U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
FULL BOARD MEETING

SUBJECT: PALEOHYDROLOGY - AGE CONTROL FROM U-SERIES AND ^{14}C DATING OF CALCITE AND OPAL IN THE ESF

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PALEOHYDROLOGY - A DEFINITION

"Palæohydrogeology is a combination of observations on hydrochemical and isotopic differences in various groundwater zones or bodies, mineralogic data on the rock formations and hydraulic properties of the same formations, which are then compiled to allow interpretation of the evolution of the rock-water system over long time periods in the past."

". . . it is asserted that a well-founded palæohydrogeological interpretation may form the only convincing basis from which to evaluate a predictive performance assessment."

Chapman and McEwen (1993) "The Application of Palaeohydrogeological Information to Repository Performance Assessment"

PALEOHYDROLOGICAL RECORDS

- Low-temperature mineral deposits in rock mass (e.g. calcite and opal) which mark paleoflow pathways of percolation

- Ancient spring deposits (old ground-water discharge sites)

- Lake and playa deposits (climate records)

- Alteration zones in the rocks above the water table (high water marks or evidence of perched water zones)

- Perched water (left over from an earlier hydrologic regime)

YMP DATING PROGRAM

In November 1995, YMP expanded a coordinated isotopic dating program to study the physical records of percolation through the rock mass

- Los Alamos National Laboratory began a ^{36}Cl study of pore and fracture water/salts in the ESF coupled with a modeling study to explain the distribution of ^{36}Cl in the rock mass

- U.S. Geological Survey increased its efforts in dating calcite and opal deposits using the U-series and ^{14}C methods, and continued an isotopic tracer study of calcite using strontium, oxygen, and carbon isotopes

OBJECTIVES

- To establish a credible time framework (history) of deposition of low-temperature calcite and opal in fractures and cavities in the repository block

- To relate ages and isotopic attributes of calcite and opal to climatic variations (determine relationship between surficial climatic conditions and flux)

- To estimate or bound the paleoflux through the repository block based on the depositional record of calcite and opal

CALCITE ($CaCO_3$) AND OPAL ($SiO_2 \cdot nH_20$)

- Low-temperature calcite and opal deposits are common in fractures and cavities at Yucca Mountain
- These minerals were deposited from water percolating through the unsaturated zone
- They contain information about the times of deposition (U-series and ^{14}C) and the isotopic attributes of the waters from which they precipitated ($\delta^{13}C$, $\delta^{18}O$,$\delta^{87}Sr$, $^{234}U/^{238}U$)
- The mass of calcite and opal per unit volume of host rock is related to the past water flux which transported the requisite ions to depositional sites

CONCLUSIONS

The collective dating results (^{36}Cl, U-series, and ^{14}C) suggest the existence of two distinct flow systems or styles in the unsaturated zone:

- Fast percolation through discrete zones (fault zones?) which contain bomb-pulse ^{36}Cl. Calcite and opal deposits are not common in these zones.

- Slow percolation through the rest of the rock mass
  - U-series ages of opal and calcite, 37 to >500 ka
  - ^{14}C ages of calcite, 16 to >40ka
  - $^{36}Cl/Cl$ ratios of pore and fracture waters (salts) mostly less than 1000×10^{-15}

CONCLUSIONS (cont'd)

- Calcite and opal were deposited under unsaturated conditions (fractures and cavities were not filled with water, deposition required open space for evaporative concentration)

- Depositional rates were slow - micrometers per thousands of years - indicative of low flux

- Mineral textures suggest low-volume water films migrating down fracture surfaces and into cavities

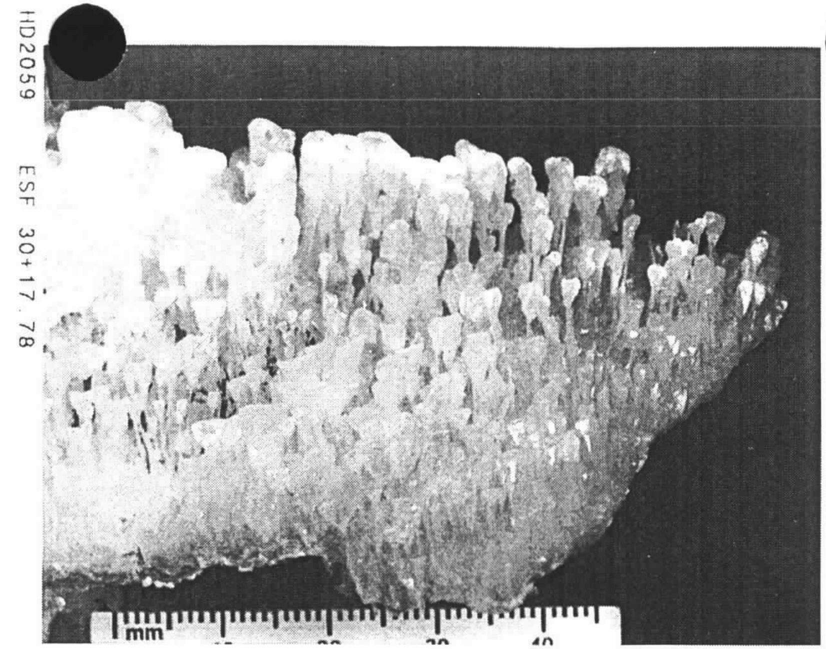
- Tracer isotopes indicate modification of infiltrating water during percolation (rock-water interaction during slow flow)

CALCITE AND OPAL OCCURRENCES

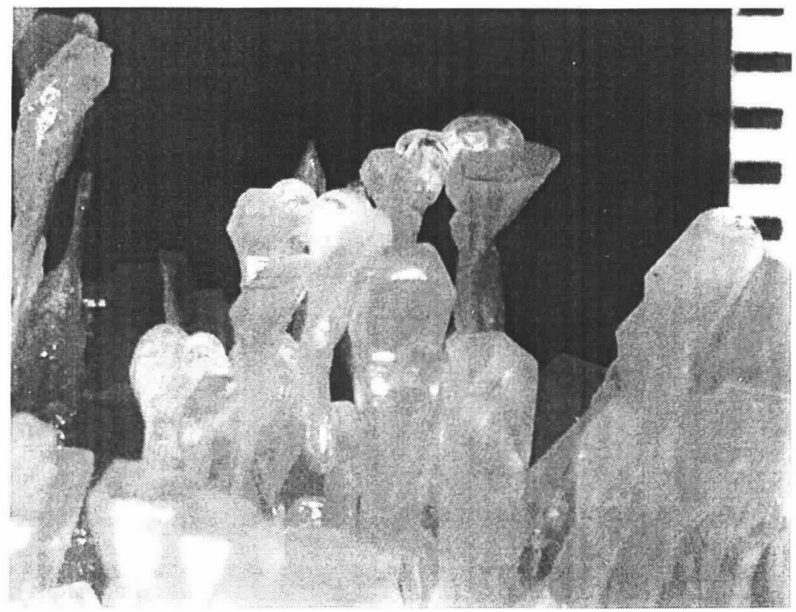
- Typically in fractures and cavities with openings greater than several millimeters
- In <u>single</u> fractures with variable openings, narrow intervals contain little or no mineralization whereas wider zones are mineralized
- Deposits occur on lower sides of openings
- Deposits are thicker and more complex on low angle features
- No "high" water marks that would indicate standing water

