PSU-Pb Geochronology of Zircon from Volcanic Ashes in the Marcellus Formation, Appalachian Basin*

Chantelle Parrish[1], Jaime Toro[1], Amy Weislogel[1], Jessica Hayward[1], and Joe Wooden[2]

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Abstract

Numerous thin volcanic ash layers are found interbedded with the upper Onondaga Formation and lower Marcellus Shale of the Appalachian basin. These ashes are believed to have been sourced from continental arc magmatism along the Acadian orogen. We have dated zircons extracted from ashes taken from cores of six wells and from one outcrop in Pennsylvania and West Virginia. The ashes range in thickness from 0.5-14 cm and are recognized by their buff color, abundant muscovite, and high U/Th ratios in spectral gamma ray logs. Sampling targeted the uppermost and lowermost ashes when possible. The age of each ash layer was determined by analyzing zircon at the USGS-Stanford SHRIMP-RG laboratory. For each sample, 12-18 spots on individual zircon crystals were analyzed. Recycled or reworked older zircon crystals are absent from the samples suggesting a primary origin as air-fall deposits. Each ash typically contains euhedral Middle Devonian volcanic zircons that are either prismatic or equant in habit and exhibit oscillatory zoning in cathodoluminescence images. Equant zircon crystals tend to contain Proterozoic inherited cores that record the age of the crust underlying the arc. Individual concordant 206Pb/238U ages from zircon crystals within a single ash may vary over a range of as much as 23 My, but typically there is a cluster of younger ages that we interpret as the best estimate of the age of eruption, which would be coeval with depositional age in the basin. Mean eruption ages of ashes near the base of the Marcellus Shale range from 402.0 ± 1.8 Ma to 388.0 ± 1.5 Ma (Emsian to Givetian) in five wells. This indicates either that the basal Marcellus Shale was deposited diachronously across the study area or that ashes were not preserved uniformly across the study area. This result should be tested by dating zircon from ashes within the upper Onondaga to determine if the younger basal Marcellus Shale deposits are underlain by Onondaga strata that preserve older ashes. If age-equivalent ashes are found in basal Marcellus and upper Onondaga deposits, this can place important constraints on lateral facies variations that could complicate lithostratigraphic correlations and formation contact picks based on well log data. Estimates of Marcellus sedimentation rates, from wells where the uppermost and lowermost ashes are 7-9 feet apart, are from 0.6-1.6 ft/my (19-49 cm/my). We will refine our dating by using high-resolution TIMS geochronology on selected zircons.

U-Pb Geochronology of Zircon from Volcanic Ashes in the Marcellus Formation, Appalachian Basin

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Abstract

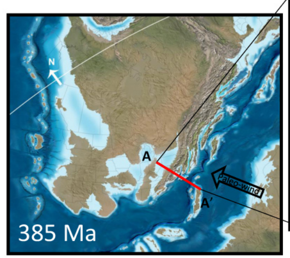
Numerous thin volcanic ash layers are found interbedded with the upper Onondaga Formation and lower Marcellus Shale of the Appalachian basin. These ashes are believed to have been sourced from continental arc magmatism along the Acadian orogen during the Middle Devonian. These beds form key stratigraphic markers for regional correlation, allow for geochemical analysis of parent magma, and most importantly, can provide geochronologic dates used in determining depositional rates and stratigraphic relations.

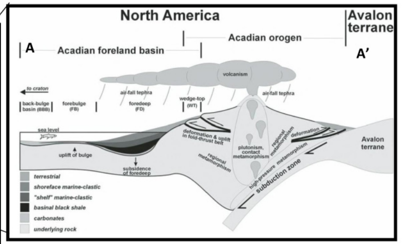
Zircons were extracted from ashes found in 6 well cores in Pennsylvania and West Virginia. The ashes range in thickness from 0.5-14 cm and are recognized by their buff color, abundant muscovite and pyrite, and high U/Th ratios in spectral gamma ray logs. The U-Pb age of each ash layer was determined by analyzing 12-18 spots on individual zircon crystals at the USGS-Stanford SHRIMP-RG laboratory. Recycled or reworked older zircon crystals are absent from the samples suggesting a primary origin as air-fall deposits. Concordant $^{206}Pb/^{238}U$ ages from zircon crystals within a single ash vary over a range of as much as 23 My which could represent the residence time of the zircon crystals within the Acadian magmatic system. Typically there is a cluster of younger ages that we interpret as the best estimate of the age of eruption and coeval with depositional age in the basin. Mean eruption ages of ashes near the base of the Marcellus Shale range from 402.0 ± 1.8 Ma to 388.0 ± 1.5 Ma (Emsian to Givetian) in 5 wells. This indicates that either the basal Marcellus Shale was deposited diachronously or that ashes were not preserved uniformly across the study area. Estimates of compacted Marcellus sedimentation rates, from wells where the uppermost and lowermost ashes are 7-9 feet apart, are from 0.6-1.6 ft/my (19-49 cm/my).

Wells on the western-most side of the study area in northern West Virginia yield consistently older ages than the rest of the wells. However, this age distribution is inconsistent with the simplistic model of Appalachian basin fill where the oldest sediments are expected closer to the eastern margin.
Some wells also showed stratigraphically younger ashes yielding older ages than underlying ashes, although most overlap within age error, possibly due to complexity in basin structure and bathymetry influencing sedimentation patterns.

Background

The Acadian orogeny persisted from 400 to 325 million years ago with several episodes of tectonic subsidence and quiescence. Oblique convergence of Avalonian and/or a series of terranes with the northeastern portion of Laurentia caused subsidence of an adjacent foreland basin which became the depositional location for the Marcellus Shale and Onondaga Limestone. As a product of subduction and lithospheric loading, explosive volcanic events occurred on the continental margin and sent eruption columns into the atmosphere allowing ash to be carried the West and Southwest, and deposited and preserved within the Onondaga and Marcellus formations. Upon cooling, these volcanic glass layers became unstable and devitrified to smectitic clays during diagenesis and are termed a K-bentonite. These layers contain valuable zircon crystals that are used for U-Pb dating.

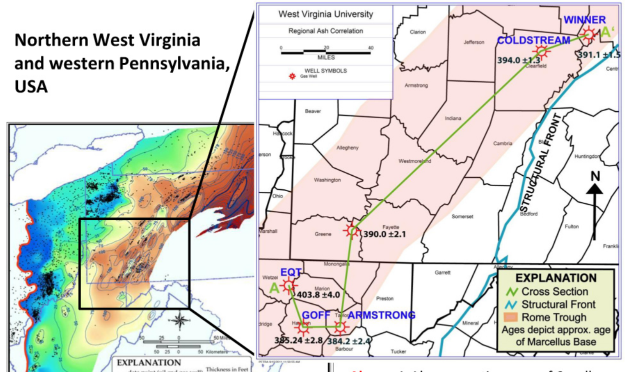




Images modified from Blakey, 2005 (left) and Ver Straeten &Griffing, 1994 (above). Arrow (left) indicates approximate paleo-wind direction after Parrish, 1982.

