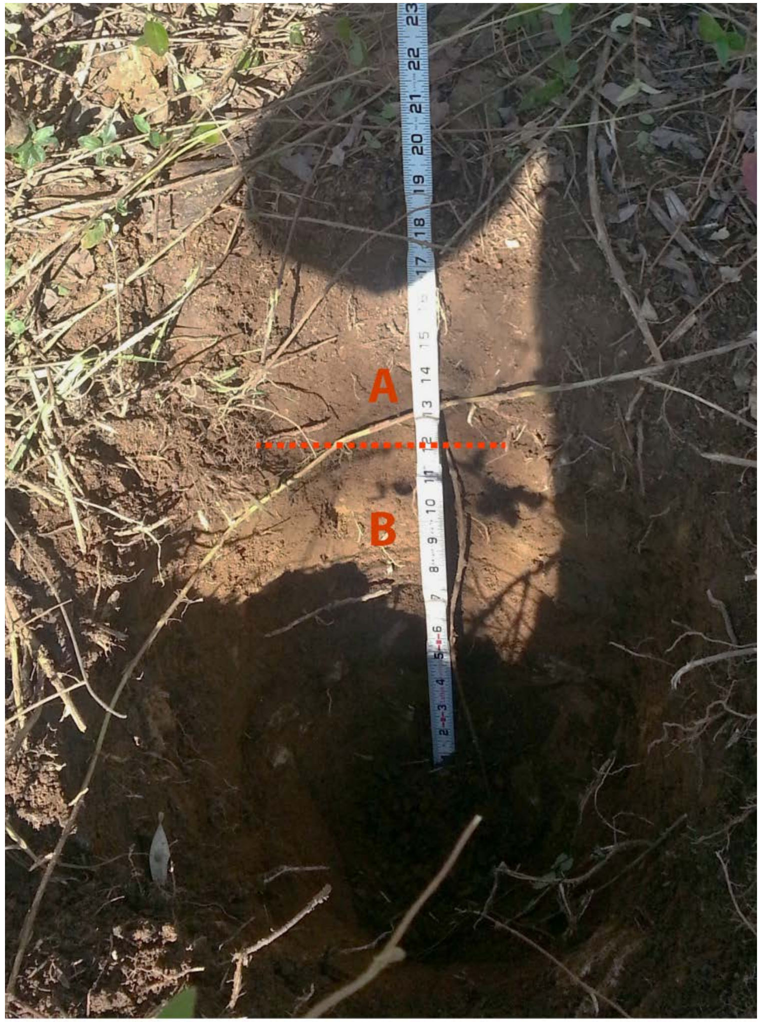




Field Site 2: Highway Outcrop
Sampling

- Alfisol soils atop Hermitage Fm. (Oh) Ordovician sandy and argillaceous limestone bedrock

Field Site 2:
Sampling of alfisol



Field Site 2: Obc sample

- Bigby-Cannon Limestone (Obc) Ordovician phosphatic calcarenite/limestone
- Located 0.15km away from the Hermitage-Alfisol sample site

Xiaomei Wang and Jenna Nam

Loess outcrop in Meeman Shelby Park, Memphis, TN

Bulk Soil Properties

Site	Sample	Munsell Color	ρ (g/cm^3)	Mean grain size (μm)	Soil Texture (USDA)
1	B1	10YR 6/3	1.5 ± 0.2	43	Silt
1	B2	10YR 5/6	1.5 ± 0.2	19.9	Silt
2	W840	7.5YR 5/4	1.8 ± 0.2	29.3	Silt Loam

Bulk Properties

Sample	% Insol. Residue	$\epsilon_{Zr, w}$	CIA %	% OC
B1	NA	0.81	73	0.69
B2	NA	0.76	84	0.63
W840	NA	0.68	76	1.81
Mfp	99%	NA	78	
Oh	28%	NA	70	
Obc	15%		60	
PL	82%			3.92
RS	99%			0.25
HR	99%			1.02

Major element compositions

Original name	Loveland loess	Roxana silt	Peoria loess	Harpeth R.	Mfp	B1	B2	Oh	Obc	W840
SiO2	88.92	77.26	69.46	81.87	87.33	86.14	78.12	24.2	5.67	67.32
TiO2	0.32	0.87	0.71	0.99	0.33	1.03	0.99	0.2	0.04	0.64
Al2O3	5.29	10.05	9.10	7.16	5.13	5.14	8.76	4.02	1.04	6.34
TFe2O3	1.75	3.91	3.21	3.42	2.58	2.36	4.39	1.62	0.49	3.21
MnO	<0.01	0.06	0.08	0.04	<0.01	0.02	0.02	0.16	0.05	0.15
MgO	0.21	0.68	2.83	0.37	0.46	0.24	0.43	1.19	2.68	0.47
CaO	0.48	0.49	3.89	0.39	0.19	0.1	0.09	36.57	48.2	7.7
Na2O	0.04	0.48	1.33	0.32	0.09	0.37	0.27	0.13	0.11	0.25
K2O	0.19	1.66	2.07	1.1	1.05	1.03	0.95	1.19	0.3	1.09
P2O5	0.03	0.06	0.11	0.24	0.05	0.04	0.08	1.69	2.81	5.96
LOI	2.61	4.30	7.17	4.29	2.97	3.31	5.76	29.28	38.31	6.75
TOTAL	99.84	99.81	99.95	100.19	100.18	99.78	99.86	100.25	99.7	99.88

Powder XRD Results

- W840 soil has same minerals as Oh bedrock
- B1 and B2 soils do not have the same minerals as Mfp bedrock

Sample	Quartz	Microcline	Albite	HAp	Chlorite	Amphibole	Sum
B1	95	4	1	0	0	0	100
B2	95	2	1	0	2	0	100
Mfp	100	0	0	0	0	0	100
Obc	38	8	11	35	8	0	100
W840	92	2	2	4	0	0	100
Oh	87	3	1	9	0	0	100
HR	97	2	1	0	0	0	100
PL	90	2	5	0	2	1	100
RS	97	2	1	0	0	0	100
LL	98	0	0	0	2	0	100