HD2059: Calcite + opal coating floor of large lithophysal cavity

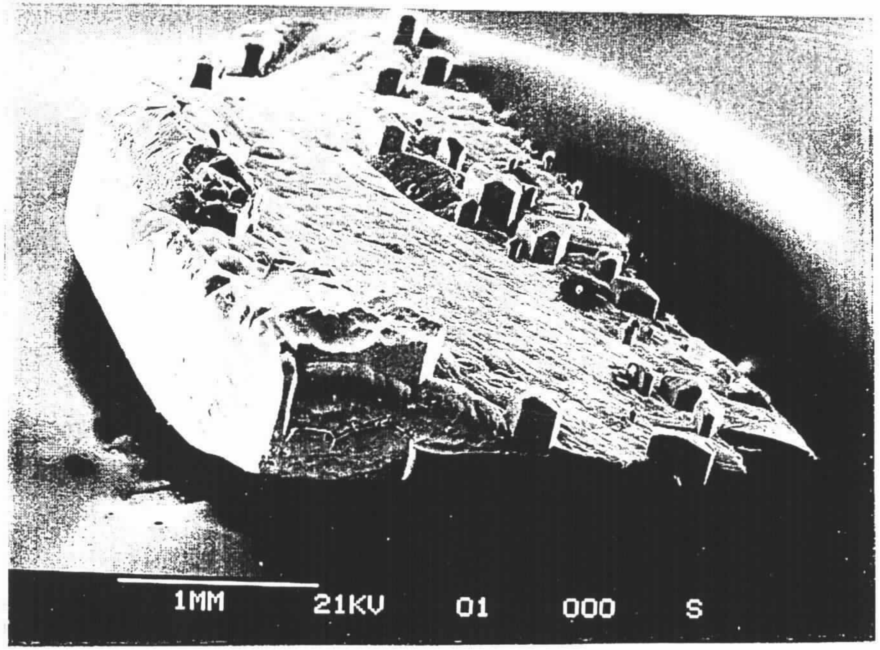
Slab of secondary mineral coating consisting of more-massive, basal calcite with later delicate, thin blades of calcite and latest opal (green-fluorescing under UV light) at blade tips.



Magnified view of upper right portion of sample shown above. Latest opal occurs as water-clear, green-fluorescing (photographed under UV light) bulbous, mammilary-like clusters clearly on top of gray, angular, scepter-head calcite crystals which in turn have developed at the outer tips of thin (<0.5 mm thick) blades of earlier calcite. Scale on right is in millimeters.



A



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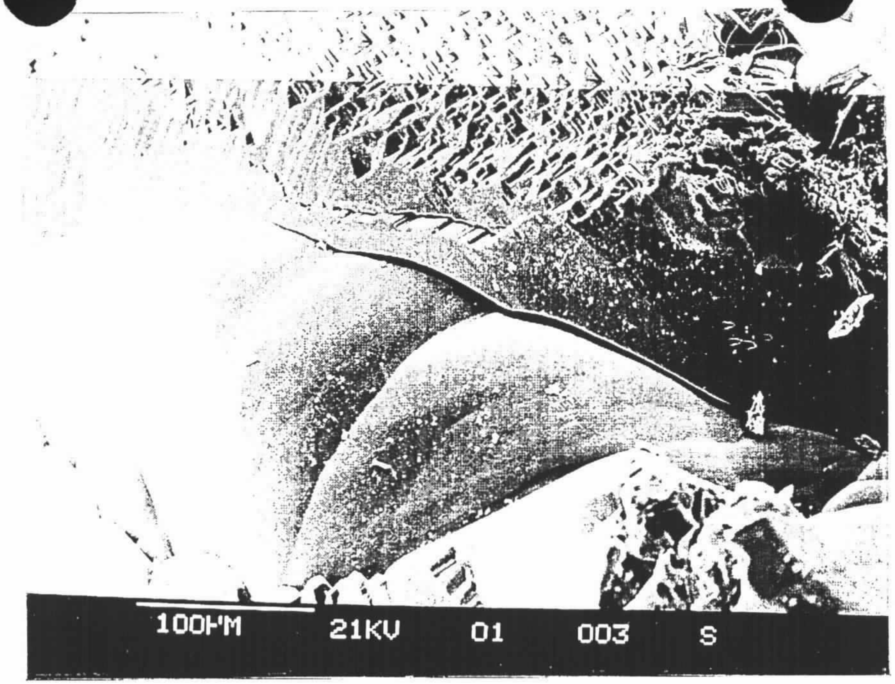
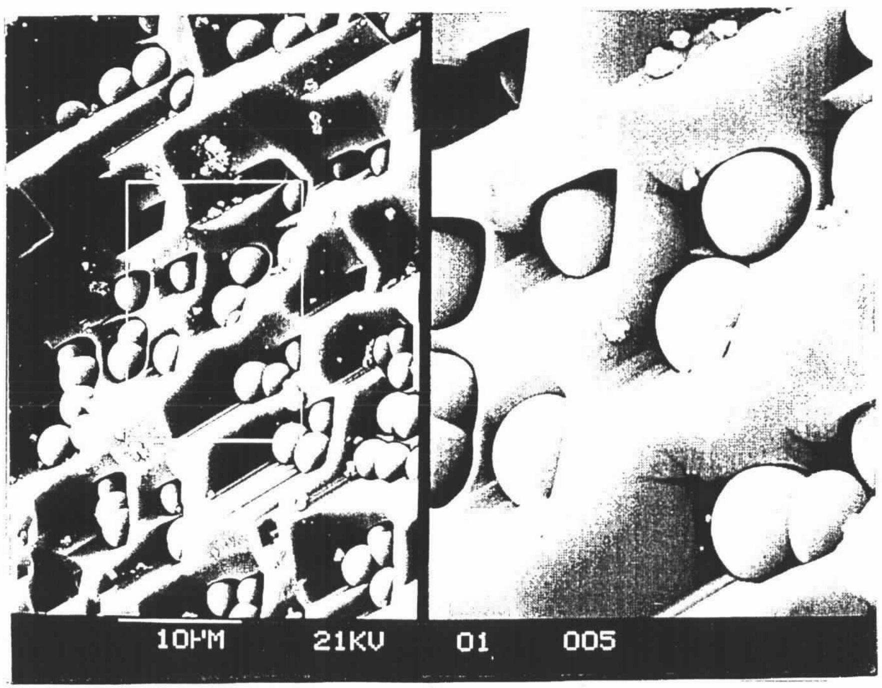


C



Sample HD2057, ESF 29+62.2; Secondary electron images of calcite and opal from a secondary mineral coating that floors the open-space created by intersecting sub-horizontal and sub-vertical fractures.

A. Individual narrow blade of calcite with thin coating of botryoidal opal followed by growth of scepter-head calcite at blade tip and small euhedral calcite crystals perpendicular to blade axis. White bar at bottom of image represents 1 mm.

B. Magnification of top of scepter-head blade-tip on far left side of image in A. Rounded, undulating surface of earlier opal-coated blade is overgrown by later calcite which shows areas with abundant crystal defects (angular pits in upper-central portion of image). Note gap between younger calcite and opal substrate. White bar at bottom of image represents 100 microns.