Study Area

Northern West Virginia and western Pennsylvania, USA



Above: Marcellus Shale organic-thickness map. Warmer colors represent thicker intervals. (Modified from Erenpriess, M.S., et al., 2011)

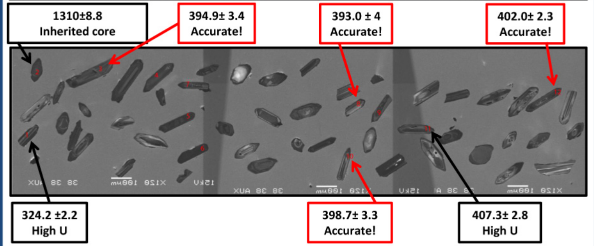
Above: A-A' cross section map of 6 well locations showing their location relative to the major structural features of the area, and the approximate ages of the base of the Marcellus.

U-Pb Dating

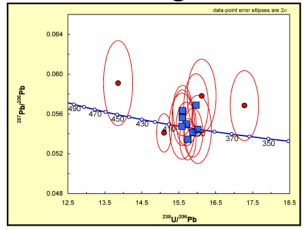
U-Pb dating analysis was completed by a Sensitive High Resolution Ion Micro Probe Reverse Geometry (SHRIMP RG) method at USGS- Stanford University Laboratory

Zircon Analysis

Eighteen zircon grains were removed from the 2nd ash layer of the Goff well at 7231.24 ft. The upper photo was captured by transmitted light microphotography. The lower photo was taken with a Scanning Electron Microscopy - Cathodoluminescence (SEM-CL) to visualize internal features.

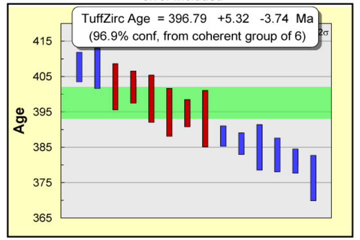


Goff #55 Age Data



Above: Concordia Diagram, blue squares represent ages used in calculations. Red points are dismissed due to high uranium or lead loss

Below: Average age of 14 zircons with weighted means and error included



Overall Age Data

Tioga Ashes- Dated				
Well Name	Sample ID	Ash # (depth in ft)	Ash Thickness (inches)	Average $^{206}Pb/^{238}U$ Age (Ma)
EQT 511391	EQT1	1 (7114.9)	0.47	403.8 ±4.0
	EQT2	2 (7117.05)	2.36	402.1 ± 1.8
Goff #55	Goff1	1 (7227.45)	3.15	385.24 ±2.8
	Goff2	2 (7231.24)	0.866	396.79 ±2.6
Armstrong #1	Arm1	1 (7755.27)	0.24	384.2 ±2.4
	Arm7	7 (7780.46)	0.48	380.9 ±2.0
St. Whipkey #1	Whip2	2 (7893.6)	2.17	390.0 ±2.1
	Whip4	4 (7897.5)	0.787	389.9 ±2.1
Coldstream #1	Cold1	1 (7156.7)	1.18	400.74 ±2.2
	Cold2	2 (7157.2)	1.97	394.0 ±1.3
	Cold3	4 (7162.4)	3.94	398.5 ±1.3
	Cold4	5 (7163.5)	0.98	396.7 ±2
Winner 4-8	Win23	1 (8023.5)	0.88	383.6 ±1.4
	Win32	2 (8032.6)	2.76	391.1 ±1.5
	Win35	3 (8035.4)	1.57	391.0 ±3.1
	Win41	4 (8041.5)	5.51	388.6 ± 1.5

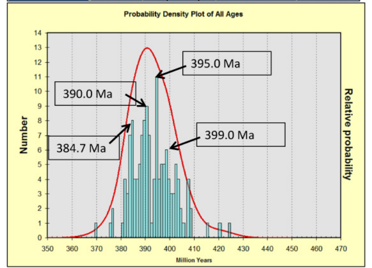


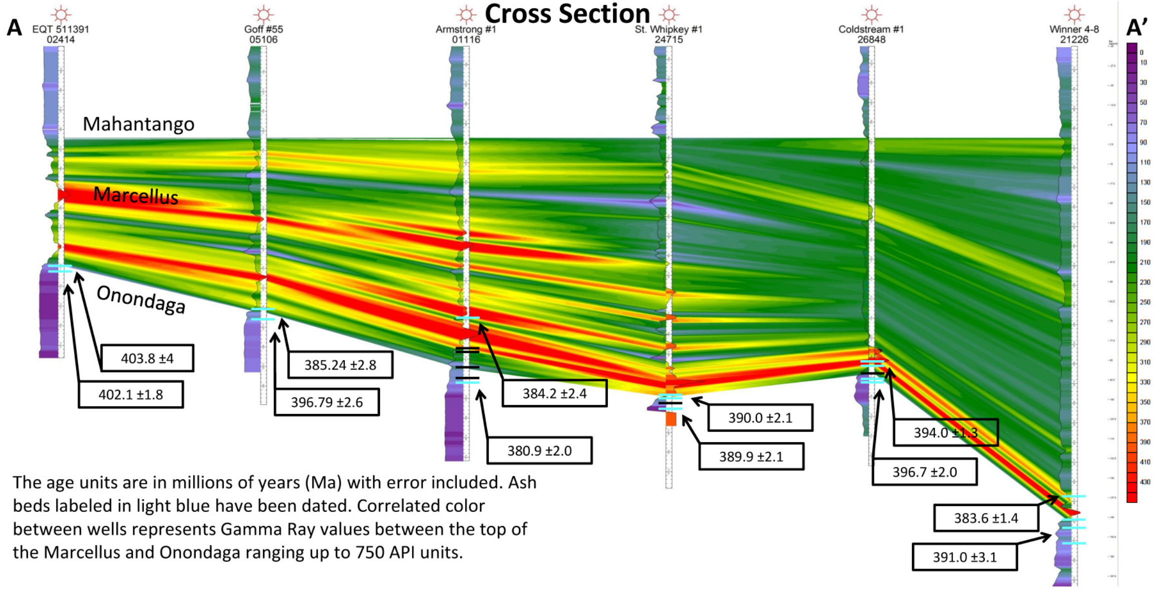
Table summary:

Includes all six wells studied with well names and sample IDs. Ash number is labeled at depth found in cores and ash thickness is measured in inches. The average ages are listed per ash horizon with error

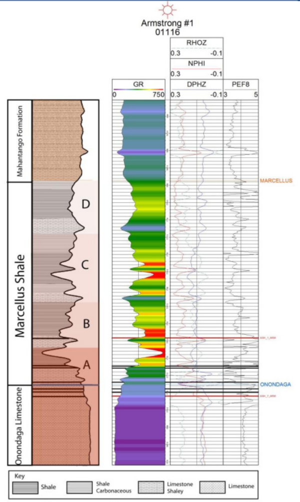
Probability Density Plot:

Major peaks for individual zircon ages with no respect to ash layer: **383.4**, **384.7**, **390.0**, **395.0**, **399.0**, **402.9**, and **408.0** Ma

Cross Section



The age units are in millions of years (Ma) with error included. Ash beds labeled in light blue have been dated. Correlated color between wells represents Gamma Ray values between the top of the Marcellus and Onondaga ranging up to 750 API units.



The Marcellus interval is coarsening upward from black shale to limey shale units. Marcellus is shown separated into four parasequences, A, B, C, D. The top of each parasequence is marked by the base of the limey unit.

Conclusions

- Each ash horizon represents 1 eruption, however, multiple ash falls can occur within one eruption as evidenced by fining-upwards graded beds within single ash horizons.
- Zircon ages in one ash horizon vary over a range of 10 -20 million years which may represent longevity of arc magmatic system.
- Youngest concordant populations represent eruption ages.
- Distinct age groups exist from zircon U-Pb ages representing possible major eruptions at 384.7, 390.0, 395.0 and 399 Ma
- The base of the Marcellus is diachronous as shown by mean eruption ages of ashes near the base of the Marcellus Shale ranging from 402.0 ± 1.8 Ma to 388.0 ± 1.5 Ma (Emsian to Givetian) in 5 wells.
- Oldest ash ages lie on western side of the basin, opposite of the simplistic Appalachian basin fill model, suggesting basin structure and bathymetry complexities which influenced sedimentation regimes.

Acknowledgements

Recognize other authors: Dr. Jaime Toro, Jessica Hayward and Dr. Amy Weislogel at WVU. A special thanks to Joe Wooden at the USGS-SHRIMP Lab and to Energy Corporation of America, Petroleum Development Corporation, EQT Corporation, Enerplus and CORELAB for access to core.

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Erenpriess, M.S., et al. (2011). "Regional organic-thickness map of the Marcellus Shale with additional organic-rich shales beds in the Hamilton Group included for New York, Pennsylvania, and West Virginia". Ohio Department of Natural Resources, Division of Geological Survey.

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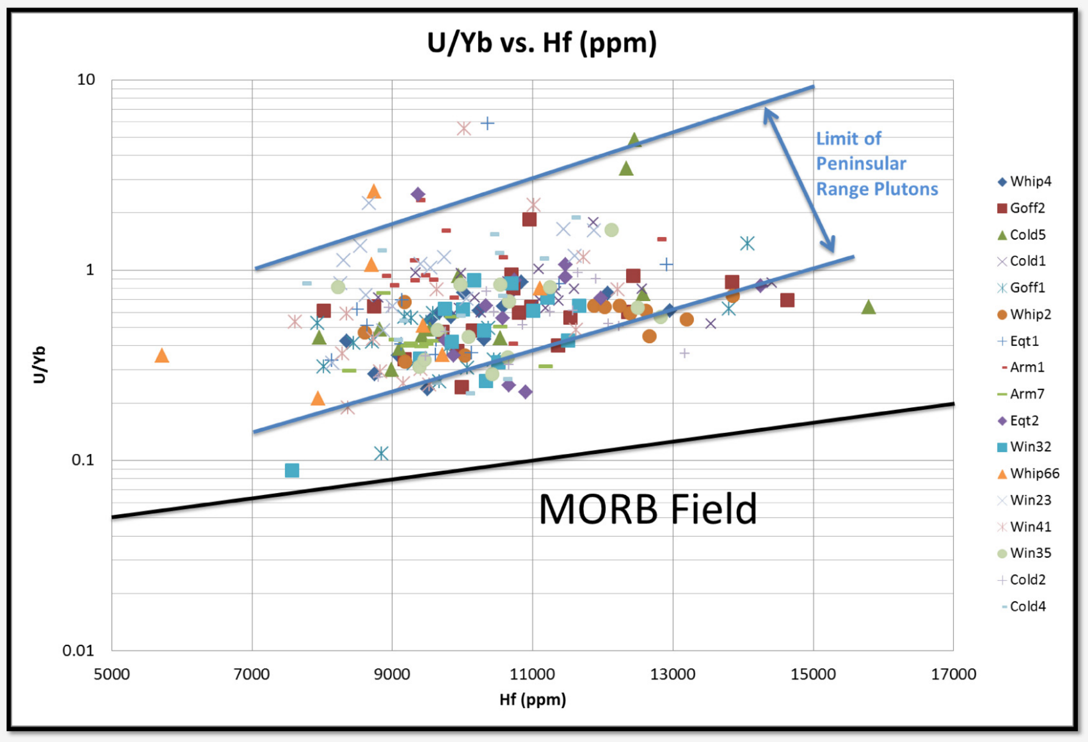
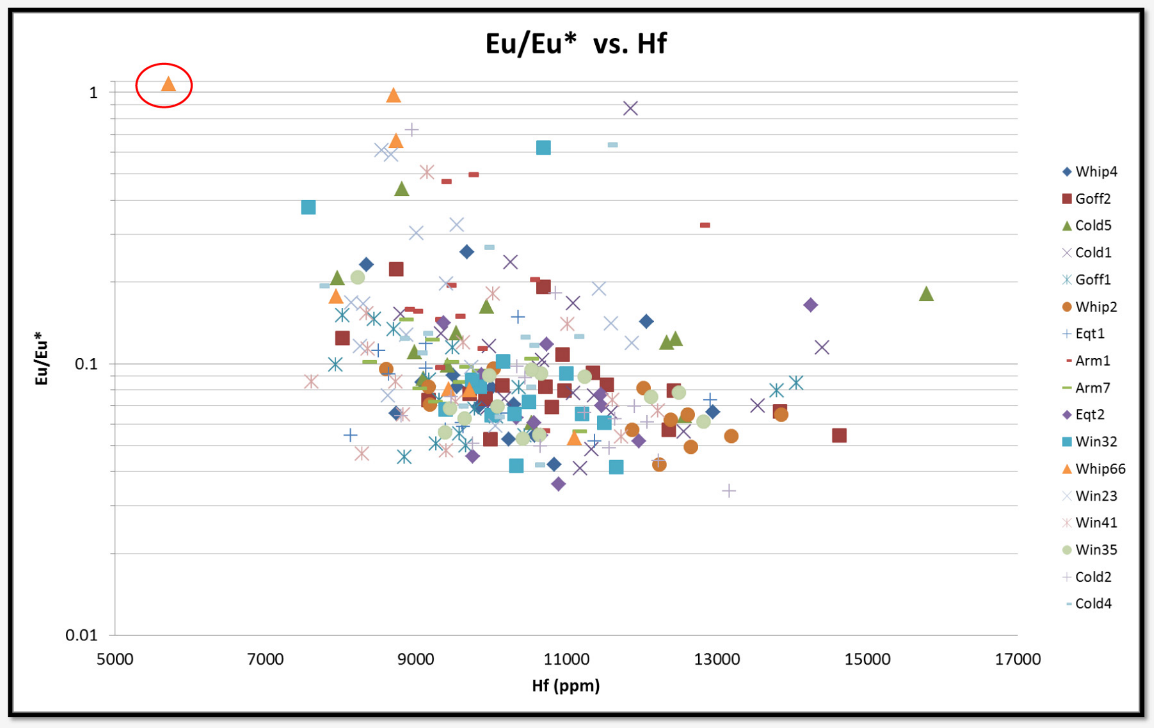
Way, J.H.; Smith, R.C.; Roden, M. (1986). "Detailed correlations across 175 miles of the Valley and Ridge of Pennsylvania using 7 ash beds in the Tioga Zone". *Selected geology of Bedford and Huntington Counties*. 51st Annual Field Conference of Pennsylvania Geologists. U.S. Geological Survey. pp. 55–72.