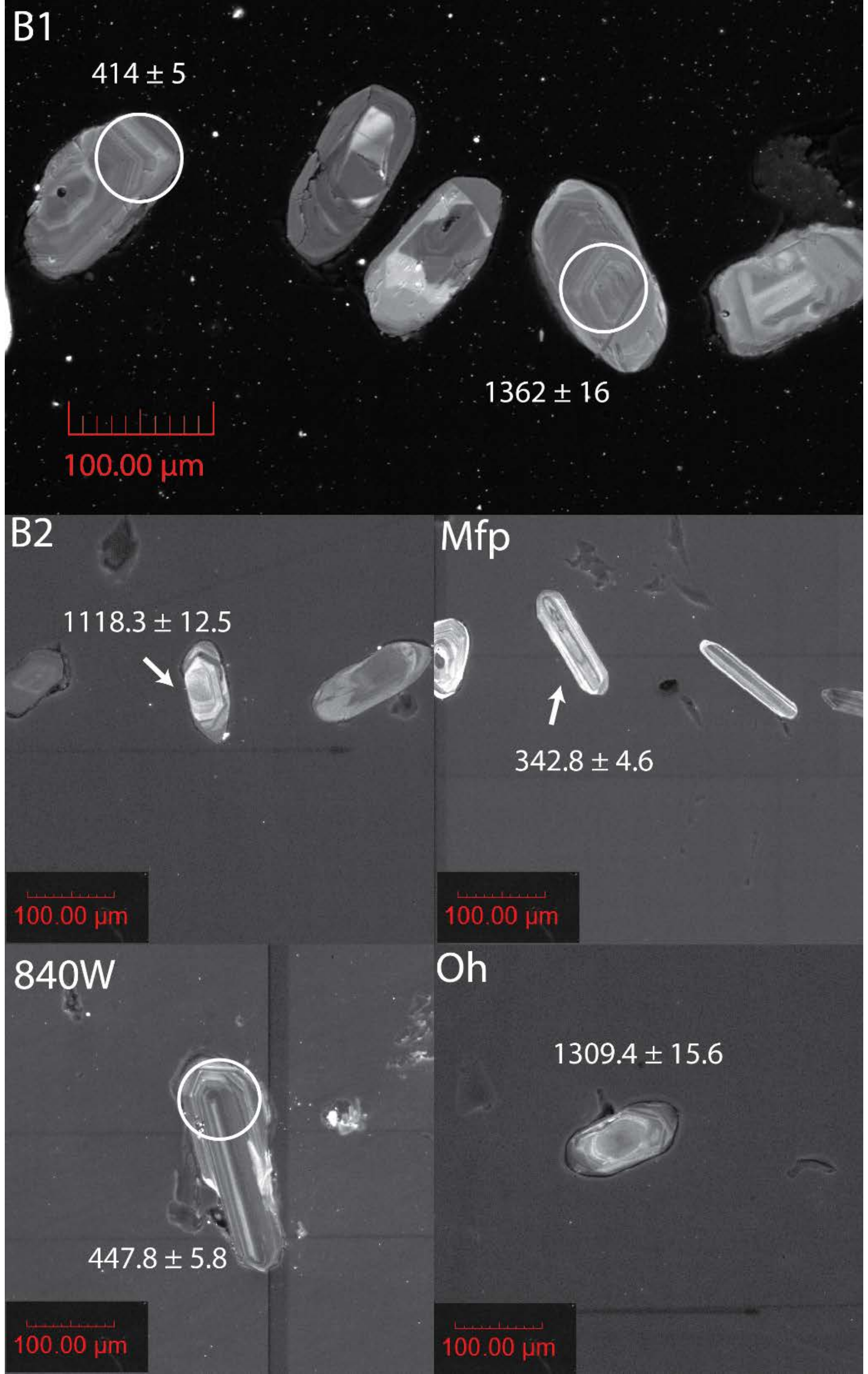
Geochronological Methods

- CL imaging – zoning and inclusions
- ThermoFisher iCAP Qc quadrupole ICP-MS with CETAC autosampler and Photon Machine Excite 193nm excimer laser ablation system
- 50 x 50 µm spot size
- Data processed in Glitter, then ET_Redux v. 3.6.25
- Analyses that were > 20% positively or negatively discordant were rejected, where % discordance was calculated as

  $100-(100*(^{206}Pb/^{238}U \text{ date})/(^{207}Pb/^{206}Pb \text{ date}))$

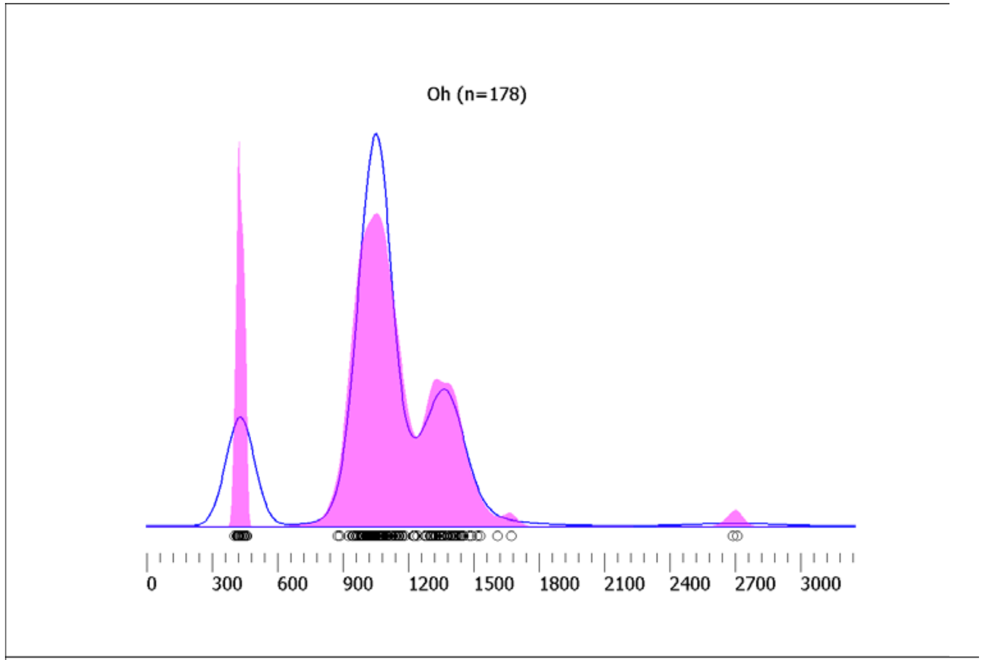
- Age spectra plotted as kernel density estimates using "DensityPlotter" program of Vermeesch (2012)