C. Magnification of angular pits in the upper-central portion of image B. Pits contain one or more tiny opal balls shown enlarged on right side of image. Angular calcite has sharp corners and edges indicative of crystal growth rather than corrosion. Pits may form after deposition of 1 to 3 micron opal balls due to commonly-observed reluctance of calcite to form in contact with preexisting opal. White bar at bottom of image represents 10 microns for left-hand image.

MICROSAMPLING AND AGE RESOLUTION

- Submicron growth layer of both calcite and opal requires fine-scale sampling

- Sampling resolution is limited by analytical requirements - 10-20 mg of calcite for ^{14}C, 50-100 mg of calcite for U-series, 0.1-2 mg of opal for U-series

- Even smallest samples probably integrate over finite intervals of growth history and therefore yield composite ages

- Depositional histories can still be established by composite ages

HD2059: Calcite + opal coating floor of large lithophysal cavity

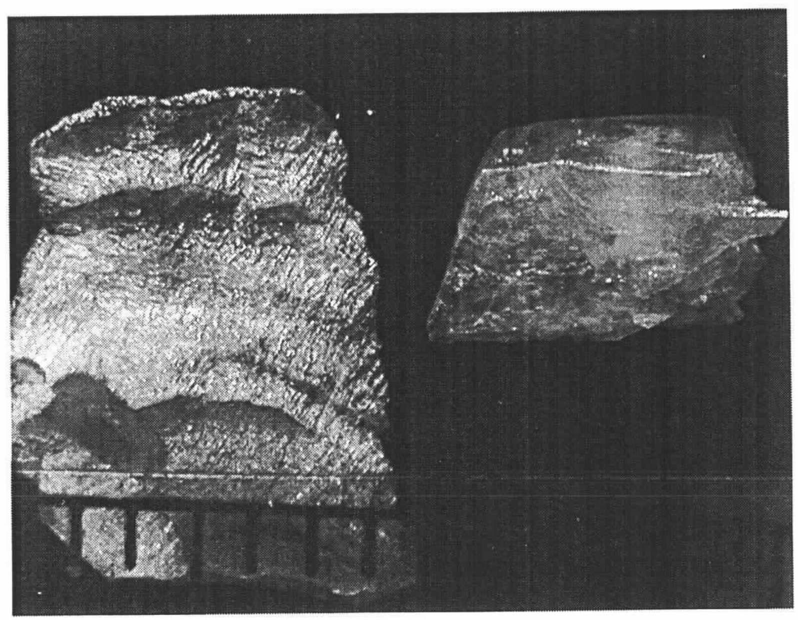
Very thin, fragile bladed calcite showing banded growth layers

HD2059 ESF 30+17.78 SPC00503986

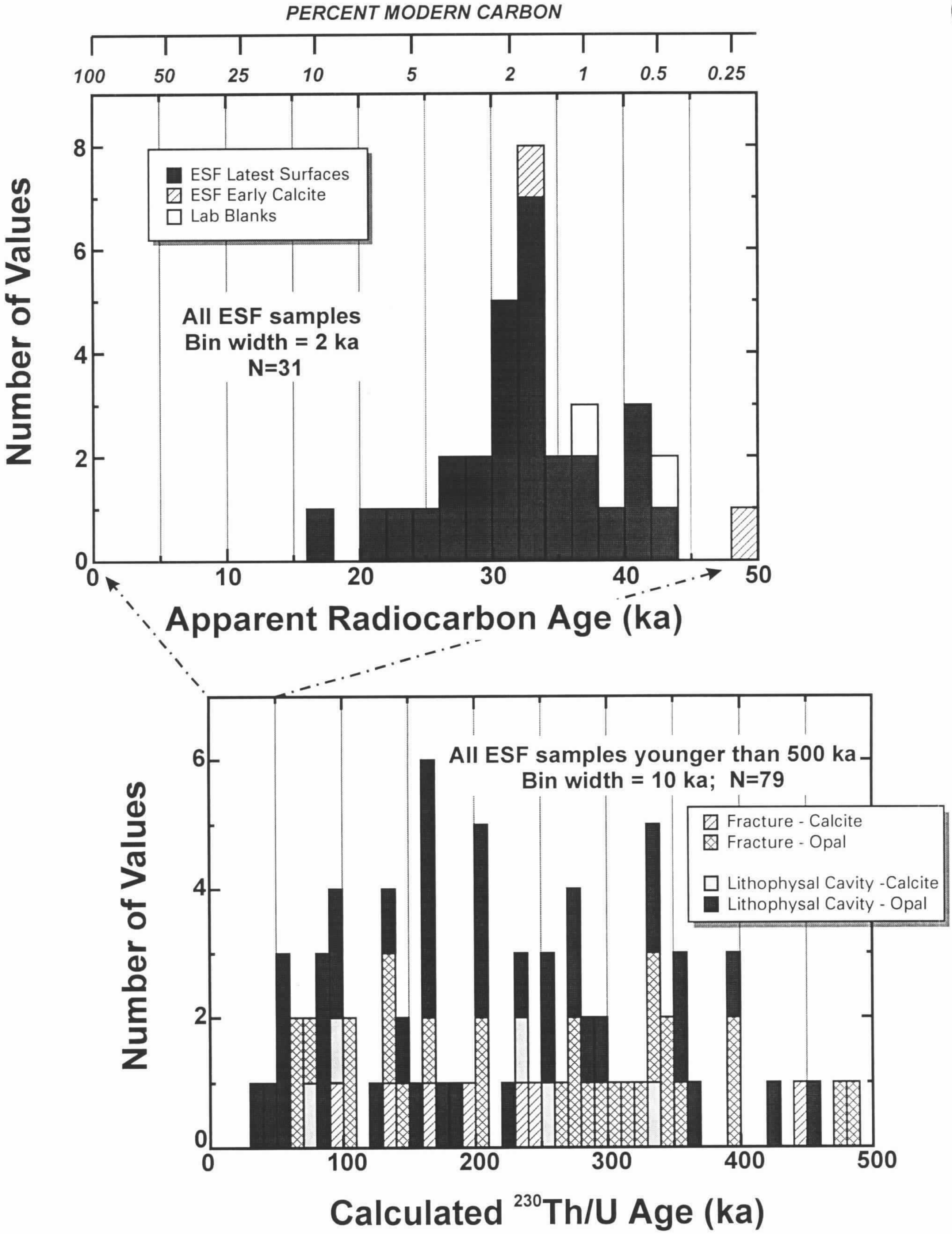
Calcite blade tips: last 1 or 2 growth bands
U-series: **74.8±1.3 ka** IR=4.7
^{14}C: **38.0±1.0 ka**

