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CHEM.3040 - FORENSIC SCIENCE II
DEMISE OF THE ICE MAN

I. Introduction

The body of a prehistoric human (the *Ice Man*) was discovered in the Tyrolean Alps. Forensic evidence suggested that he had suffered a violent death. It was also apparent that he was far from his home, perhaps on a hunting trip. The body was well-preserved and therefore amenable to a variety of forensic investigations. In this exercise we will investigate how isotopic data were used to determine where the ice man lived. Before you start the exercise you should review the pdf file – Demise of the Ice Man – which is found on the course web site.

II. Ar-Ar Mica Ages

IIa. *Introduction*

During examination of the remains of Ice Man, a sample of the Ice Man's intestinal content was screened for cereal fragments. The intestinal sample also contained 12 100- to 400 µm white micas (muscovite) that are believed to have been ingested as a result of the grinding of cereal or from drinking water.

Soil is formed by the weathering of rock material. This weathering can be of two types: (1) physical during which the original rock material is broken into smaller fragments and (2) chemical in which various mineral undergo partial or complete breakdown. Some minerals, such as quartz and mica, are resistant to chemical weathering while other minerals, such as olivine or pyroxene, are easily weathered. The mica found in the intestines of the Ice Man are residual from the weathering of the country rock (the rock that underlies a particular region). If one can identify the rocks that were the source of the mica, one would have an idea of the area in which the Ice Man lived.

IIb. *Ar-Ar mica ages*

Using what is actually a very sophisticated technique, geologists were able to determine the age of individual mica grains. The technique they used is a variation of the K-Ar dating technique known as Ar-Ar dating. A subset of these ages is given in Table 1.

Table 1. Ar-Ar mica ages

Grain	Age (m.y.)
A	201
B	213
C	178
D	195
E	189
F	219
G	161

1. Refer to the geologic map taken from the Ice Man scientific paper which is attached to this exercise. What are the ages, or age ranges, for the following geologic units:

Polymetamorphic gneisses -

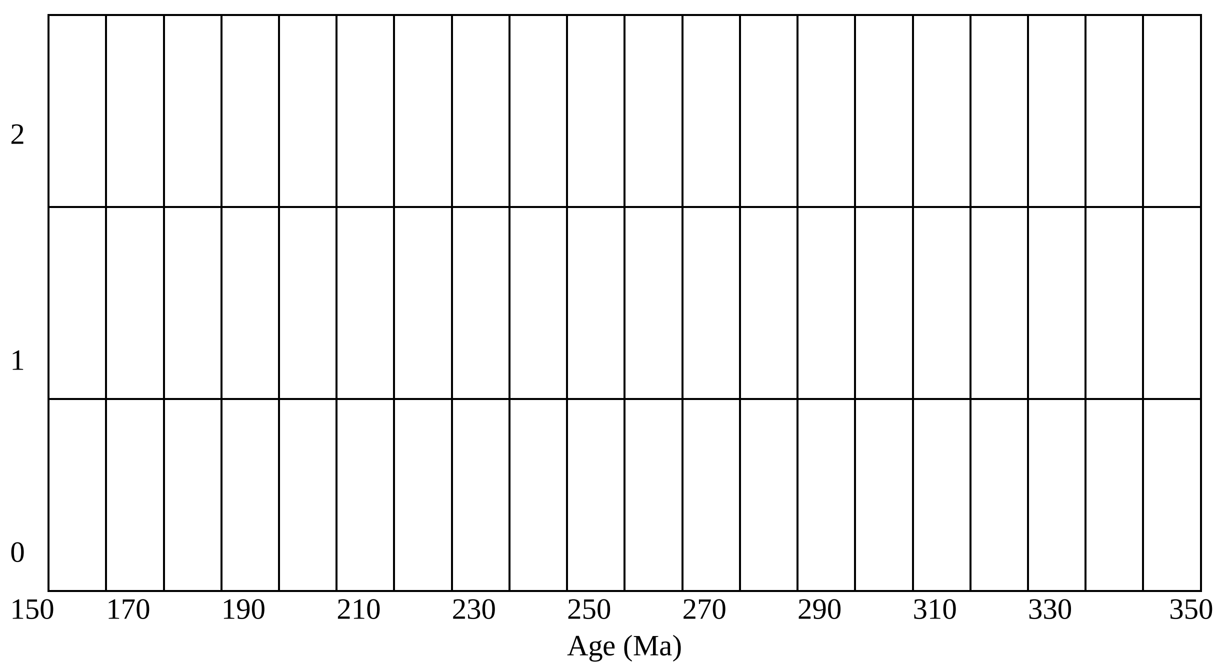
Phyllites -

Permian volcanics -

Permian granites -

Tertiary granites -

2. Plot the ages for the mica from the Ice Man's intestines on the graph below. Also plot the ages (or age ranges) for the various geologic units. Group the mica ages into 10 million year intervals. For example if there are two mica ages between 160 and 170 million years, show these as a box two units high extending from 160 to 170 million years. What you are drawing is called a histogram. Show the ages for the various geologic units either as fields or a single line, whichever is appropriate.



3. Based on these data, and the graph, which geologic unit was the most likely source for the mica grains in the Ice Man's intestines? Explain. What is the most probable home area for Ice Man? Why?

III. Demise of the Ice Man - Isotopic Evidence

IIIa. *Introduction*

Stable and radiogenic isotopic data have been used in a variety of fields to answer a wide range of scientific questions. The nucleus of an atom consists of protons (+1 charge) and neutrons (0 charge), two types of particles that have essentially the same atomic mass. The number of protons in a nucleus determines the element. For example, a nucleus with 1 proton is a hydrogen nucleus, a nucleus with 2 protons is a helium nucleus. Isotopes of an element contain the same number of protons but different numbers of neutrons. For example, there are three isotopes of hydrogen: (1) ordinary hydrogen which contains one proton and no neutrons and has an atomic mass of one; (2) deuterium which contains one proton and one neutron and has an atomic mass of two; and (3) tritium which contains one proton and two neutrons and has an atomic mass of three. The convention used to show the numbers of types of particles in a nucleus is to place the number of protons (called the atomic number) at the bottom left of the element symbol and the number of protons plus neutrons (called the atomic mass) at the upper left of the element symbol. For example, the tritium isotope is shown as ${}^{3}_{1}\mathrm{H}$.

IIIb. *Stable isotopes*

Stable isotopes are not radioactive, they do not spontaneously breakdown to other atoms. There are three isotopes of carbon: (1) carbon 12 which contains 6 protons and 6 neutrons giving an atomic mass of 12; (2) carbon 13 which contains 6 protons and 7 neutrons giving an atomic mass of 13; and (3) carbon 14 which contains 6 protons and 8 neutrons giving an atomic mass of 14. C-12 and C-13 are stable isotopes, they do not spontaneously breakdown, while C-14 is radioactive.

Stable isotopes that have large differences in mass may be fractionated during physical, chemical, or biological processes. Oxygen has three isotopes: ${}^{16}O$, ${}^{17}O$, and ${}^{18}O$. Consider a water molecule (H_2O). Let's suppose that we had two water molecules. One consists of two ${}^{1}H$ atoms and one ${}^{16}O$ atom and the other of two ${}^{1}H$ atoms and one ${}^{18}O$ atoms. The atomic mass of the first water molecule is 18 while the atomic mass of the second water molecule is 20, approximately a 10% difference. During evaporation the lighter molecule would preferentially evaporate and the water vapor would be richer in the lighter molecule relative to the water liquid. We measure this fractionation, in parts per thousand, relative to a standard. In the case of oxygen the standard is SMOW (Standard Mean Ocean Water). For oxygen the fractionation is indicated by the nomenclature $\delta^{18}O$. Positive values for this term mean that the sample is richer in the heavier isotope than the standard (the sample is said to be isotopically heavy) while negative values mean that the sample is richer in the lighter isotope than the standard (the sample is said to be isotopically light). We will use these differences to tell us something about where the Ice Man lived.