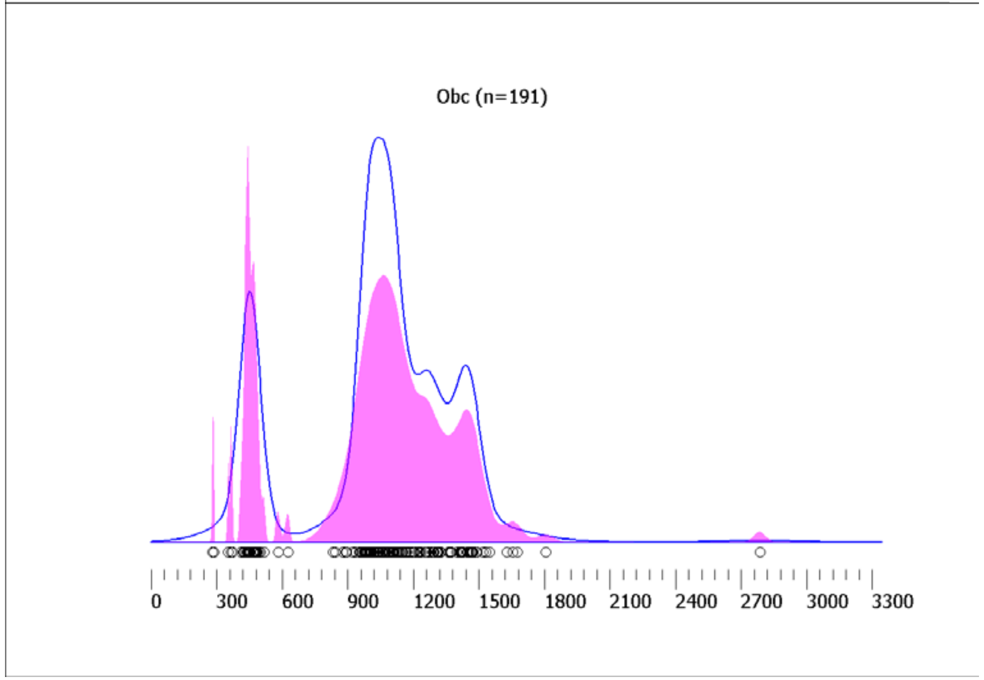
Zircon CL Images

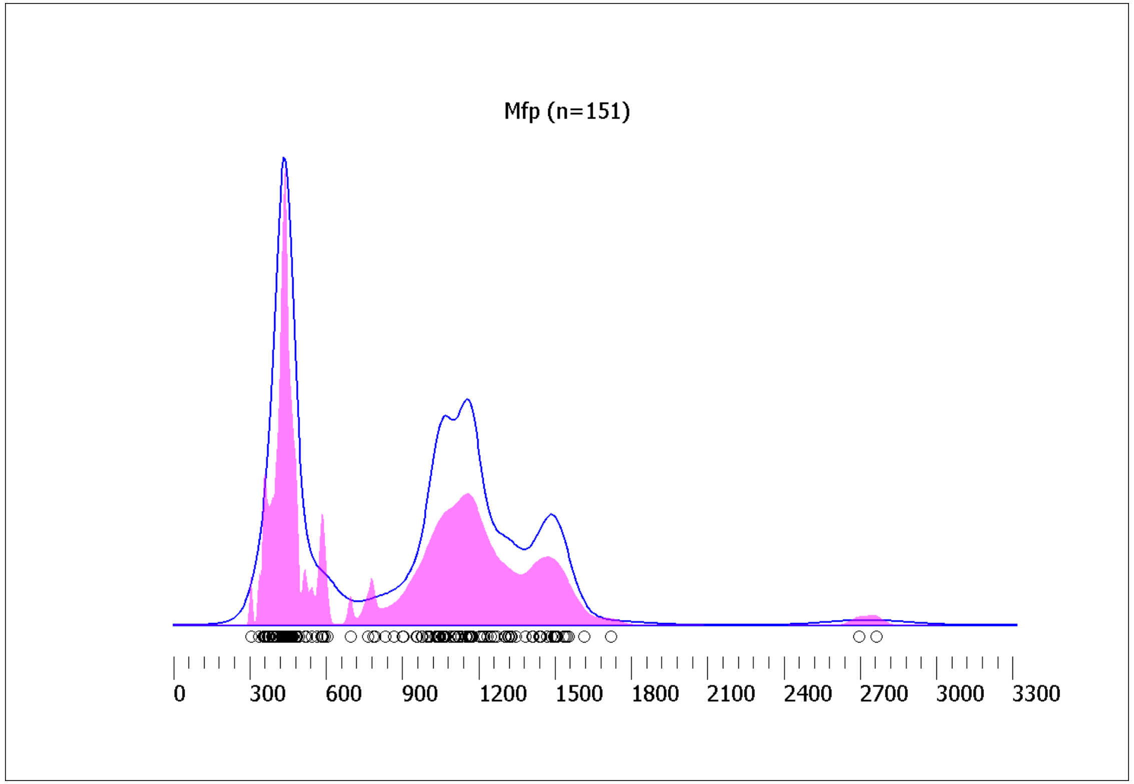


Bedrock Units

- Taconic orogeny: 430-450 Ma
- 1000-1100 Ma ages consistent with previous ages from southern Appalachians

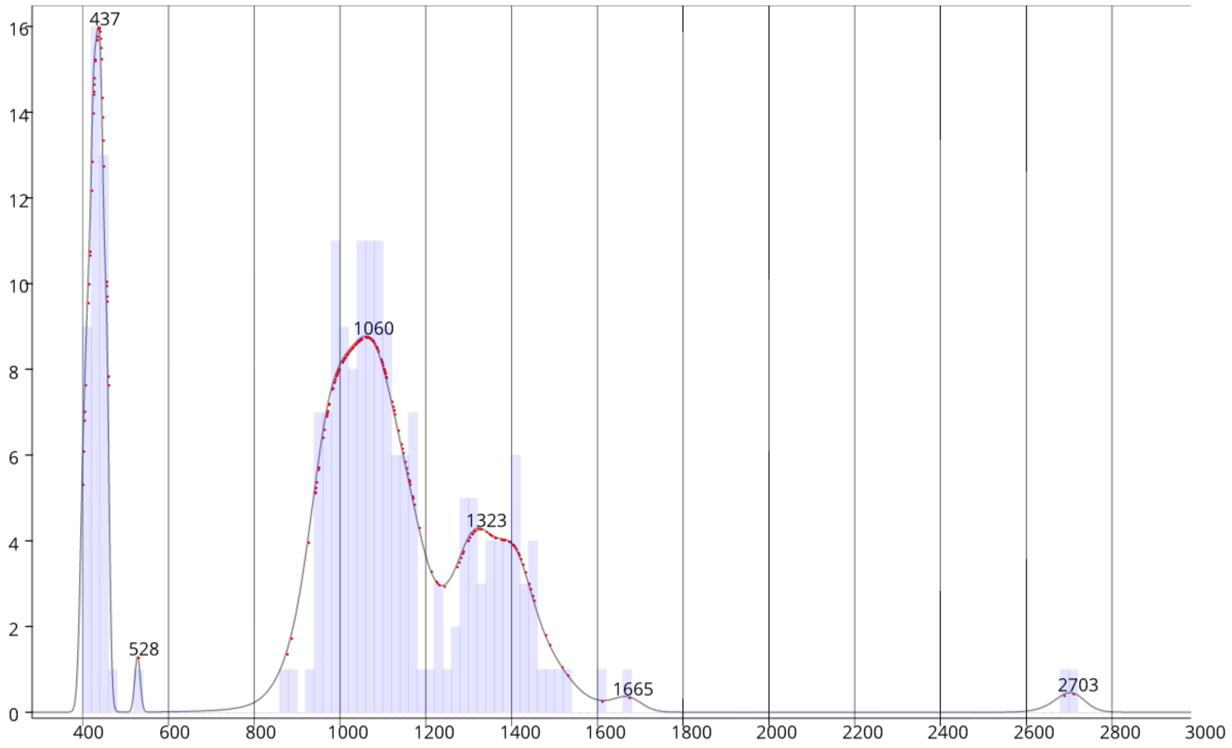






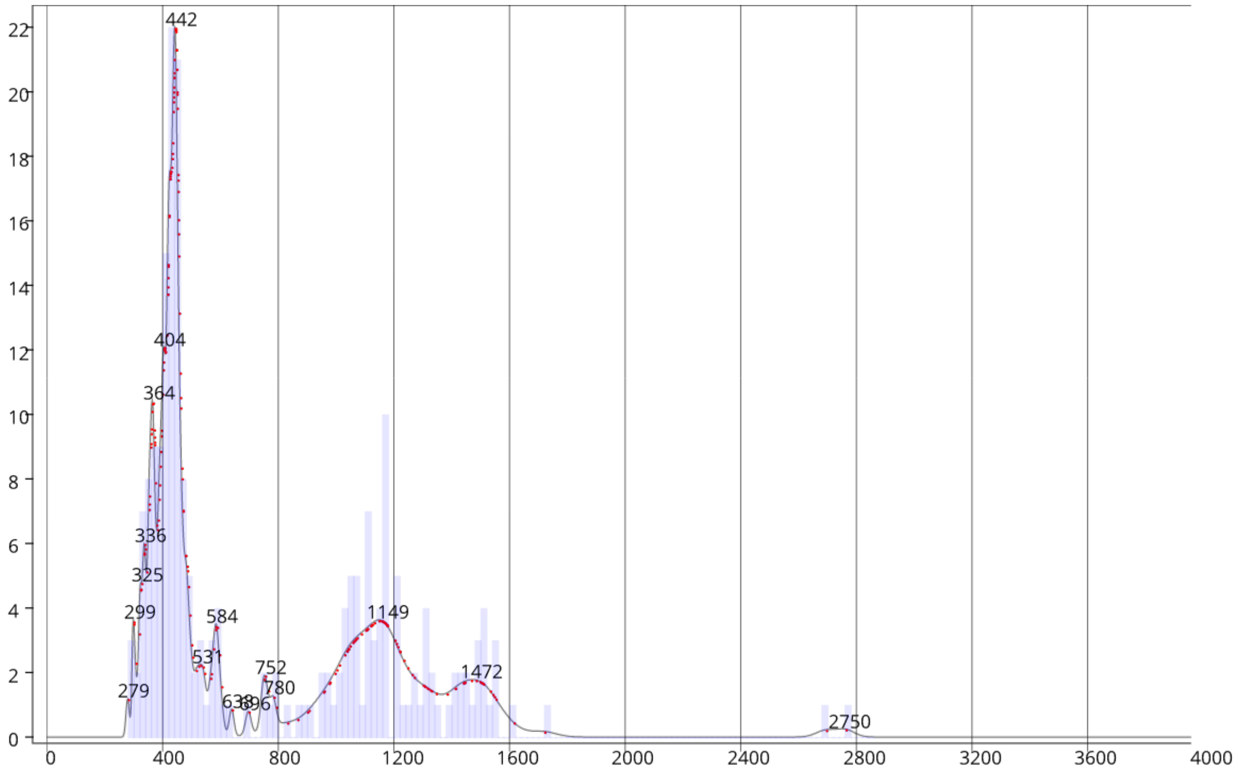
Pink represent probability density function, blue line represents the kernel density estimate (Vermeesch, 2012).