Zircon Rare Earth Geochemistry



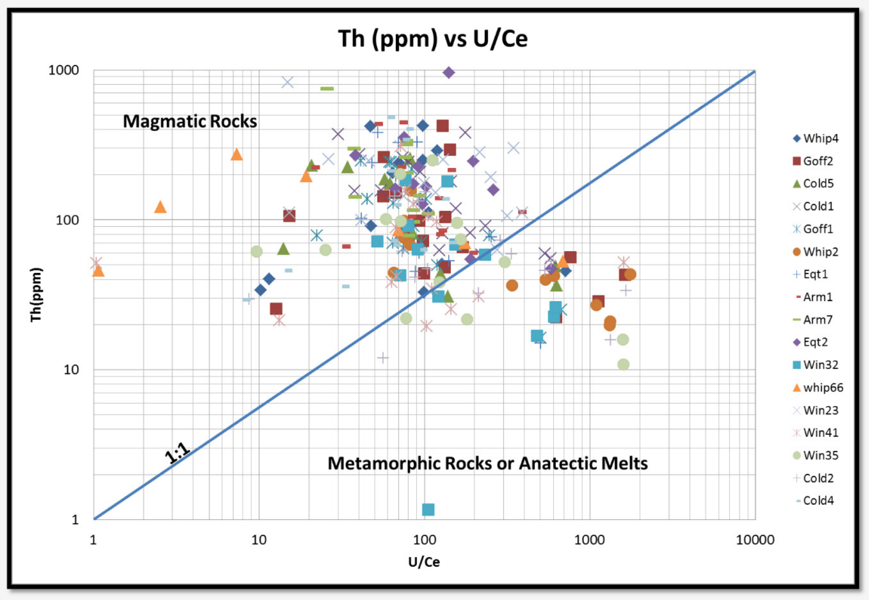
- Falls within the "Continental Granitoid" field (10,000-15,000).
- Zircons from continental arc system are distinct from oceanic crust zircons and largely overlap the continental granitoid field.
- *U/Yb ratios for zircons:*
  - •Ocean gabbros (0.18)
  - •Continental granitoids (1.07)
  - •Kimberlites (2.1)



Positive anomalies: Eu/Eu*= (0.9-1.7)

Negative anomalies: Eu/Eu* < 1

- Only 1 zircon with positive anomaly from Whip 66 which is the standard used in the experiment (circled in red), all other zircons are depleted with Eu or have an Eu/Eu* ratio less than one.
- Anomalies are largely controlled by feldspar in the source or melt. If magma crystallizes plagioclase, most of the Eu will form with this mineral and the rest of the magma will be depleted in Eu.
- Evidence that most of the source contained increased feldspar (Felsic melt)



- Most samples fall within the magmatic rock zone.
- Whip2, Win32, and Win35 all show increased numbers within the anatectic zone.
- Evidence for both crustal melting and a magma source, consistent with continental arc systems.