When the Ice Man was alive he drank the local water. Our bodies contain oxygen, and the oxygen in the Ice Man's body was in equilibrium with the oxygen in the drinking water. Hence, we can measure the oxygen isotopic composition of the Ice Man's teeth and bones and from these measurements determine the oxygen isotopic composition of his drinking water. Measurements of the oxygen isotopic composition of rivers in the area where the Ice Man lived showed that different rivers had different isotopic compositions. There was a regular difference in oxygen isotopic compositions for rivers on the southern and northern side of the mountains, a reflection of the differences in the isotopic composition of the rainwater.

Table 2 gives the results of the oxygen isotopic measurements of the Ice Man's teeth and bones and the various river waters. Because there is an altitude effect, the elevation for each river water sample is given in the data table. Note that $\delta^{18}O$ values for all these samples are isotopically negative indicating that the samples are isotopically lighter than the standard.

Table 2. Stable isotope data

Sample ID	River and/or Valley	Elevation (m)	$\delta^{18}O$ (SMOW)
Iceman			
3, dental enamel			-10.98
41g2, dental enamel			-10.56
Z2KN4a, trabecular bone			-11.31
Z2KN4b, trabecular bone			-11.48
Z2KN5a, cortical bone			-11.63
Z2KN5b, cortical bone			-11.66
Southern rivers			
E1230	Eisack/Isarco	234	-12.14
E1500	Eisack/Isarco	506	-12.20
E1750	Eisack/Isarco	752	-12.19
E11000	Eisack/Isarco	1005	-12.37
E11350	Eisack/Isarco	1348	-12.46
R1660	Rienz (Puster valley)	658	-11.94
R1750	Rienz (Puster valley)	750	-12.34
R11000	Rienz (Puster valley)	1000	-11.54
R11200	Rienz (Puster valley)	1200	-11.74
R11220	Rienz (Puster valley)	1220	-11.54
UT280	Ulten valley	275	-12.00
UT750	Ulten valley	735	-12.02
UT1000	Ulten valley	1070	-12.20
UT1500	Ulten valley	1464	-12.82
UT1900	Ulten valley	1880	-12.56
S500	Schnals valley	562	-13.09
ST1000	Schnals valley	1002	-13.28
ST1500	Schnals valley	1501	-13.67
ST2000	Schnals valley	2002	-14.27
Northern rivers			
IN600	Inn	608	-14.40
IN750	Inn	750	-14.57
IN1000	Inn	990	-14.18
IN1500	Inn	1474	-14.54
OT700	Ötz valley	700	-14.82
OT1000	Ötz valley	1024	-15.09
OT1500	Ötz valley	1484	-14.95
OT1900	Ötz valley	1950	-15.58

4. Plot the data for the river water samples on Figure 1. For each river connect the data points.

5. Show the isotopic ratios for the teeth and bone samples from the Ice Man as fields drawn across the entire diagram. You don't have any elevation data for the Ice Man samples, hence you can't make a plot of isotopic ratios versus elevation.

6. Locate each of the valleys (or rivers) on the geologic map that accompanies the Ice Man study. Which rivers (areas) have isotopic characteristics most similar to the Ice Man samples? Are these southern rivers or northern rivers?

IIIc. *Radiogenic isotopes*

Radiogenic isotopes are produced by the breakdown of radioactive parents. A number of these isotopic systems are used in the geosciences. Here we will use the rubidium (Rb) - strontium (Sr) and uranium (U) - thorium (Th) - lead (Pb) systems to determine the region in which the ice man lived.

Rubidium-Strontium. One of the isotopes of rubidium, ^{87}Rb, is radioactive and this isotope breaks down to ^{87}Sr by emitting a beta particle. A beta particle is an electron that comes from the nucleus of an atom. When a beta particle is emitted by the nucleus a neutron is converted to a proton. Hence the atomic number increases by one but the atomic mass remains the same. The half-life for the decay of ^{87}Rb is 48.8 billion years, a very long half-life. There are four isotopes of Sr: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr. Only ^{87}Sr is produced by radioactive decay, all the other strontium isotopes are stable and their concentration has remained constant. We typically measure the abundance of the isotope produced by radioactive decay relative to that of one of the stable isotopes. In the case of Sr the measured ratio is $^{87}Sr/^{86}Sr$. Various geological processes change the relative amounts of Rb and Sr. The measured isotopic ratio, $^{87}Sr/^{86}Sr$, is a function of the Rb/Sr ratio and the age of the sample. Hence, this ratio varies for different rocks formed by different processes at different times. Thus we can use the $^{87}Sr/^{86}Sr$ ratio to characterize different geologic units.