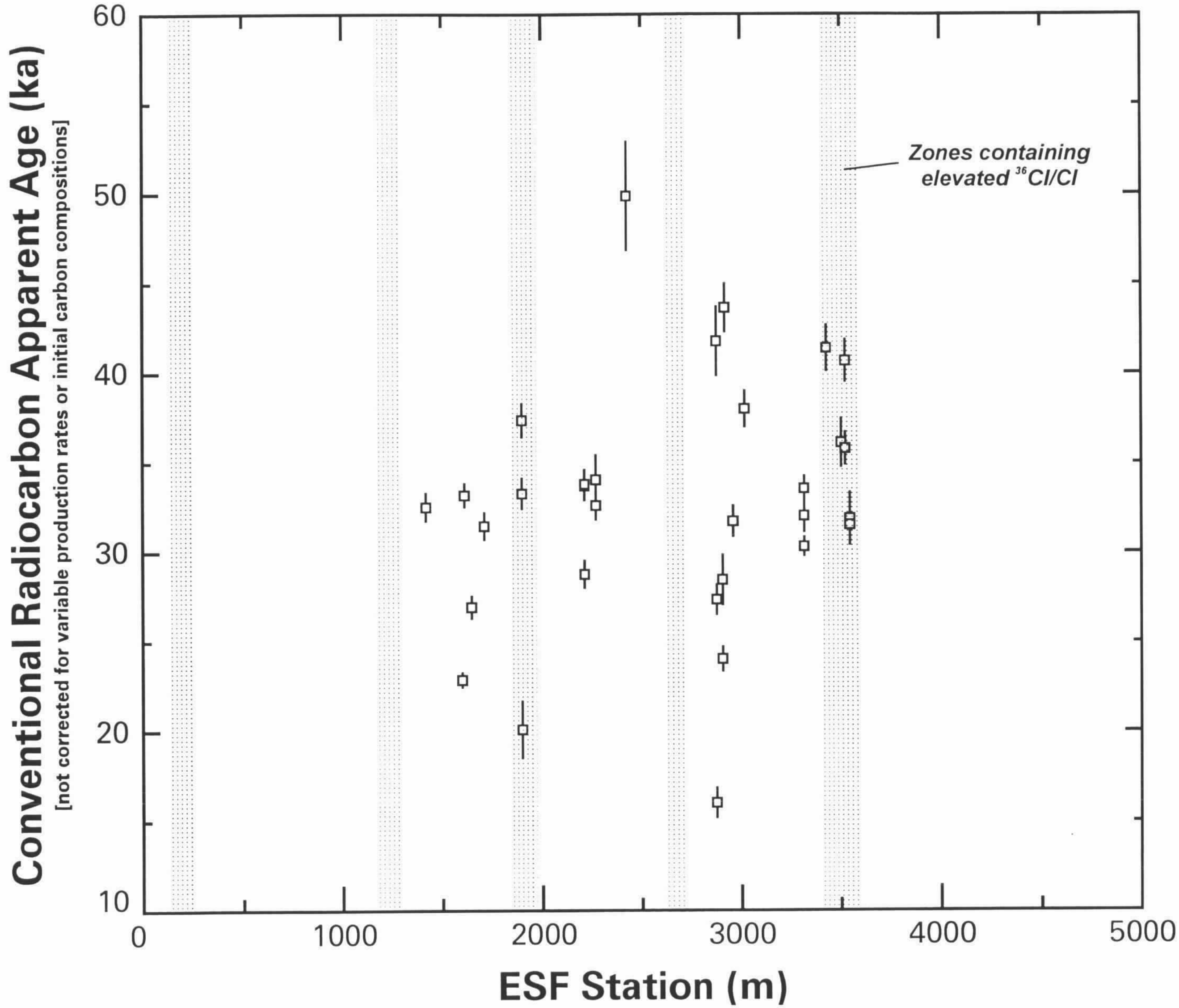
Opal bubble cluster underlying last calcite band
U-series: **96.4±1.0 ka** IR=4.76

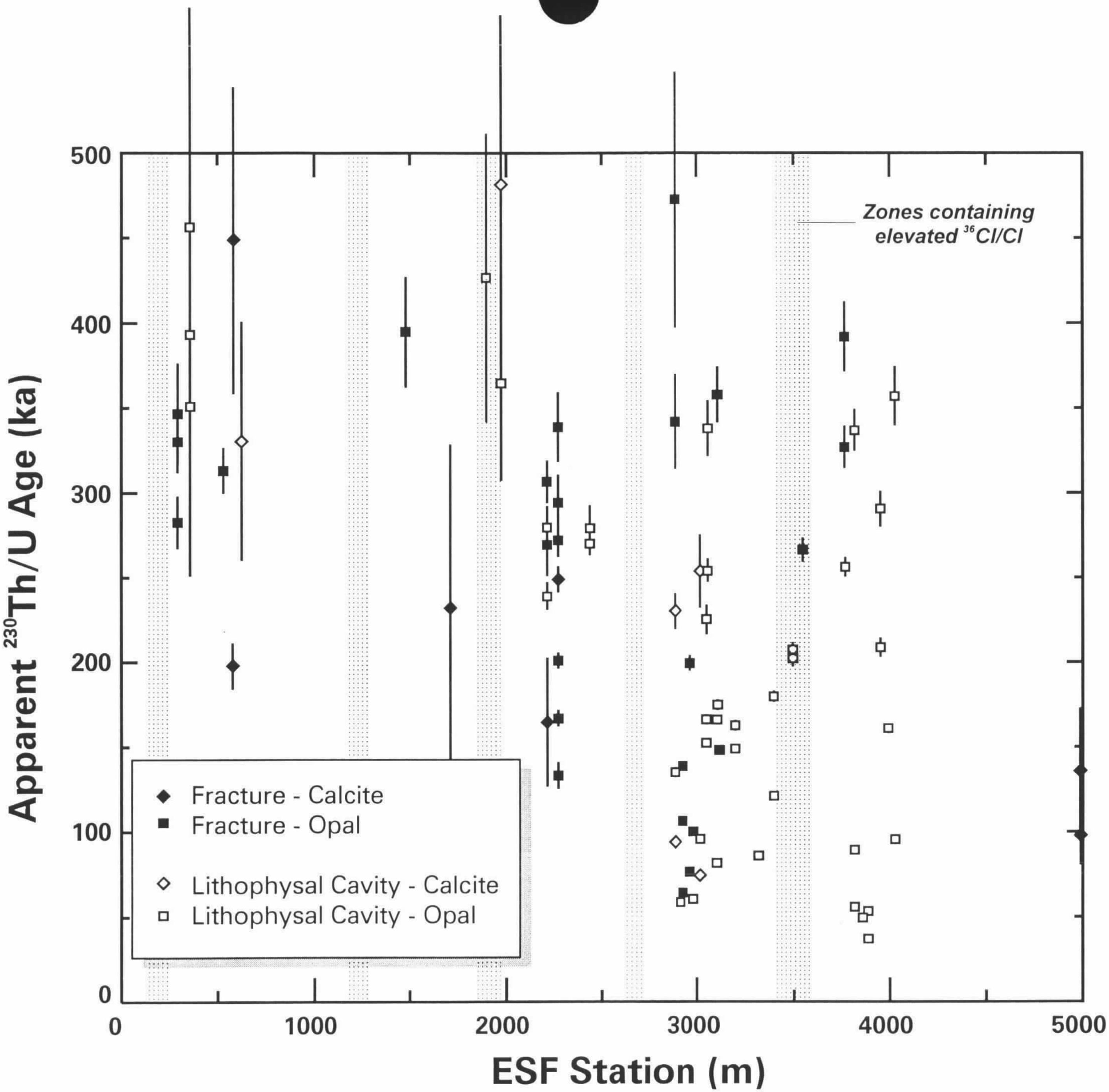
Calcite blades: composite of lower growth bands
U-series: **254±21 ka** IR=3.6