Tectonic Setting: Oh sediments



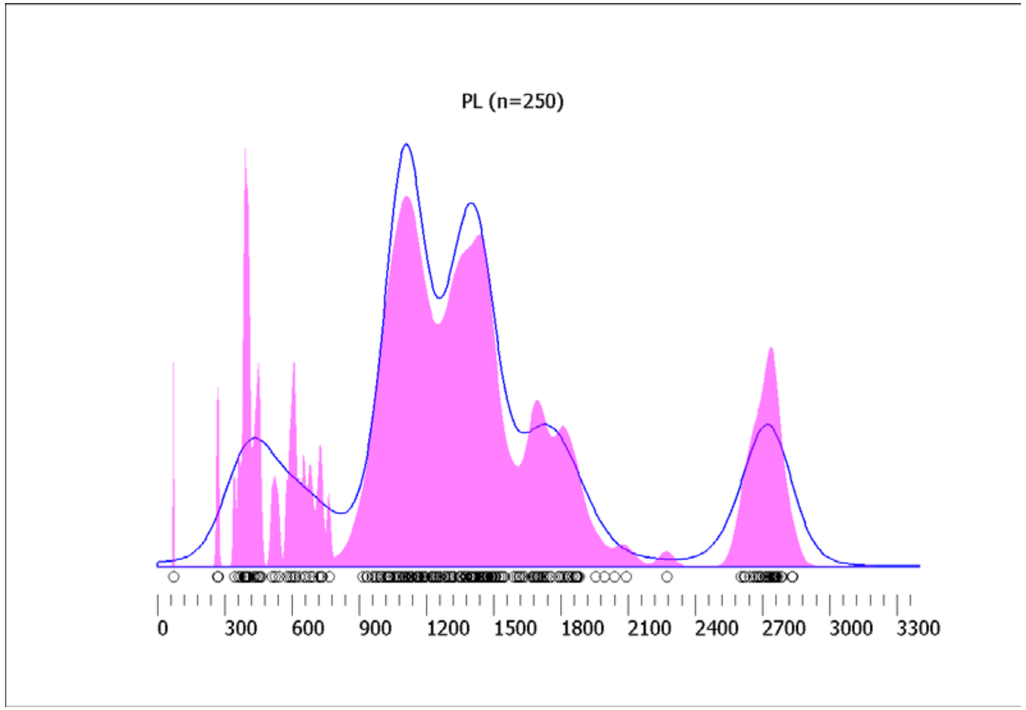
- Oh depositional age 453 Ma (Holland and Patzkowsky, 1997)
- Youngest age peak close to depositional age
- Consistent with a convergent plate margin (supra-subduction zone) setting during the Taconic orogeny.

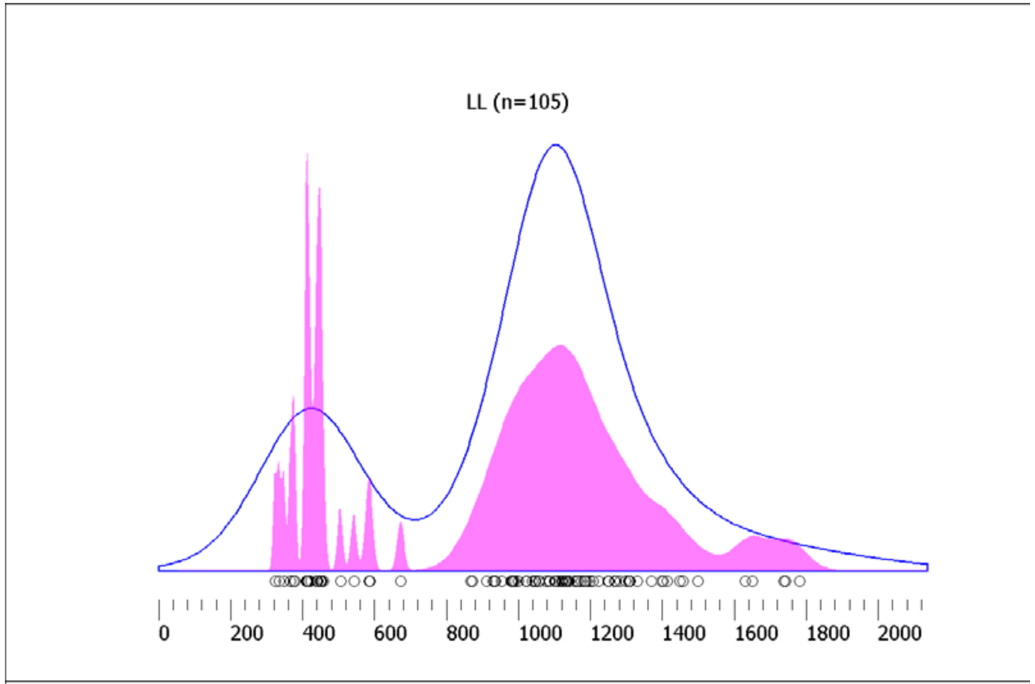
Tectonic Setting: Mfp Sediments

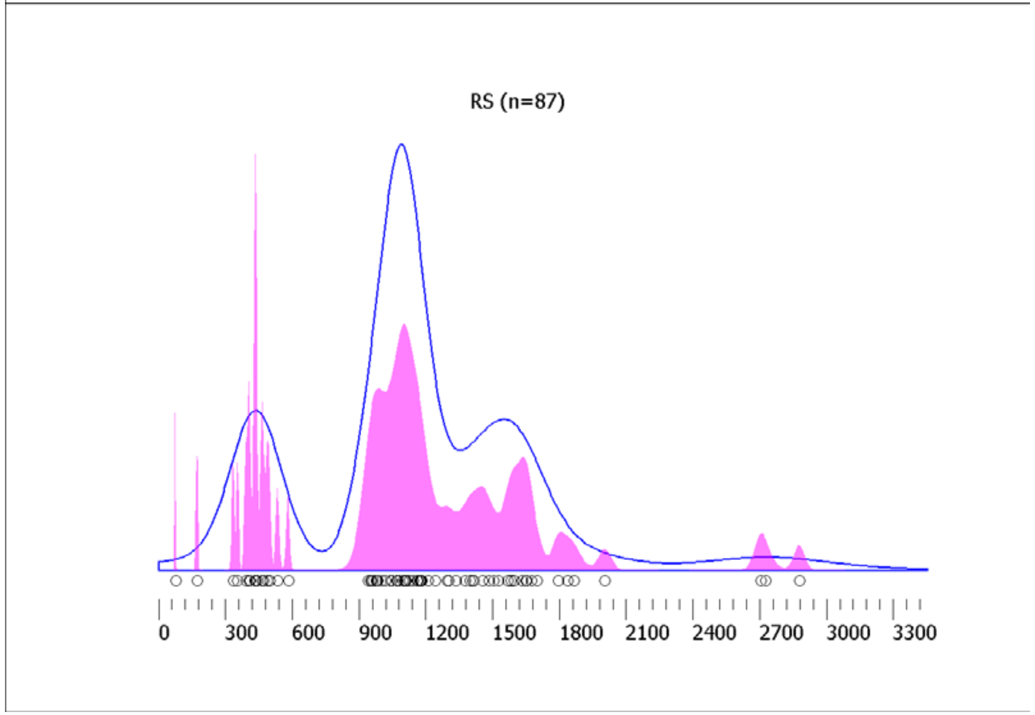


- Mfp is lower Mississippian, so depositional age ~ 350 Ma
- Youngest prominent age peak ~440 Ma
- Zircon crystals deposited ~90 Ma after crystallization
- Suggests a collisional setting, specifically the foreland basin of the Appalachians (Cawood et al., 2012).