Uranium-Thorium-Lead. Two of the isotopes of U are radioactive and so is Th. All three radioactive isotopes are at the top of long decay chains, involving the emission alpha (two protons and two neutrons emitted from the nucleus) and beta particles and eventually ending with different lead isotopes. The decay sequences are ^{238}U to ^{206}Pb with a half-life of 4.5 billion years, ^{235}U to ^{207}Pb with a half-life of 704 million years, and ^{232}Th to ^{208}Pb with a half-life of 14.0 billion years. The only isotope of Pb that is not produced by radioactive decay is ^{204}Pb and this isotope is used when we measure the lead ratios. Just as was the case for the Rb-Sr system, different geologic units have different lead isotope ratios depending on their geological history.

Soils are the result of the weathering of bedrock. Hence, soils show similar isotopic ratios to those of their rock parent. Crops grown on the soils will also have similar isotopic ratios. When the ice man ate the crops these isotopic ratios were incorporated into his teeth and bones. Thus we can correlate the isotopic ratios for Sr and Pb found in the ice man's teeth and bones with those found for the various soils. The soil isotopic ratios for Sr and Pb were determined on soil leachates. The data obtained for the Ice Man samples and various soil leachates are given in Table 3.

Table 3. Radiogenic isotope data

Sample ID	$^{87}Sr/^{86}Sr$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$
Enamel				
31G5D	0.72028	2.089	0.848	18.597
Bones				
Z2KN1 L2 (cortical)	0.71808	2.115	0.861	18.298
Z2KN2 L2 (cortical)	0.71853	2.1025	0.852	18.509
Z2KN3 D (trabecular)	0.71844	2.086	0.846	18.594
Soil leachates				
Basalts				
IS1L	0.70528	2.066	0.837	18.720
IS2L	0.70753	2.056	0.832	18.877
Carbonates				
MT1L	0.71003	1.976	0.806	19.500
VS1L	0.71363	2.092	0.848	18.480
VS2L	0.71276	2.085	0.842	18.629
Permian volcanics				
PK1L	0.71909	2.073	0.834	18.811
PK2L	0.71935	2.074	0.836	18.762
PK3L	0.71763	2.100	0.854	18.345
Gneisses, phyllites				
BA1L	0.72310	2.103	0.850	18.453
JU1L	0.72186	2.093	0.854	18.337
JU2L	0.72087	2.100	0.858	18.237
KA1L	0.72064	2.095	0.853	18.345
KA2L	0.72099	2.092	0.850	18.427
VE1L	0.72013	2.100	0.850	18.467
VE2L	0.72042	2.100	0.849	18.474
VE3L	0.72031	2.097	0.848	18.507
VP1L	0.72379	2.109	0.858	18.266
VP2L	0.72345	2.109	0.858	18.265

7. For each sample, plot the $^{87}Sr/^{86}Sr$ versus $^{206}Pb/^{204}Pb$ ratios on Figure 2. Use different symbols (or colors) for the different types of samples.