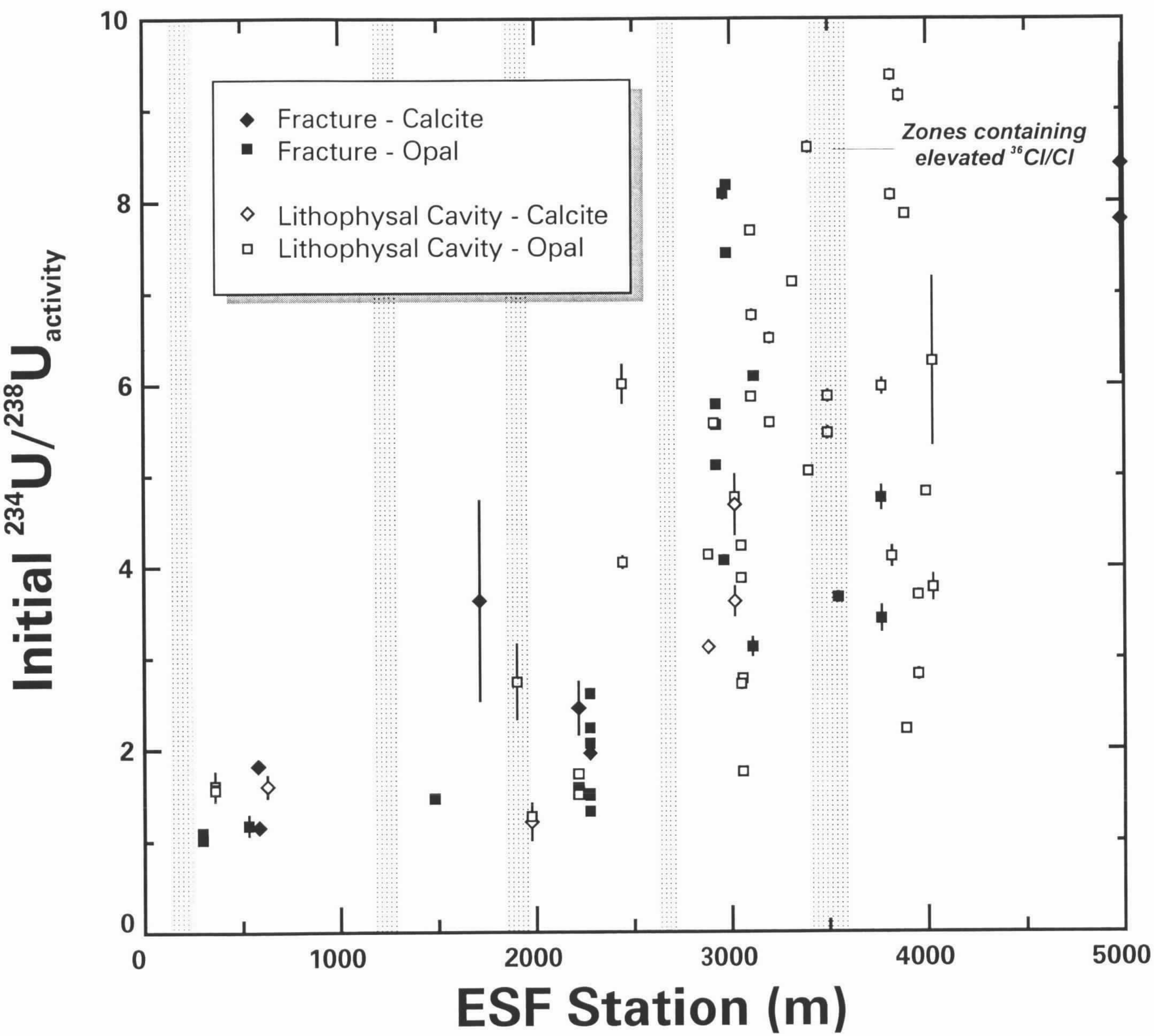
Tip of calcite blade with latest scepter-head development and underlying opal on former blade tip.


PERCENT MODERN CARBON
100
50
25
10
5
2
1
0.5
0.25
ESF Latest Surfaces
ESF Early Calcite
Lab Blanks
All ESF samples
Bin width = 2 ka
N=31
Number of Values
0
2
4
6
8
0
10
20
30
40
50
Apparent Radiocarbon Age (ka)
All ESF samples younger than 500 ka
Bin width = 10 ka; N=79
Fracture - Calcite
Fracture - Opal
Lithophysal Cavity -Calcite
Lithophysal Cavity - Opal
Number of Values
0
2
4
6
0
100
200
300
400
500
Calculated 230Th/U Age (ka)


Conventional Radiocarbon Apparent Age (ka)
[not corrected for variable production rates or initial carbon compositions]
Zones containing elevated $^{36}Cl/Cl$
ESF Station (m)
60
50
40
30
20
10
0
1000
2000
3000
4000
5000



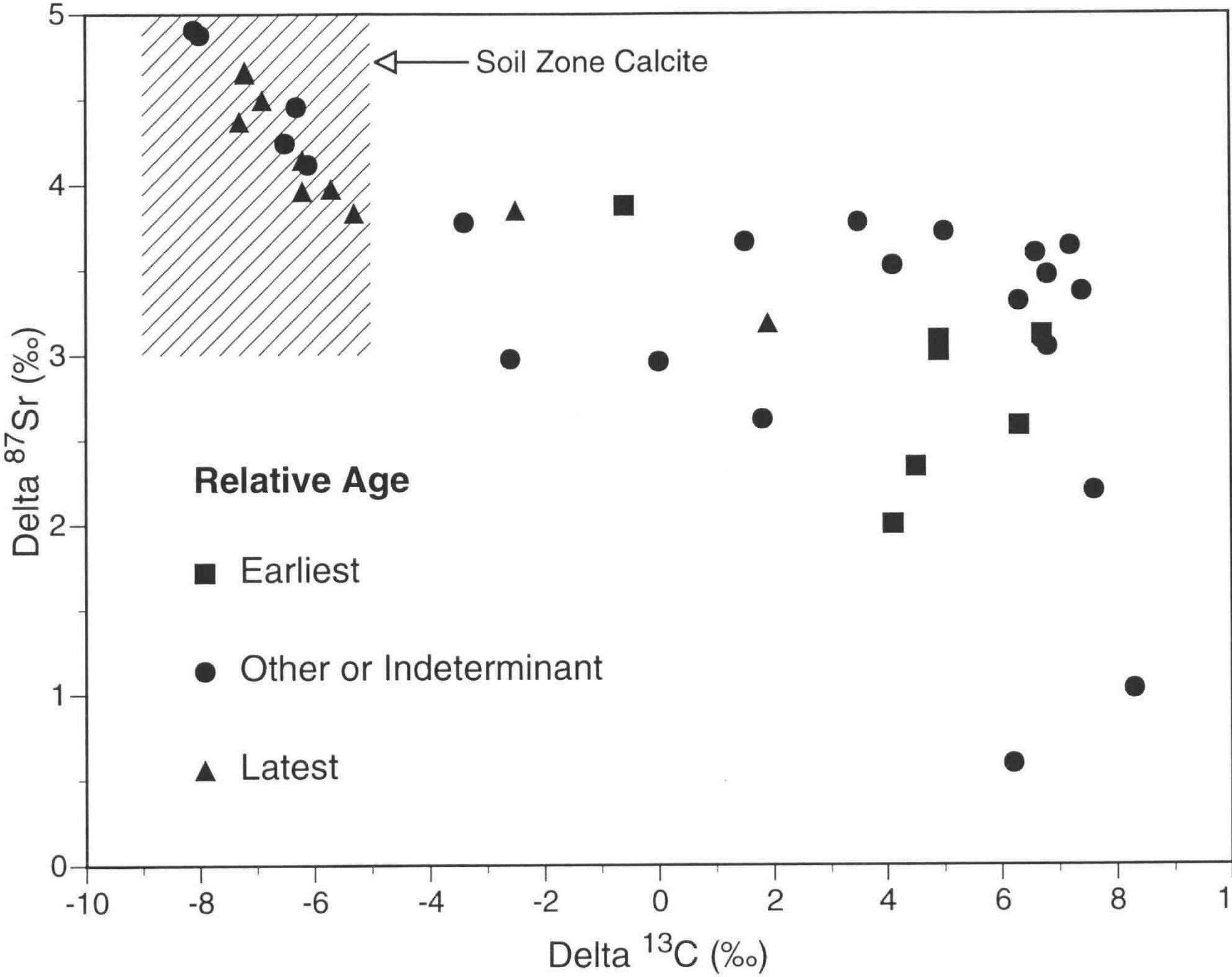
Zones containing elevated ³⁶Cl/Cl
Fracture - Calcite
Fracture - Opal
Lithophysal Cavity - Calcite
Lithophysal Cavity - Opal
Apparent ²³⁰Th/U Age (ka)
ESF Station (m)
0
100
200
300
400
500
0
1000
2000
3000
4000
5000