Loess samples







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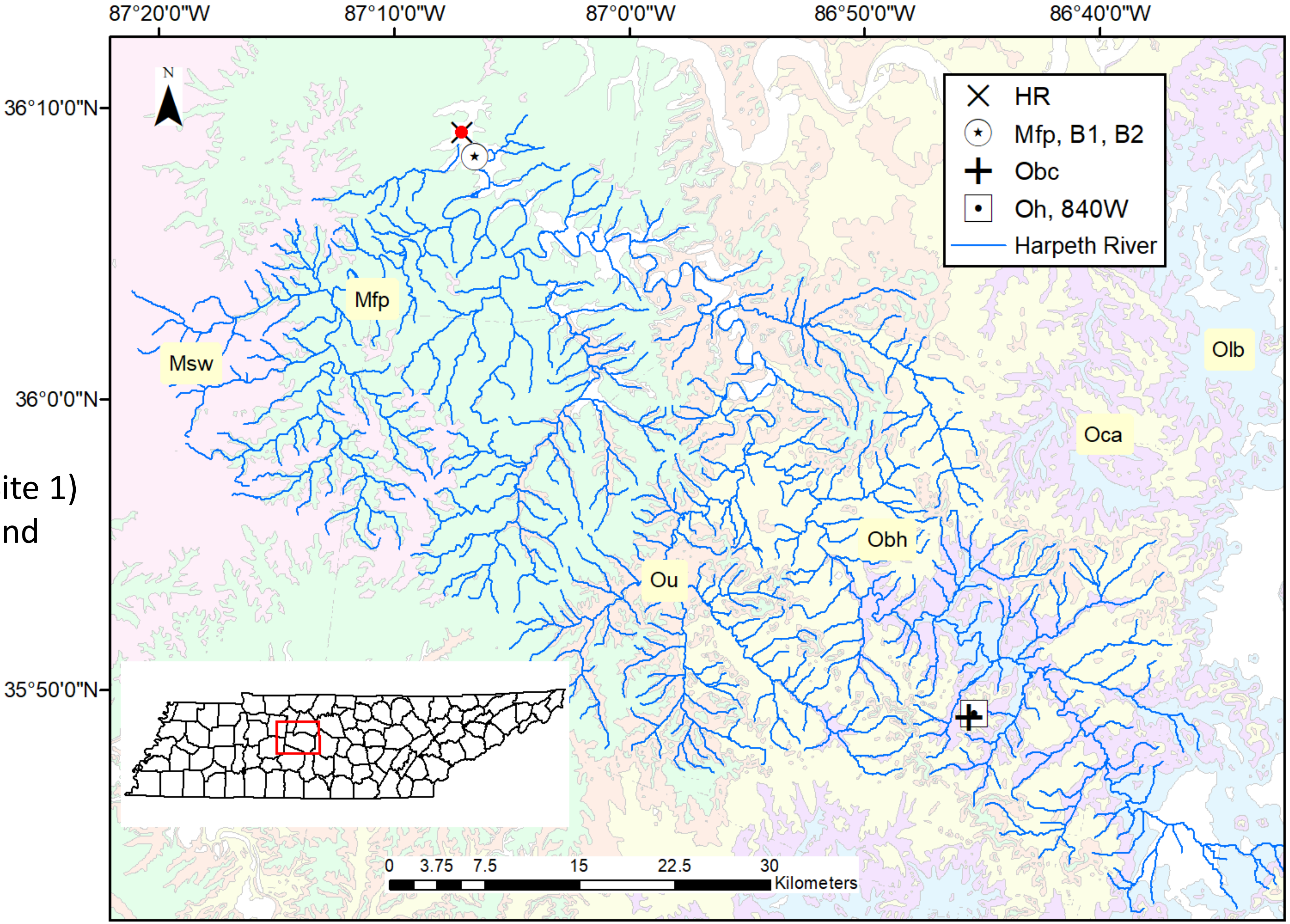
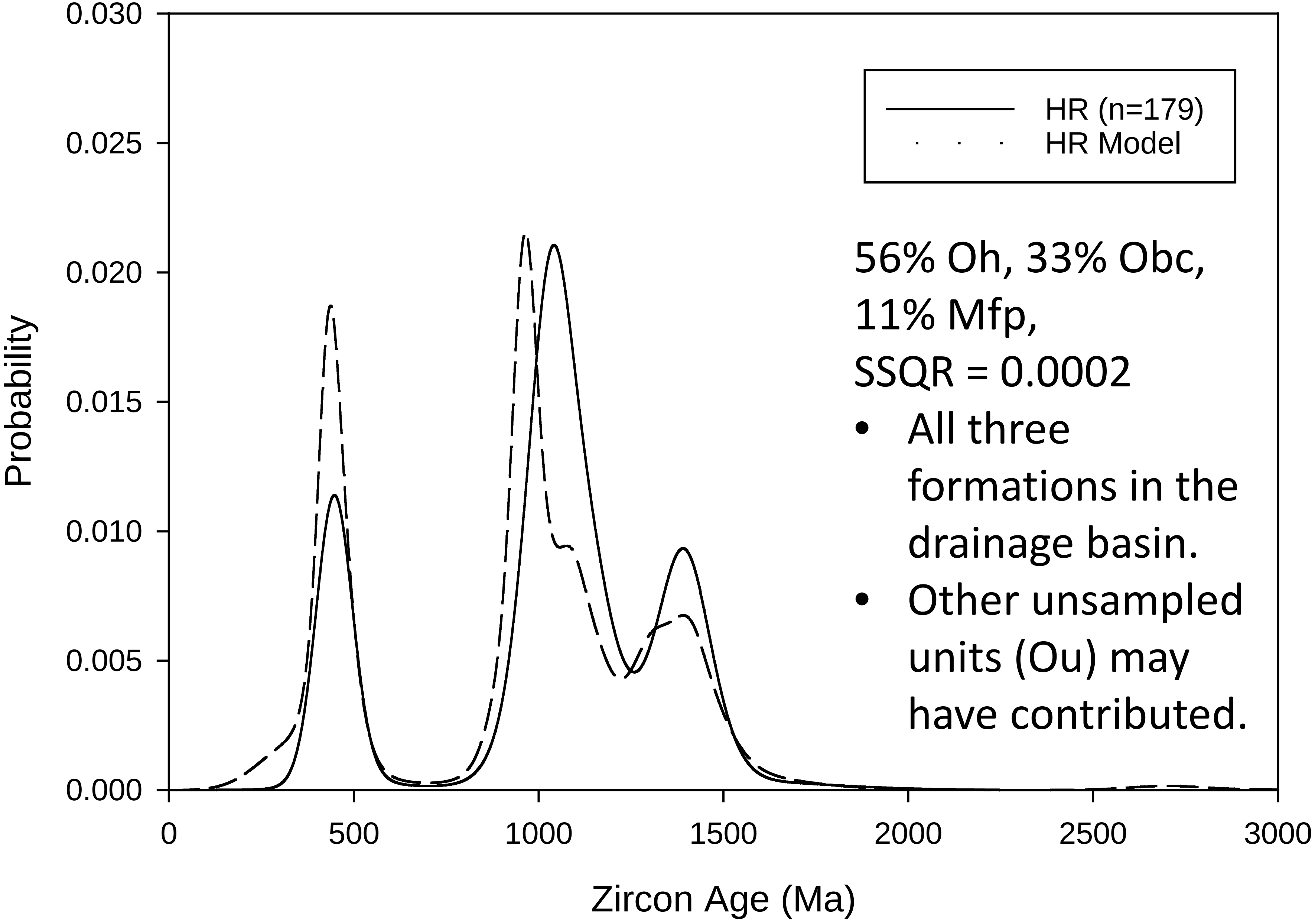