Tioga Ashes- Dated				
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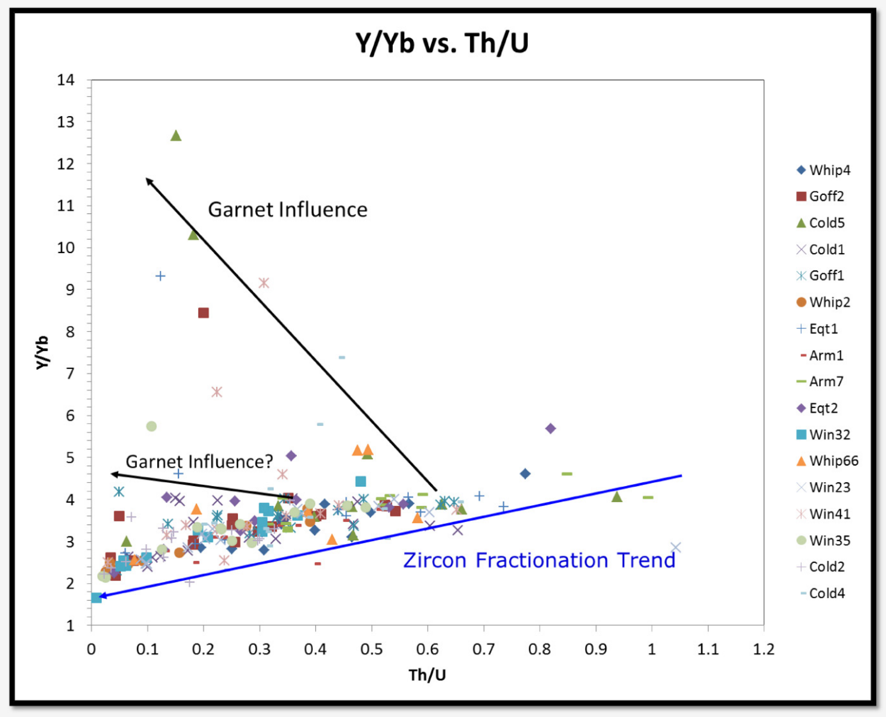
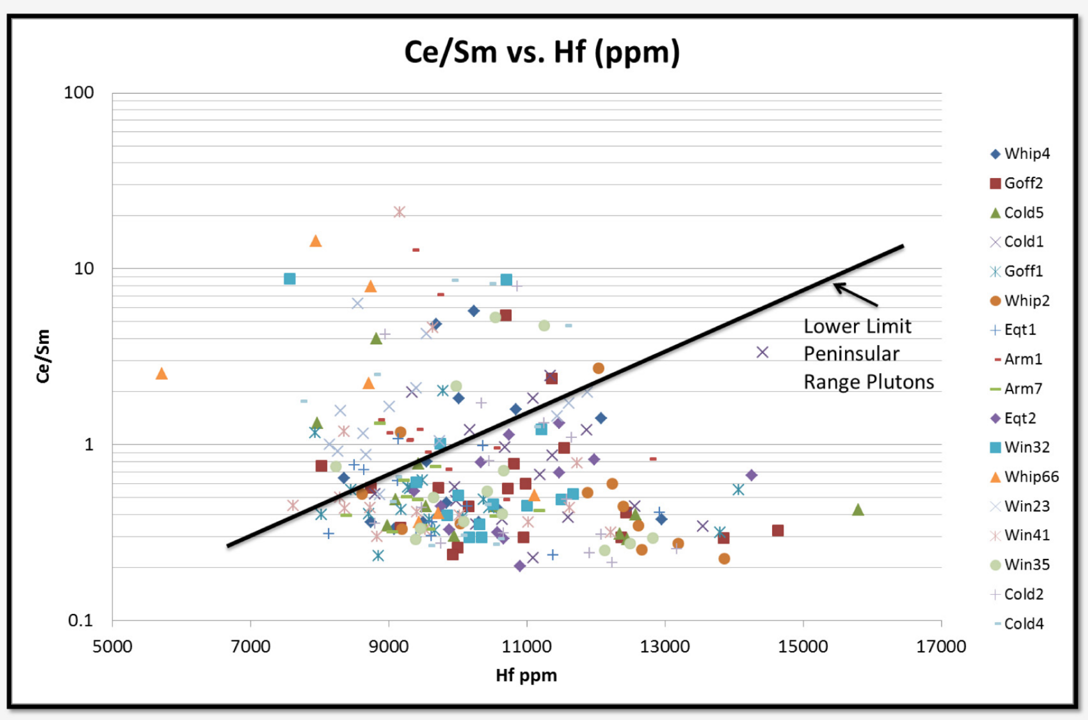
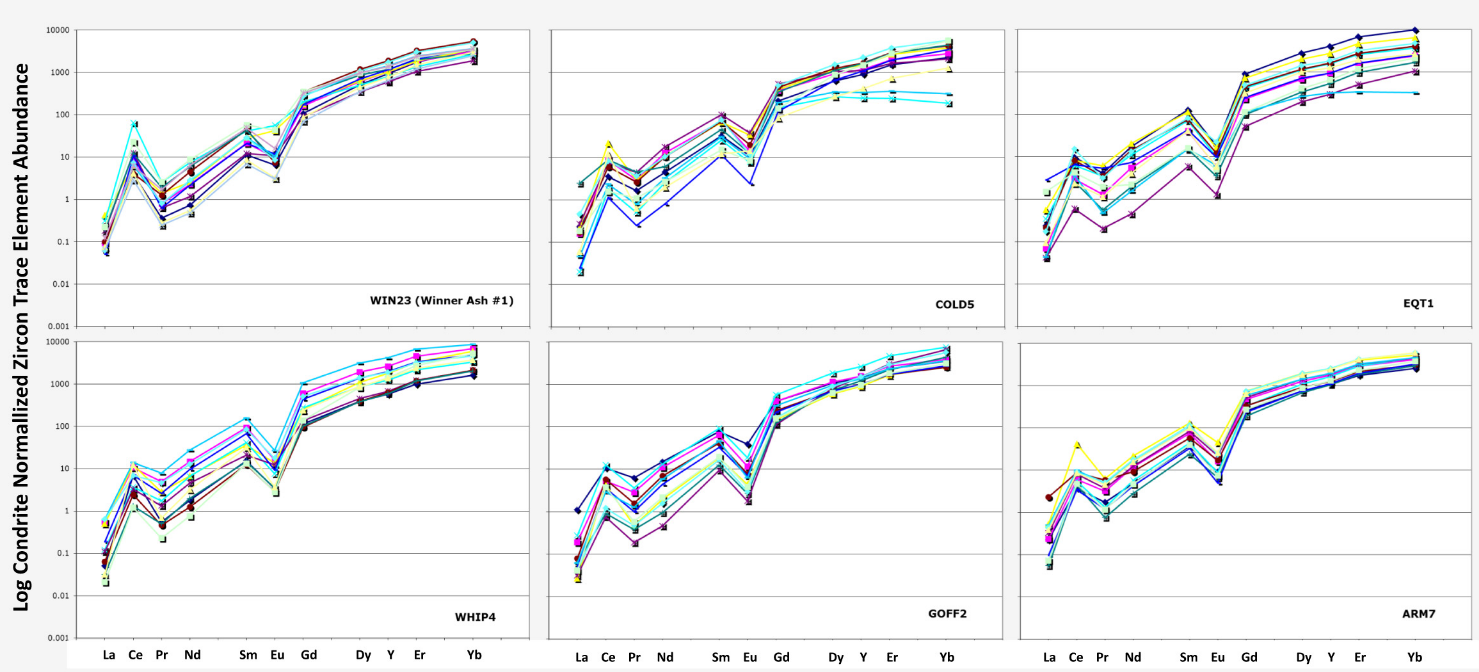


- Most samples are moderately fractionated.
- Cold5, Win41 and Cold4 show increased garnet influence. Goff2 and EQT2 show both increased fractionation and garnet influence.
- Increased fractionation from Arm7 to Arm1.
- Evidence for evolution of melt source(s) over time



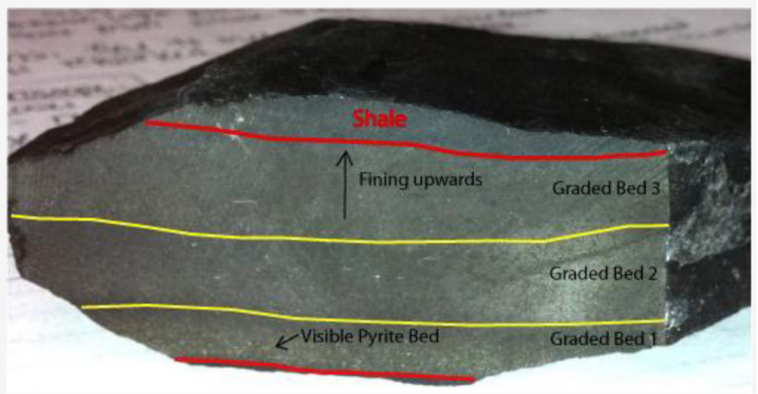
- Anomaly: Most points fall under lower limit for Peninsular Range Plutons.
- Ce was pulled out in the melt by some mineral(s) during fractionation.
- This anomaly could possibly help identify pluton body/eruption source.