8. Draw fields showing the range of isotopic ratios for each geologic area.

9. Compare the isotopic ratios measured for the Ice Man to those of the different geologic areas.

10. Based on the stable and radiogenic isotopic data, in which area did the Ice Man spend most of his life? Explain?

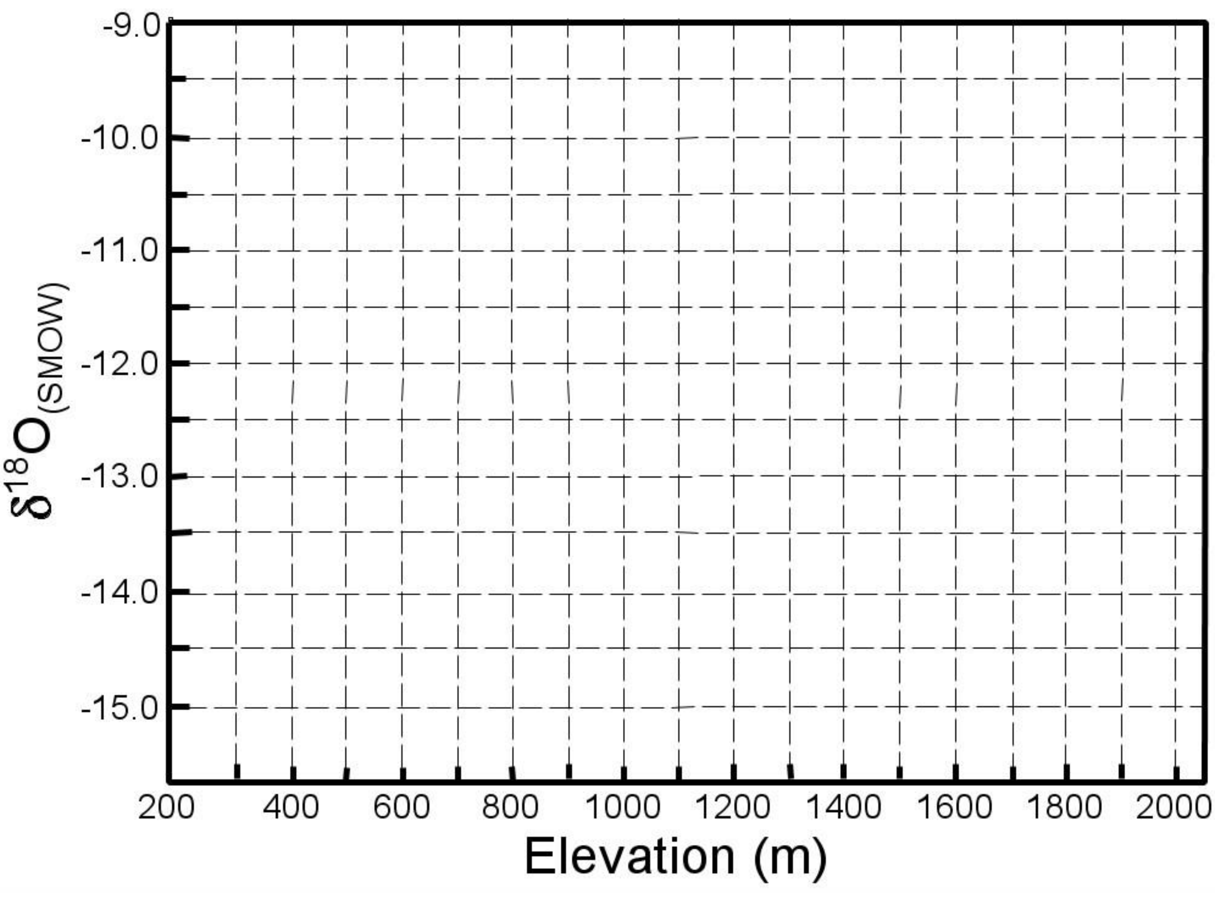


Figure 1. Graph for plotting stable isotope data.