Harpeth River Age Spectra

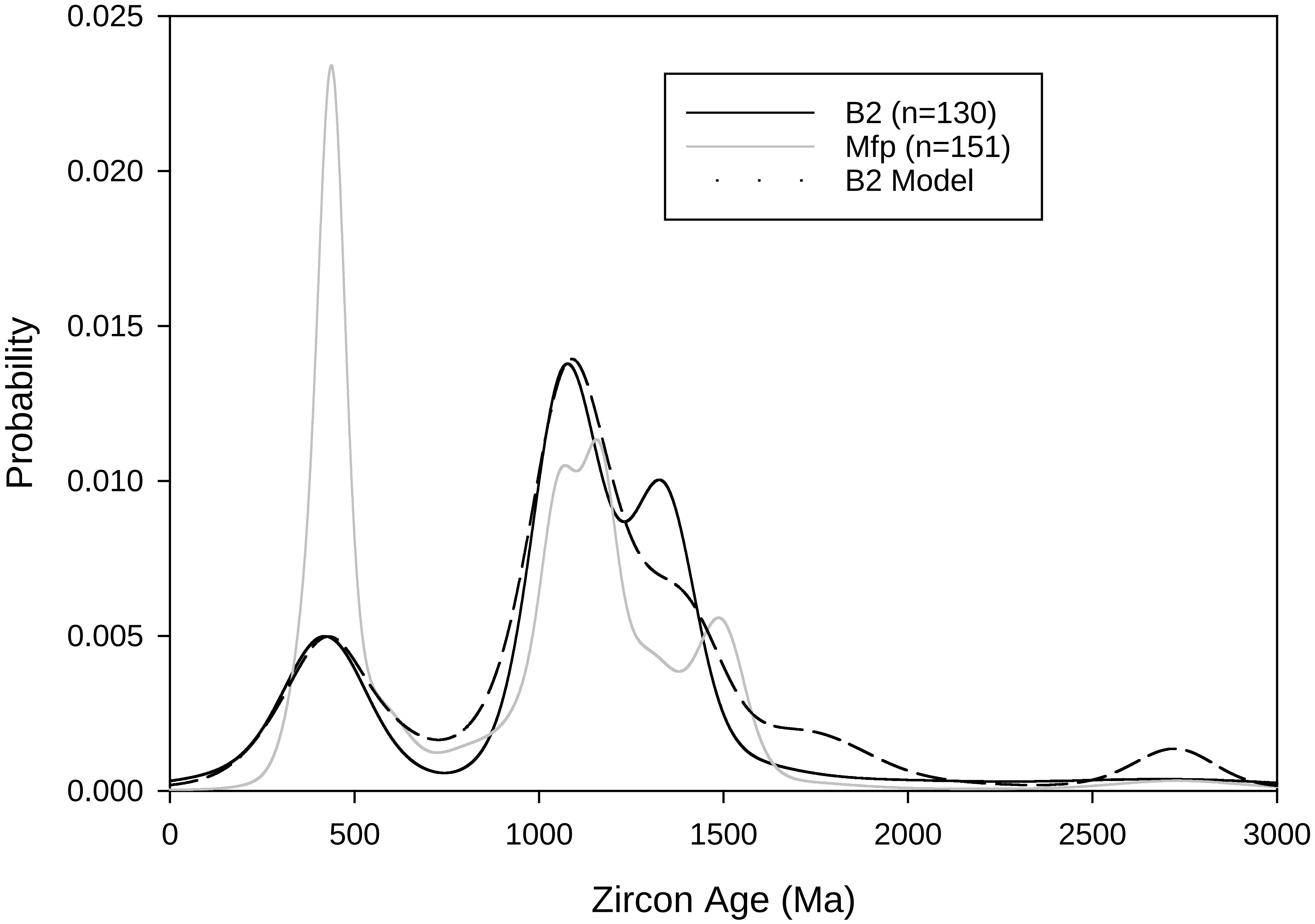


56% Oh, 33% Obc, 11% Mfp, SSQR = 0.0002

- All three formations in the drainage basin.
- Other unsampled units (Ou) may have contributed.

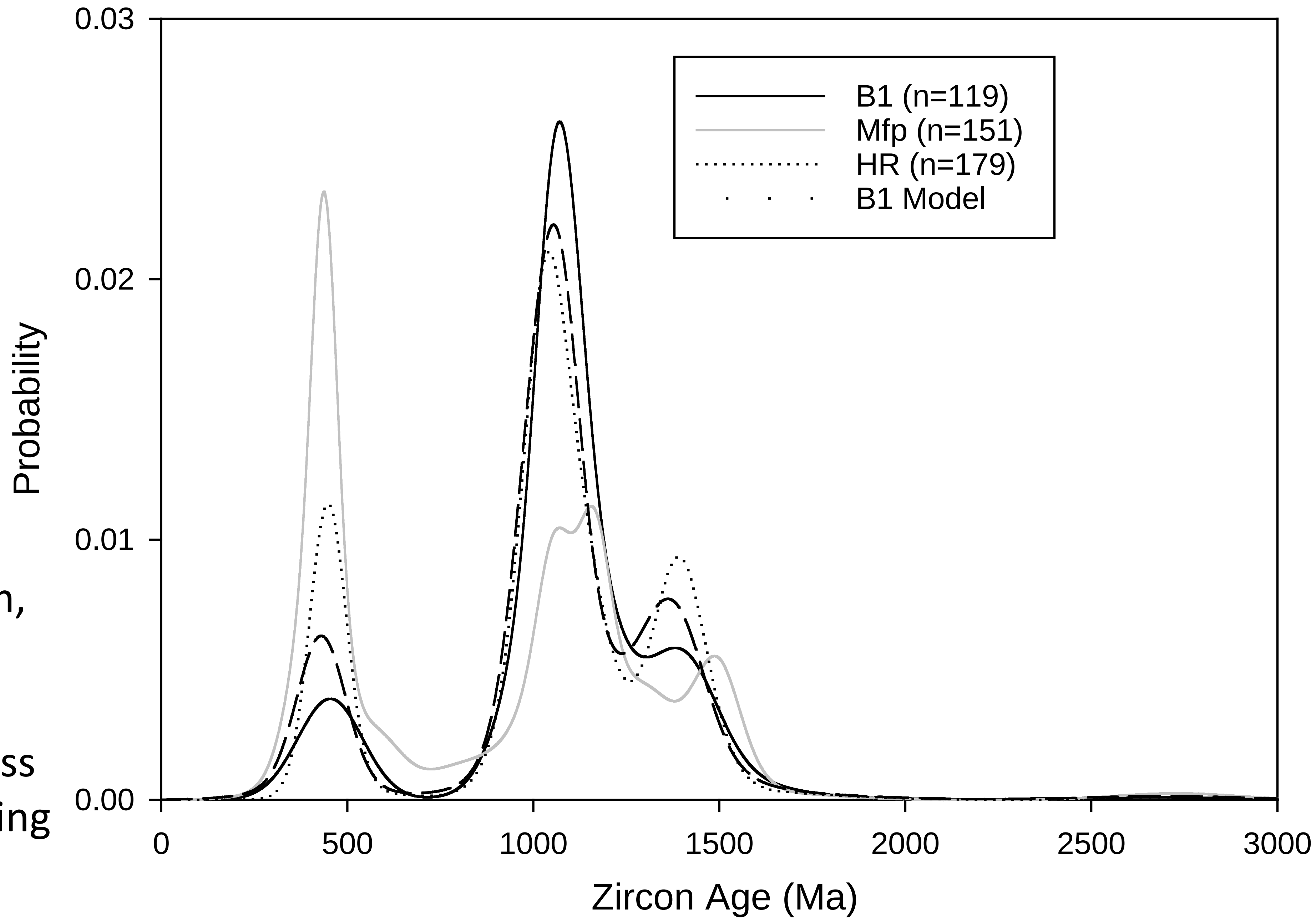
Deep layer B2 Age Spectra

47% LL, 29% PL, 24% Oh
SSQR = 0.00028
Since Oh is deep beneath the surface at site 1, must have been deposited as HR alluvium.