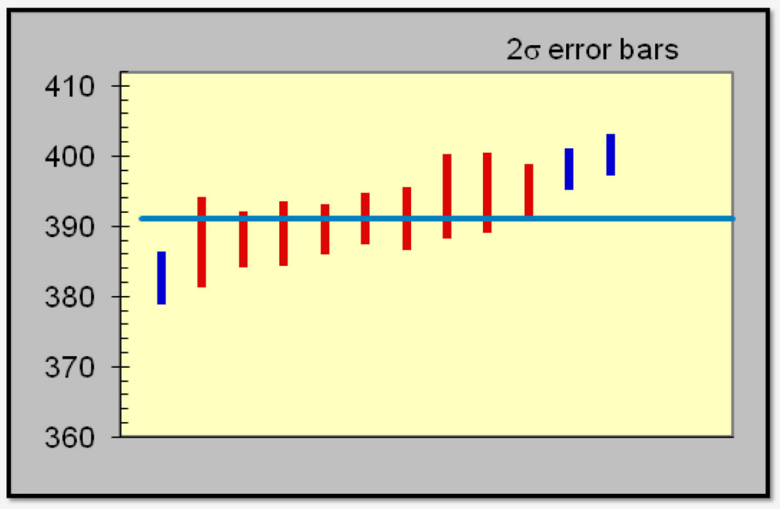
- Rare earth element diagrams corresponding to U-Pb SHRIMP analyses of zircon. Trace element abundances are chondrite-normalized (McDonough and Sun, 1995) and given in ppm.
- Samples show similar trends suggesting somewhat similar eruption sources?

Additional Data

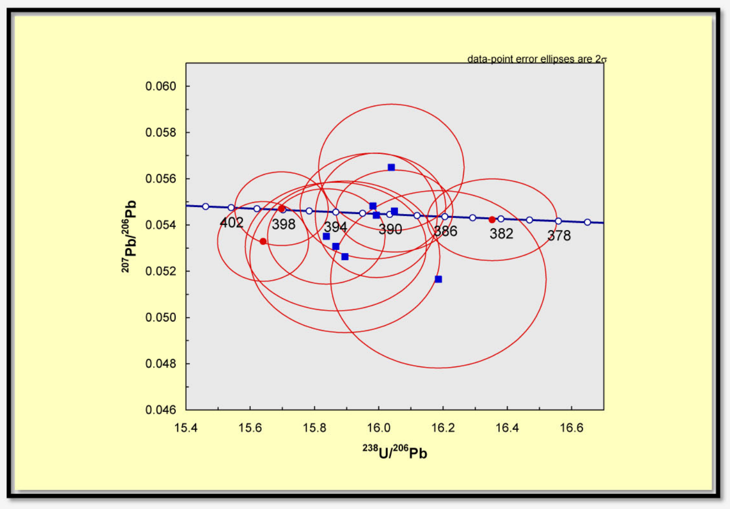
Winner Ash 2 Example



Winner 4-8 well Ash 2 (WIN32 at 8032.6') core image displaying three cyclic graded beds, fining upwards, with visible pyrite and mica grains. Graded beds may represent multiple ash fall events.

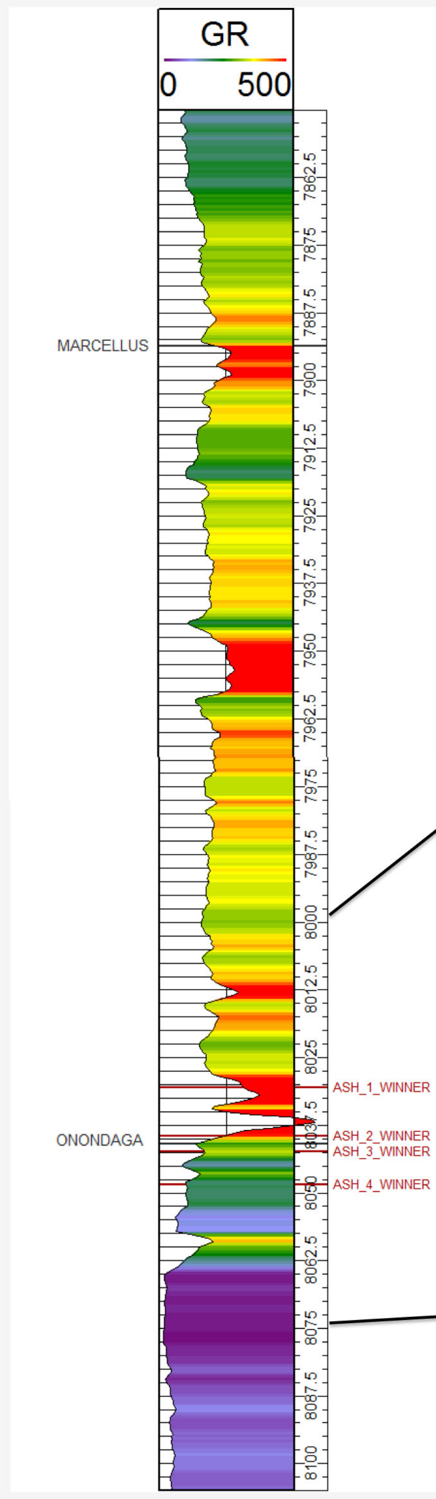


Above: Average age of 12 zircons with weighted means and error included. Average age of this ash layer is 391.1 ± 1.5.



Above: Concordia Diagram, blue squares represent ages used in calculations. Red points are dismissed due to high uranium or lead loss.