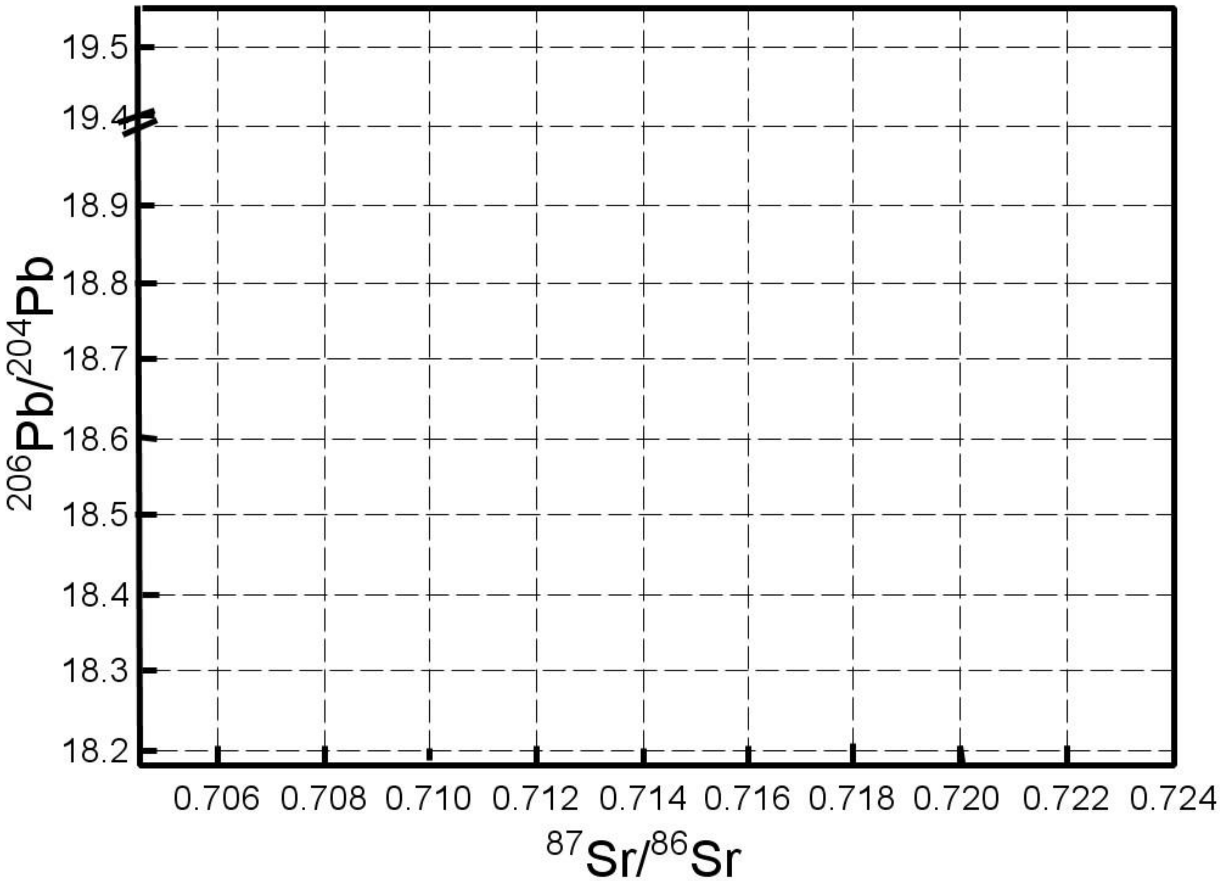
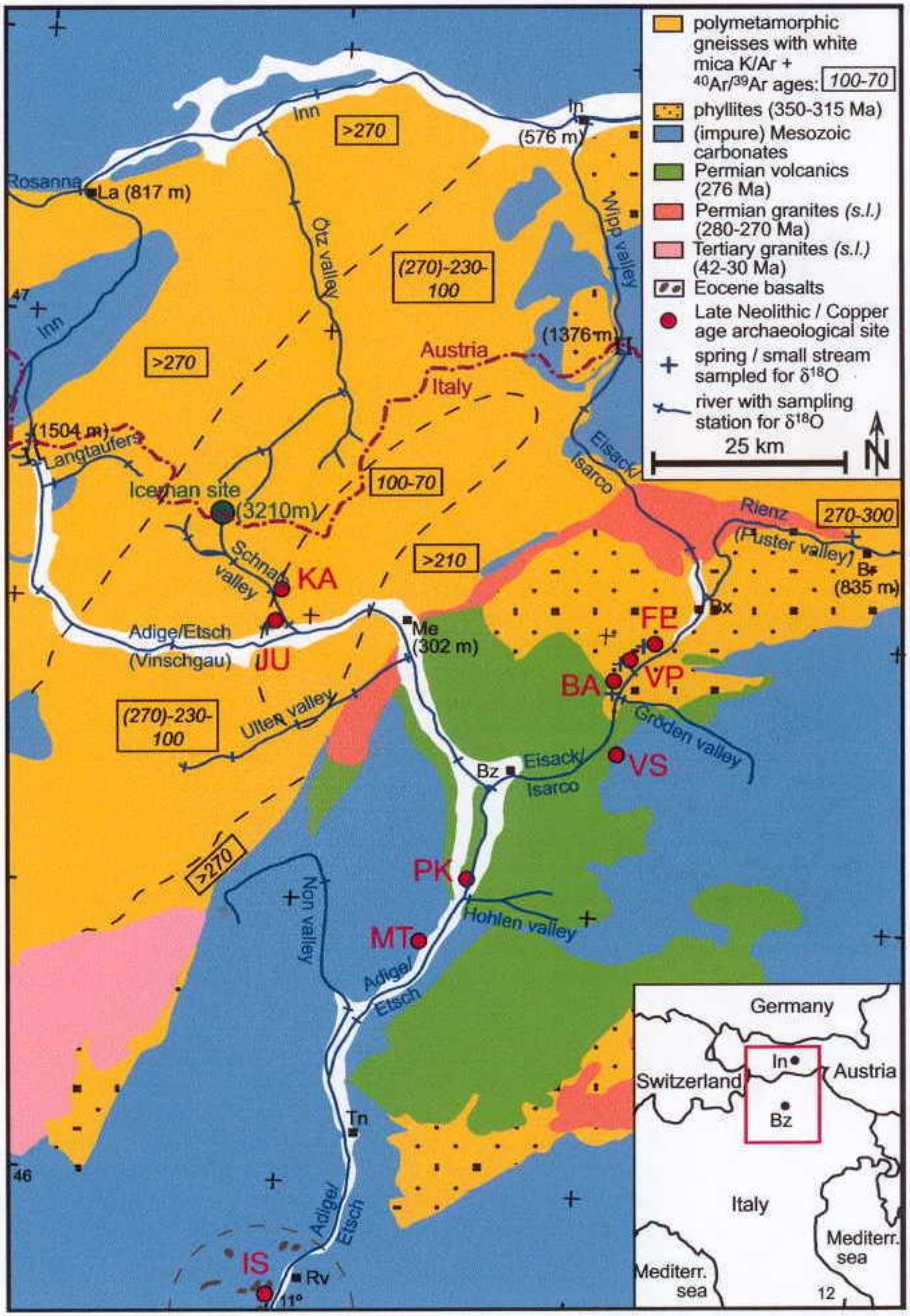


Figure 2. Graph for plotting radiogenic isotope data



polymetamorphic gneisses with white mica K/Ar + 40Ar/39Ar ages: 100-70
phyllites (350-315 Ma)
(impure) Mesozoic carbonates
Permian volcanics (276 Ma)
Permian granites (s.l.) (280-270 Ma)
Tertiary granites (s.l.) (42-30 Ma)
Eocene basalts
Late Neolithic / Copper age archaeological site
spring / small stream sampled for δ18O
river with sampling station for δ18O
25 km
N
Inn
>270
In
(576 m)
Rosanna
La (817 m)
Ötz valley
(270)-230-100
Wipp valley
47
(1376 m)
Austria
Italy
(1504 m)
Langtaufers
Iceman site
(3210m)
100-70
Eisack/Isarco
Rienz
(Puster valley)
270-300
Br
(835 m)
Schnals valley
KA
>210
Bx
FE
Adige/Etsch
(Vinschgau)
JU
Me
(302 m)
VP
BA
Ulten valley
Gröden valley
VS
Bz
Eisack/Isarco
>270
PK
Non valley
Hohlen valley
MT
Adige/Etsch
Germany
In
Austria
Switzerland
Bz
Italy
Mediterr. sea
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46
IS
Rv
11°
12