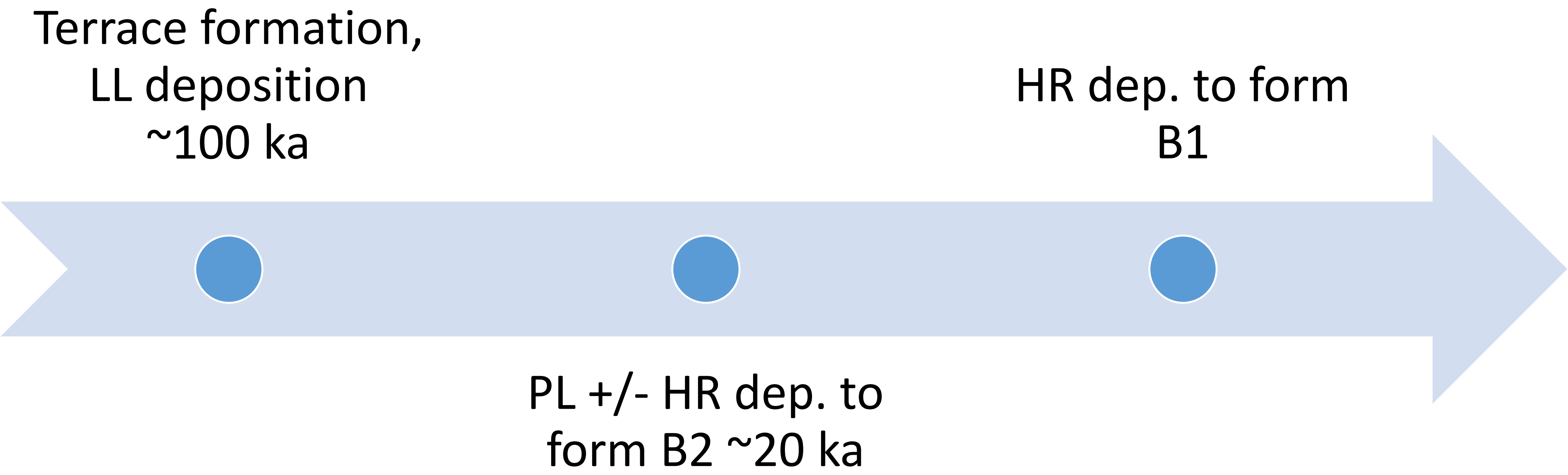


Shallow layer B1 Age Spectra

90% Oh as HR alluvium, 10% LL
SSQR = 0.0006
LL seems unlikely unless there was vertical mixing