Sedimentation Rates

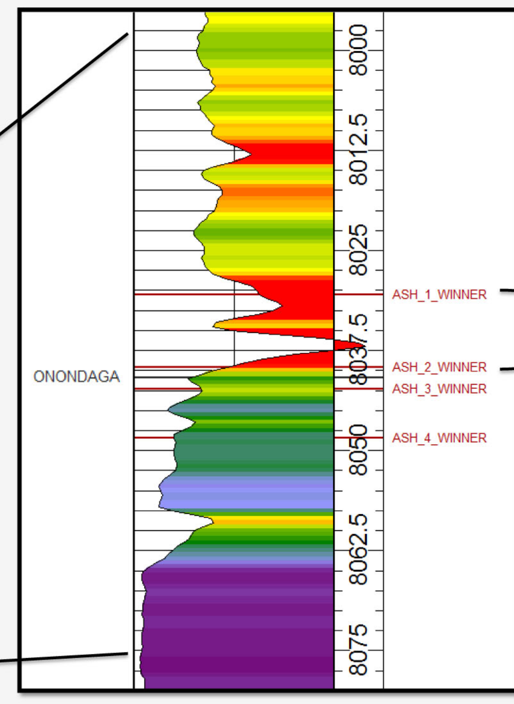


WINNER 4-8 WELL

COMPACTED SEDIMENTATION RATES:

- Measured from Ash 1 (WIN23) at 8023.5' to Ash 2 (WIN35) at 8032.6'
    - Depth difference of 9.1 feet
- Ash 1: 383.6 ± 1.4 Ma Ash 2: 391.1 ± 1.5 Ma
    - Age difference of 7.5 million years
- Compacted sedimentation rate $= \frac{\text{Sed. thickness deposited}}{\text{Time}}$

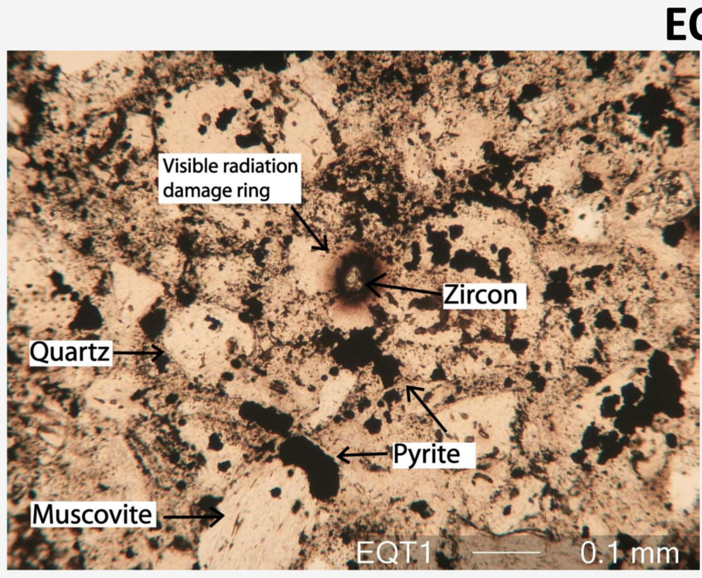
$$= \frac{9.1\text{ft}}{7.5\text{my}} = \mathbf{1.2}\ \frac{\text{ft}}{\text{my}} \text{ or } \mathbf{36.6}\ \frac{\text{cm}}{\text{my}}$$



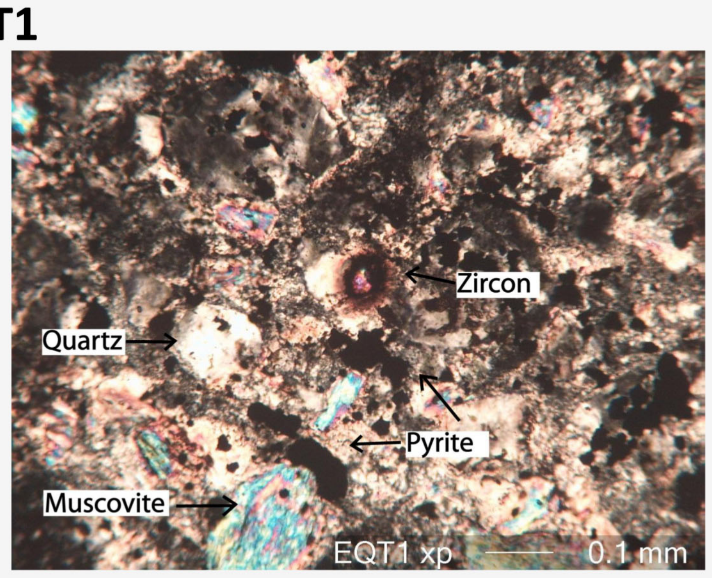
9.1 feet of sediments deposited and compacted over 7.5 million years

Petrography

EQT1



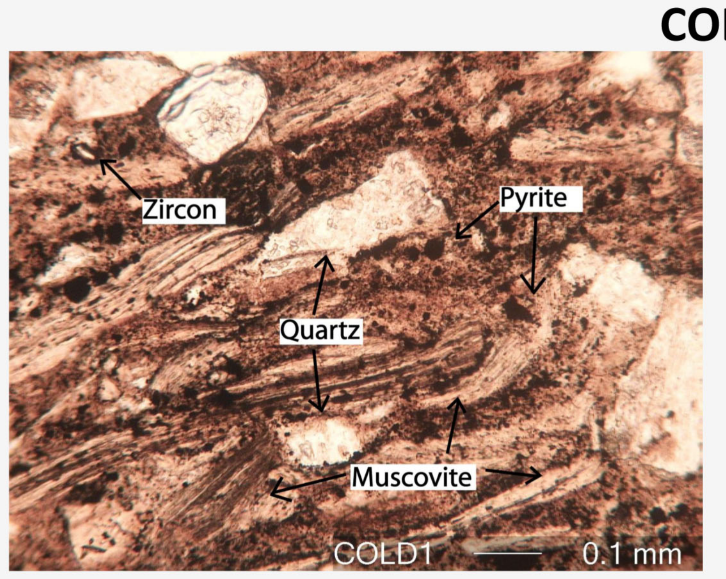
EQT1 in plain polarized light.



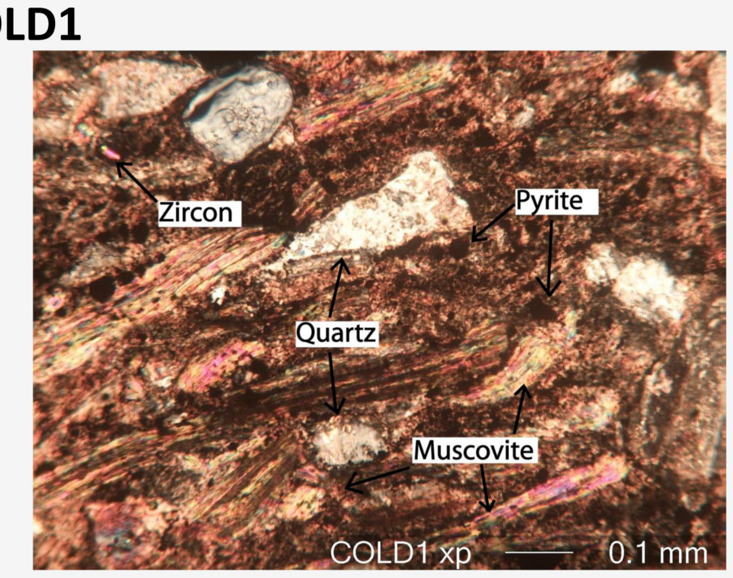
EQT1 with crossed polars.