Fracture - Calcite
Fracture - Opal
Lithophysal Cavity - Calcite
Lithophysal Cavity - Opal
Zones containing elevated $^{36}Cl/Cl$
Initial $^{234}U/^{238}U_{activity}$
ESF Station (m)
0
2
4
6
8
10
0
1000
2000
3000
4000
5000

Calcite Deposits Contain Coherent and Correlated Isotopic Signals

- Tracer isotopes (Sr, O, C) link calcite subsurface deposits with surface sources and climate conditions
- Tracer isotopes indicate past temporal variability in surface conditions and sources
- Isotopic variations are currently in the context of 'relative' ages
- Isotopic dating will be place tracer isotope signals in a real time framework

Tracer Isotopes Relate Latest Calcite in ESF to Surficial Calcite



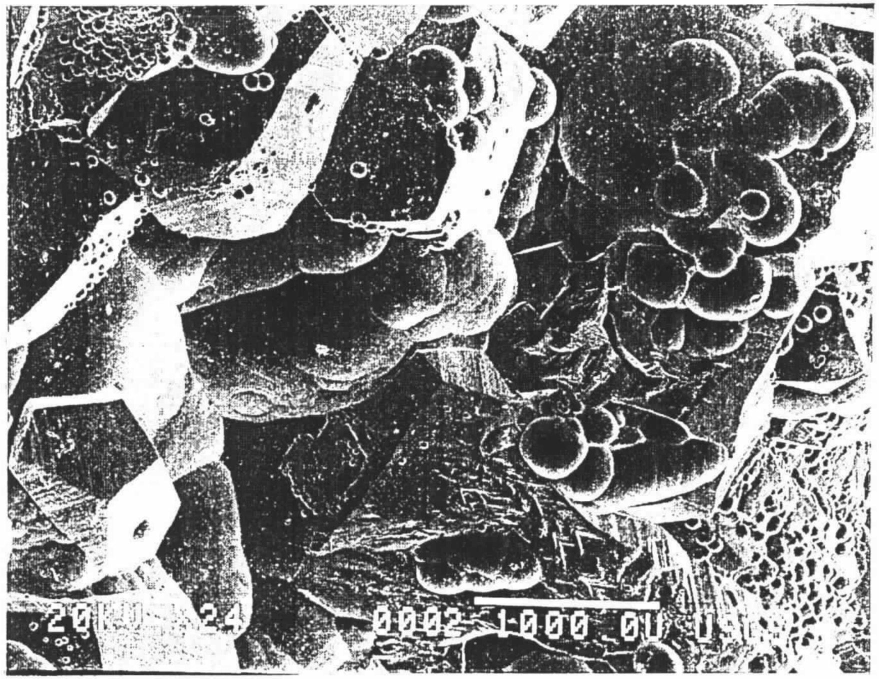
ESTIMATING WATER FLUX

- Determine abundance of calcite and opal in ESF
- Determine level of mineral saturation in possible input water
- Estimate amount of evaporative concentration necessary for calcite-opal deposition
- Establish age-distribution model of calcite and opal deposition
- Calculate flux required to deposit minerals

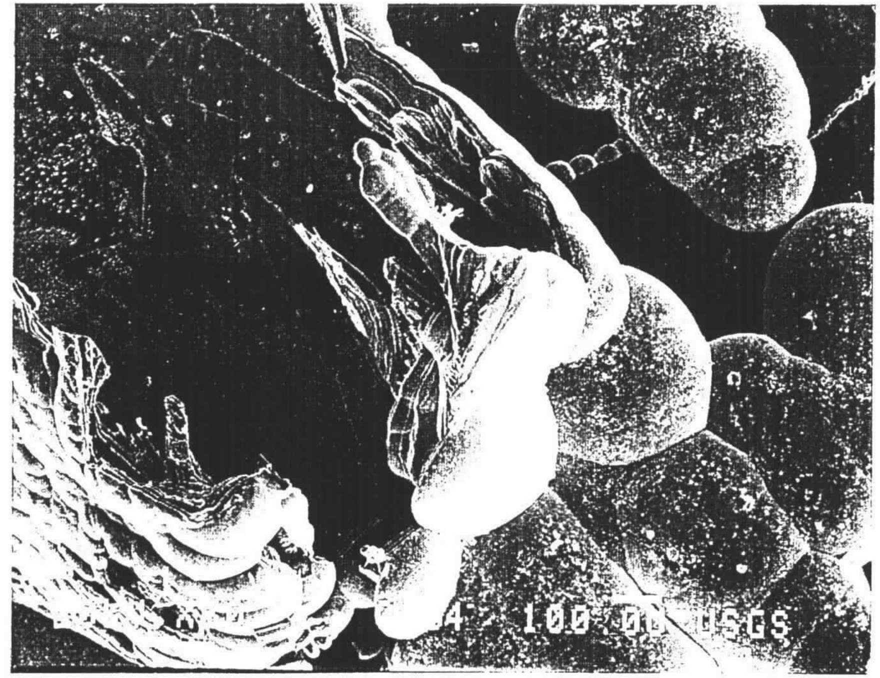
SUPPLEMENTAL SLIDE

- Photomicrographs of sample at Station 22 + 72 showing intimate relationships between calcite (crystalline) and opal (bulbous masses), and fine-scale growth layering in opal

A



B



C

Sample HD2008, ESF 22+72; Secondary electron images of calcite and opal coating a steeply-dipping fracture.

A. Free-face surface with an early stage of broadly-rounded opal (left center and center of image) overgrown by later blocky calcite with latest small bubbles of opal on both earlier calcite and opal. Apparent ^{230}Th/U ages span a wide range from about 300 ka for early-opal to 130 ka for the smallest late-opal bubbles. White bar at bottom of image represents 1 mm.