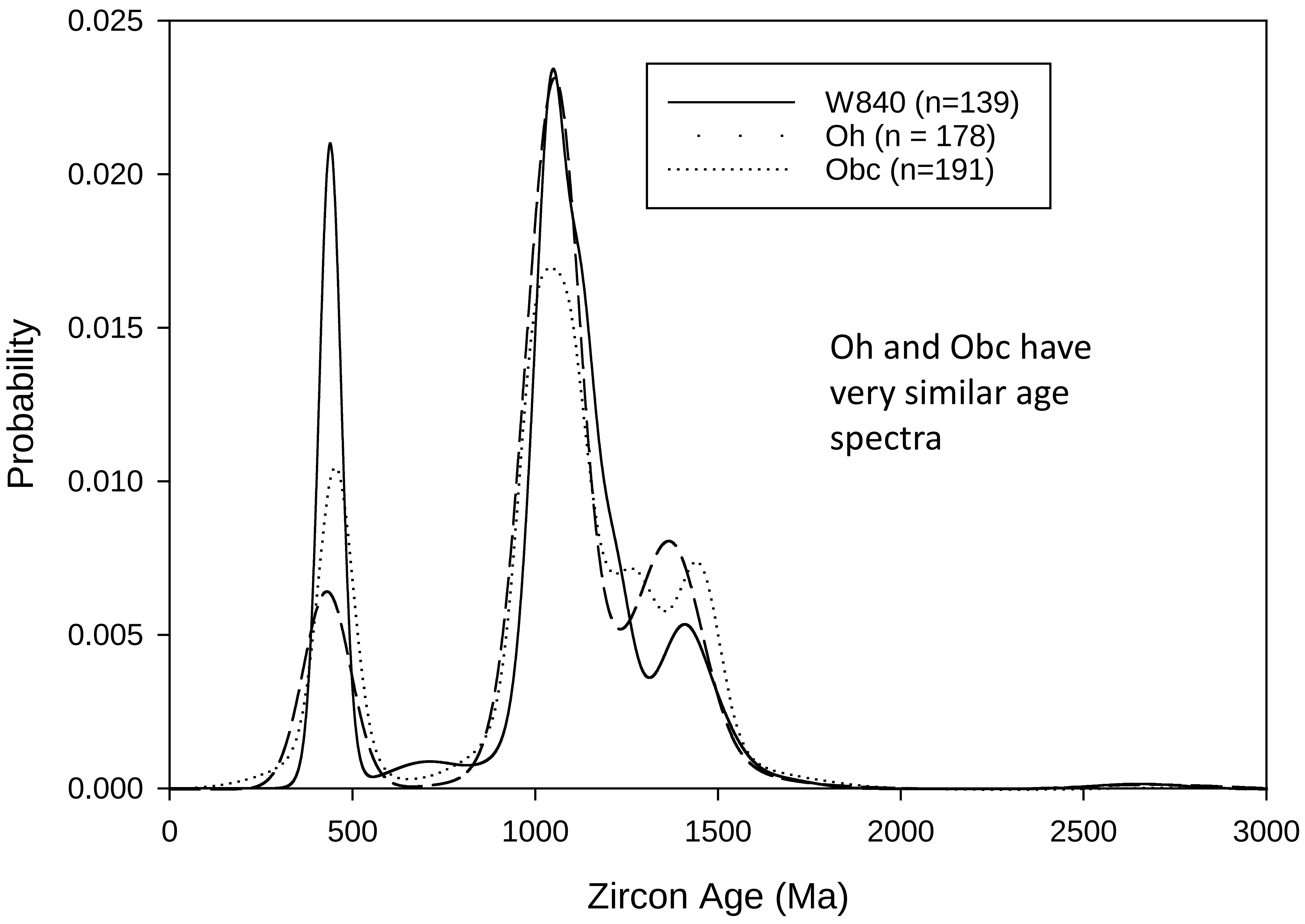


Timeline for Site 1



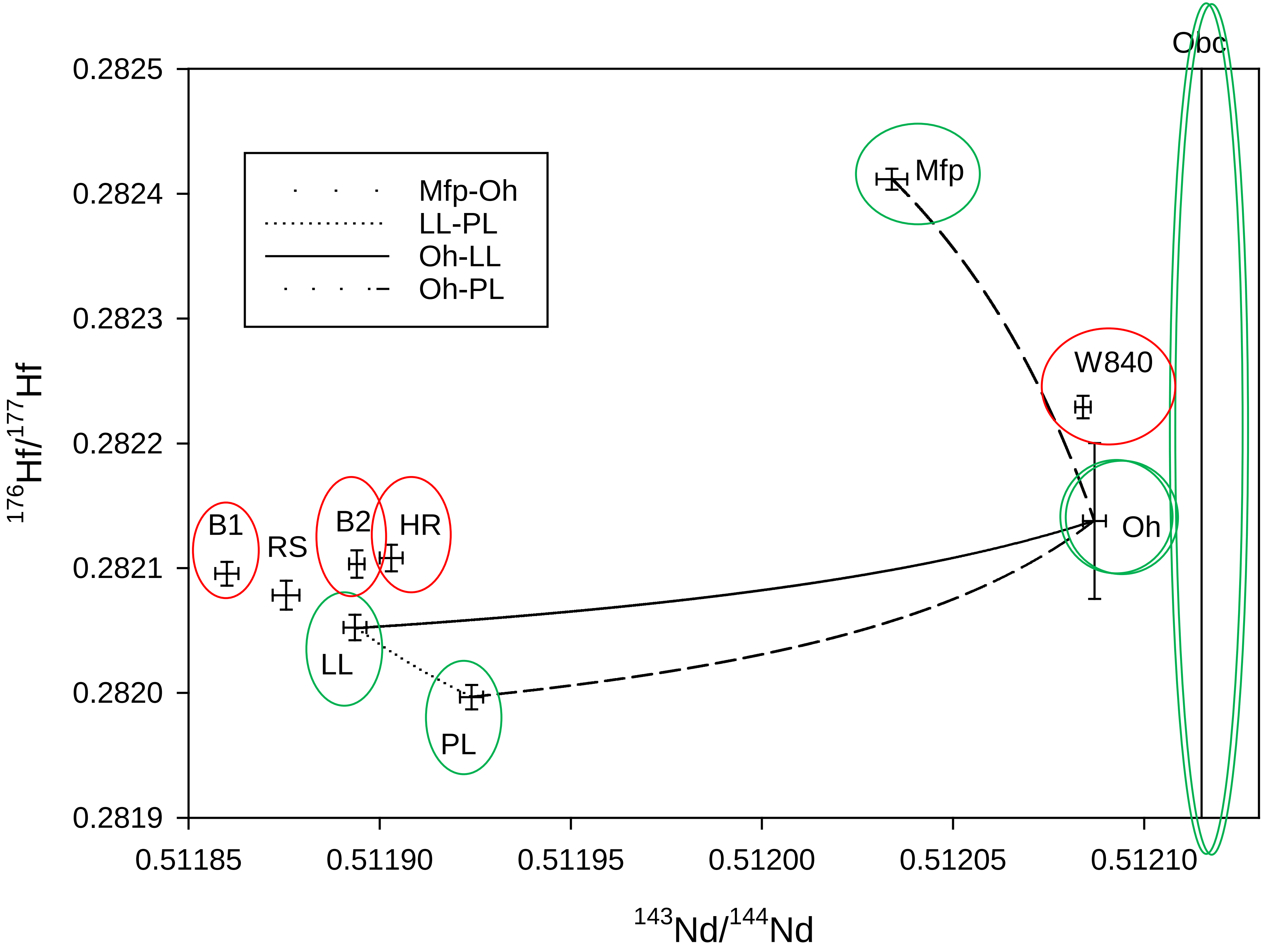
Site 2 W840 Soil Age Spectra

82% Obc,
18% Oh ± Mfp
SSQR = 0.001



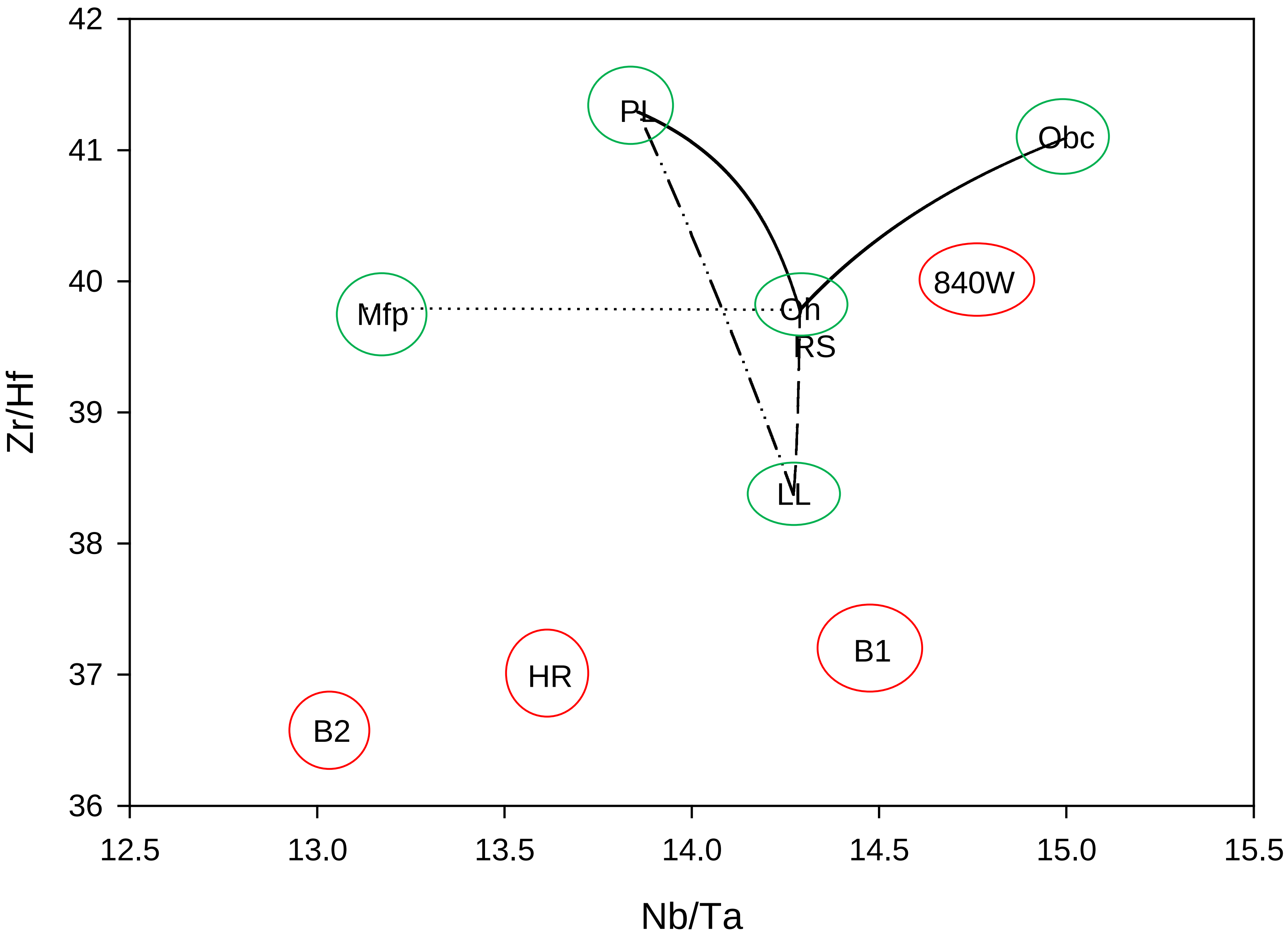
Oh and Obc have very similar age spectra

Bulk Isotope Results



B1 and B2 not close to Mfp

Trace Element Results



Evidence Consistent With Genetic Relationship?

Parent-soil pair	Mineralogy	U-Pb age spectra	$^{143}Nd/^{144}Nd$	$^{176}Hf/^{177}Hf$	Zr/ Hf	Nb/ Ta	Gd_N/Yb_N	Eu/ Eu*	τ_j§
Mfp-B1	N	N	N	N	N	N	Tie†	N	Y
Mfp-B2	N	N	N	N	N	Y	Tie	N	Y
HR-B1	Y	Y	N	Y	Y	N	Tie	Y	
HR-B2	Y	Y	Y	Y	Y	N	Tie	Y	
Oh-W840	Y	Y	Y	Y	Y	?	Y	Y	Y
Obc-W840	?	Y	N		?	?	N	N	Y
HR-W840	N	Y	N	N	N	N	N	N	
<u>Binary Mixtures</u>									
(Oh+LL)-B1	N	Y	N	Y	N	Y	N	N	
(Obc+Oh)-W840	?	Y	N	Y	Y	Y	Tie	Tie	
(PL+LL)-B2	Y	Y	Y	N	N	N	N	N	
(Mfp+Oh)-W840	Y	N	Y	Y	Y	N	Tie	Tie	

† "Y" if parent is closest of all parents to soil, or to binary mixing lines for pairs of parents. For mixtures, soil must plot in-between sources. "?" indicates ambiguous results. "Tie": Mfp and HR have equal GdN/YbN, and W840 has almost identical GdN/YbN and EuN/Eu*N as Oh.

§ Mass transfer coefficient τ calculated only for soil-bedrock pairs.

Conclusions

- Bedrock age peaks indicate source rocks for sediments formed during the Taconic orogeny, but many older zircons preserved from prior orogenies.
- Above Fort Payne chert bedrock, ultisol with exotic source:
  - Deposition of Loess and Harpeth River alluvium to form ultisol B2 soil horizon + intense weathering.
  - Deposition of Harpeth River alluvium to form ultisol B1 horizon.
- In-situ weathering of Oh + Obc to form W840 alfisol

Use of zircon U-Pb ages for soil provenance

- Zircon is recoverable from limestone.
- Zircon U-Pb geochronology is an effective tool for determining provenance of soil.
- However, best match in zircon U-Pb mixing model does not always agree with other datasets such as Nd and Hf isotopes.
  - Similar age spectra of our endmembers: all rocks formed from Appalachian sediments.
  - Harpeth River alluvium derived by erosion of those rocks with similar age spectra.
  - Loess deposits have many age peaks, some of which overlap with Appalachian sediment age peaks.

Applications to Igneous & Metamorphic Rocks

- Testing for soil formation by in-situ chemical weathering would be easier if bedrock had only one age peak, which is more likely for igneous bedrock.
- Provenance of metamorphic rocks: Compare zircon U-Pb age spectra of protolith and related metamorphic rocks. Could provide unequivocal evidence for metamorphic growth (ages younger than the youngest age in the protolith)
- Especially useful for metamorphic rocks with clastic sediment protoliths.