Zircon displays obvious radiation damage ring. Abundant pyrite and opaques in small clusters. Tattered grains suggest some reworking of the shale and ash.

COLD1



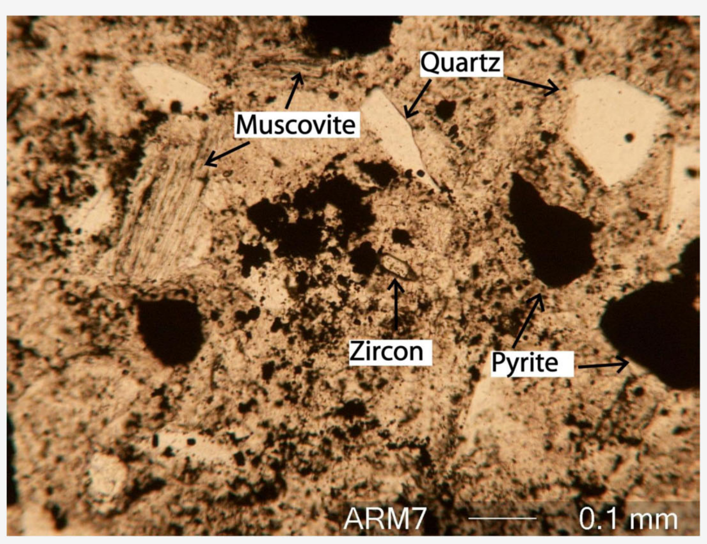
COLD1 in plain polarized light.



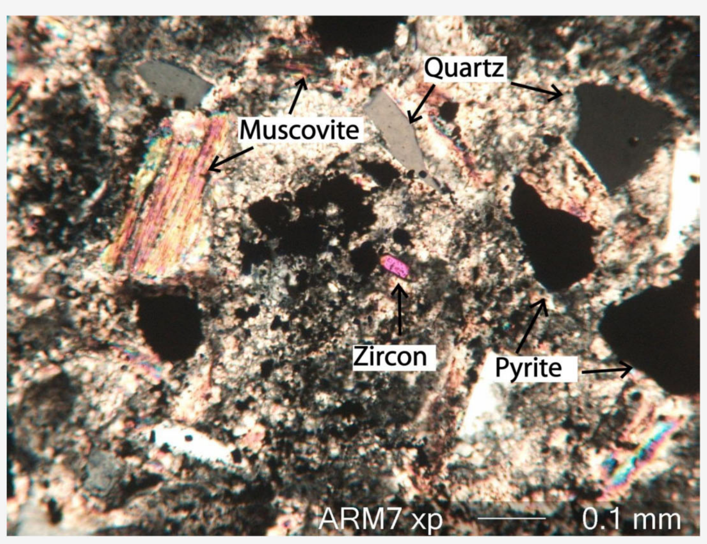
COLD1 with crossed polars.

Picture from base of ash layer. Micas are elongated and flattened along probable bedding plane and comprise most of the matrix, suggesting very little reworking at base. Relatively few opaques.

ARM7



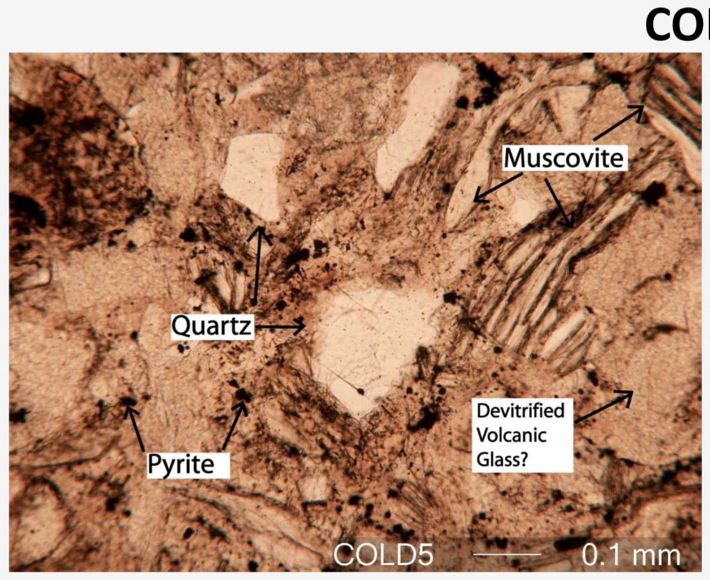
ARM7 in plain polarized light.



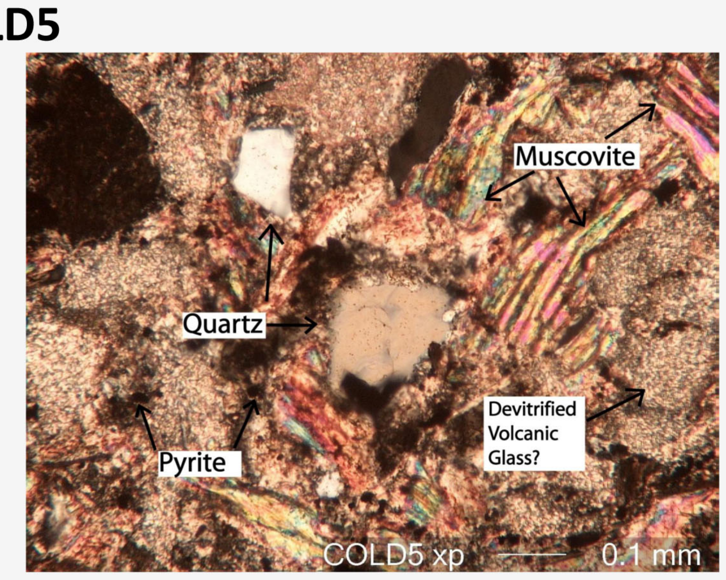
ARM7 with crossed polars.

Large micas with angular to sub-angular quartz grains and large pyrite clusterss urrounding . Small zircon near center of picture.

COLD5



COLD5 in plain polarized light.



COLD5 with crossed polars.

Many fragmented micas surrounding euhedral quartz. Plagioclase was fairly abundant in this sample. Matrix could be comprised of devitrified volcanic glass.