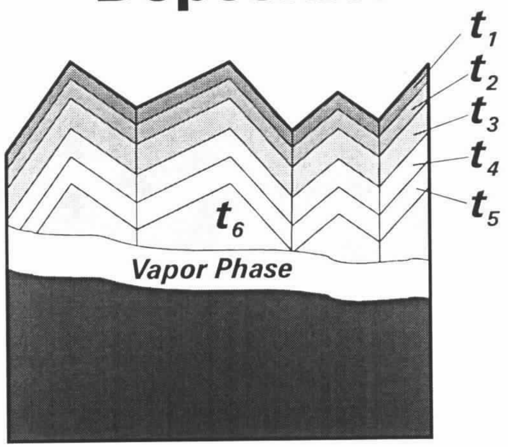
B. Image of late opal after calcite substrate was removed by laboratory acid etching. Dark area in upper left-hand corner represents void left after dissolution of blocky calcite crystal. Note rounded, coalescing bubble forms on upper surfaces, as well as multiple layers and narrow "roots" that extend below the outer surface. These latter textures indicate intimate growth relations between opal and calcite rather than distinct episodes of mono-mineralic deposition. White bar at bottom of image represents 100 microns.

C. Magnification of opal bubble near upper-central portion of image B. Opal bubbles appear to be constructed of innumerable, concentric sub-micron layers. The amount of time required for deposition of each layer is not known. White bar at bottom of image represents 100 microns.

SUPPLEMENTAL SLIDE

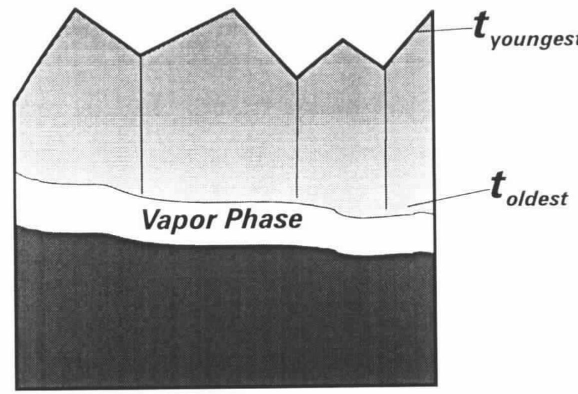
- Conceptualization of “episodic” and “continuous” deposition models

Episodic/Instantaneous Deposition



1) Layers of finite thickness.
2) Deposition rapid relative to interval between events.
3) Analysis represents individual layer.
4) Measured isotopic rations uniform throughout layer.
5) Calculated age reflects age of discrete depositional event.

Continuous Deposition



1) Layers infinitely thin.
2) Extremely low deposition rates.
3) Analysis represents multiple layers.
4) Measured isotopic rations dependent on sample thickness and growth rate.
5) Calculated age reflects mixed age intermediate between age of outermost and innermost layers.

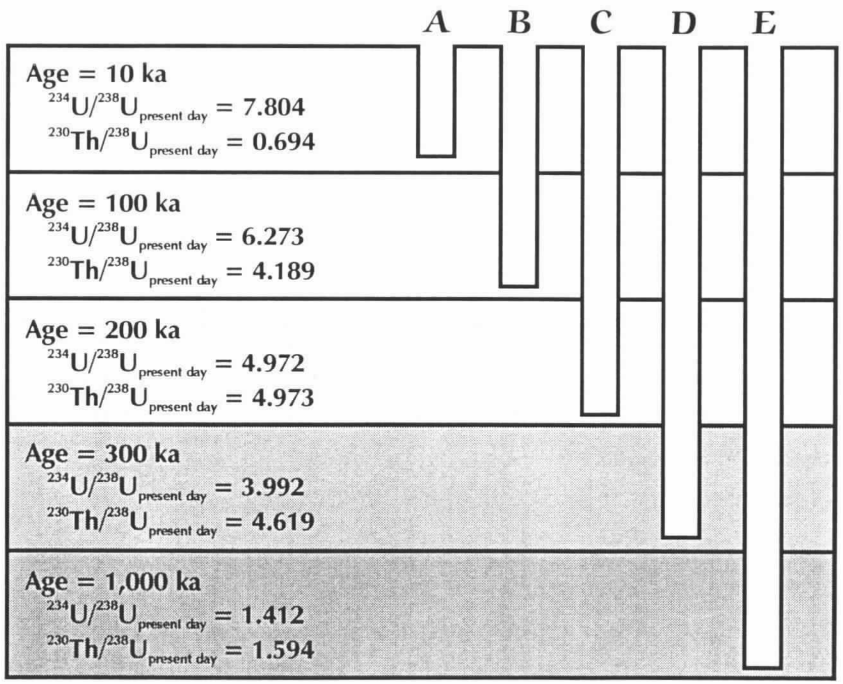
SUPPLEMENTAL SLIDE

- Illustration of effects of sampling multiple layers of different ages. Incorporation of older and younger material in sample will result in a numerical age that is younger than the mean age

Calculated Ages for mechanically-mixed layers of different ages.

Assumes:

1) Uniform U concentration in all layers
2) Constant initial $^{234}U/^{238}U$ activity of 8
3) Each layer contributes an equal mass



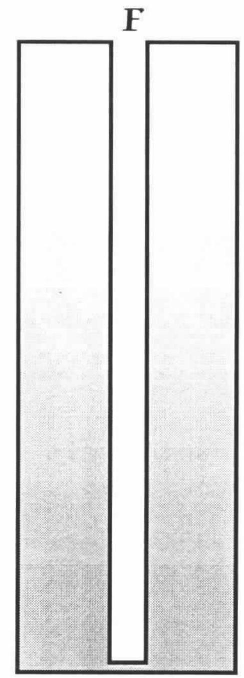
Continuous Deposition

Assumes:

1) Deposition from 0 to 1,000 ka at a constant rate

At time of deposition:

2) Constant U concentration
3) Constant initial $^{234}U/^{238}U$ = 8



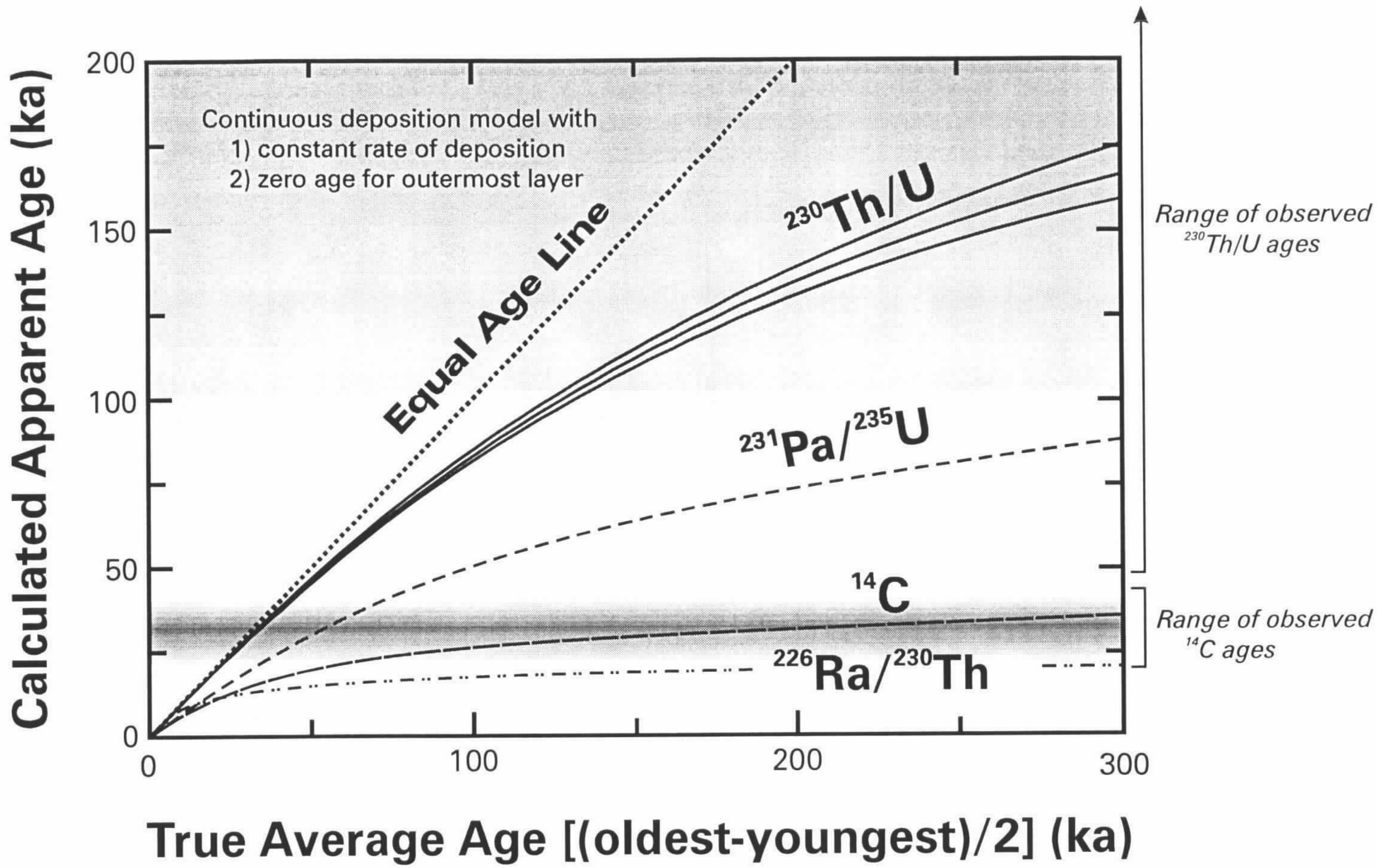
	A	B	C	D	E	F
Average Age	10	55	103	152.5	322	500
Calculated Mixed Age	10	43.5	70.9	92.0	98.4	186
Calculated Mixed Initial Ratio	8.0	7.8	7.5	7.2	6.2	4.9

SUPPLEMENTAL SLIDE

- Isotopic systematics that result from sampling that integrates over a finite growth history of mineral

- Discordance from “true” age is dependent of half lives of isotopic system

- These discordances can be used to evaluate the continuous deposition model



Effects of very slow secondary mineral growth on ages:

Calculated ages represent composite depositional events.

Younger ages obtained for smaller samples from the same surface.

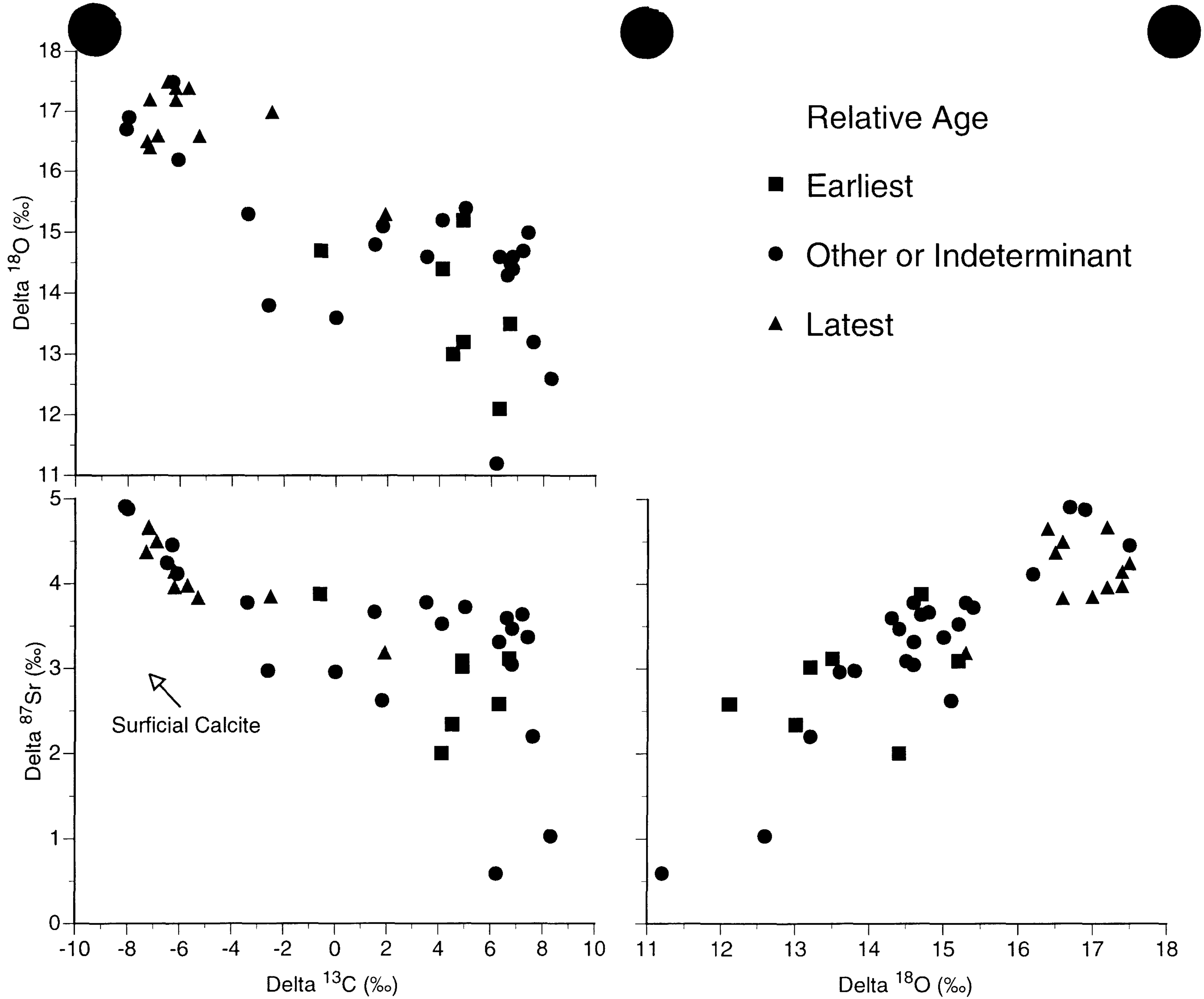
Isotopes with shorter half-lives will yield younger calculated ages for the SAME material..

Samples of outermost materials will not yield calculated ages at the upper limit of the isotopic system (^{230}Th/U $\approx$ 450 ka; ^{231}Pa/^{235}U $\approx$ 200 ka; ^{14}C $\approx$ 45 ka; ^{226}Ra/^{230}Th $\approx$ 10 ka).

SUPPLEMENTAL SLIDE

- Coherent and correlative variations in strontium, carbon, and oxygen isotopic compositions of calcite deposits

- These coherent isotopic records indicate that subsurface conditions can be related to surfical conditions (climate)



Relative Age
Earliest
Other or Indeterminant
Latest
Delta ^{18}O (‰)
Delta ^{87}Sr (‰)
Delta ^{13}C (‰)
Delta ^{18}O (‰)
Surficial Calcite