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You should know something if you want to learn something new – a story of stable isotopes

Seminar of the Institute of Physics
Jan Kochanowski University
26 April 2023

Stable isotopes – definition

- Atoms containing the same number of protons but a different number of neutrons in their nuclei
- The term "stable" is relative, depending on the detection limits of radioactive decay times. A stable isotope is defined as an isotope for which no radioactive decay has been experimentally detected
- The results of stable isotope measurements can be given as δ values or as isotope ratios

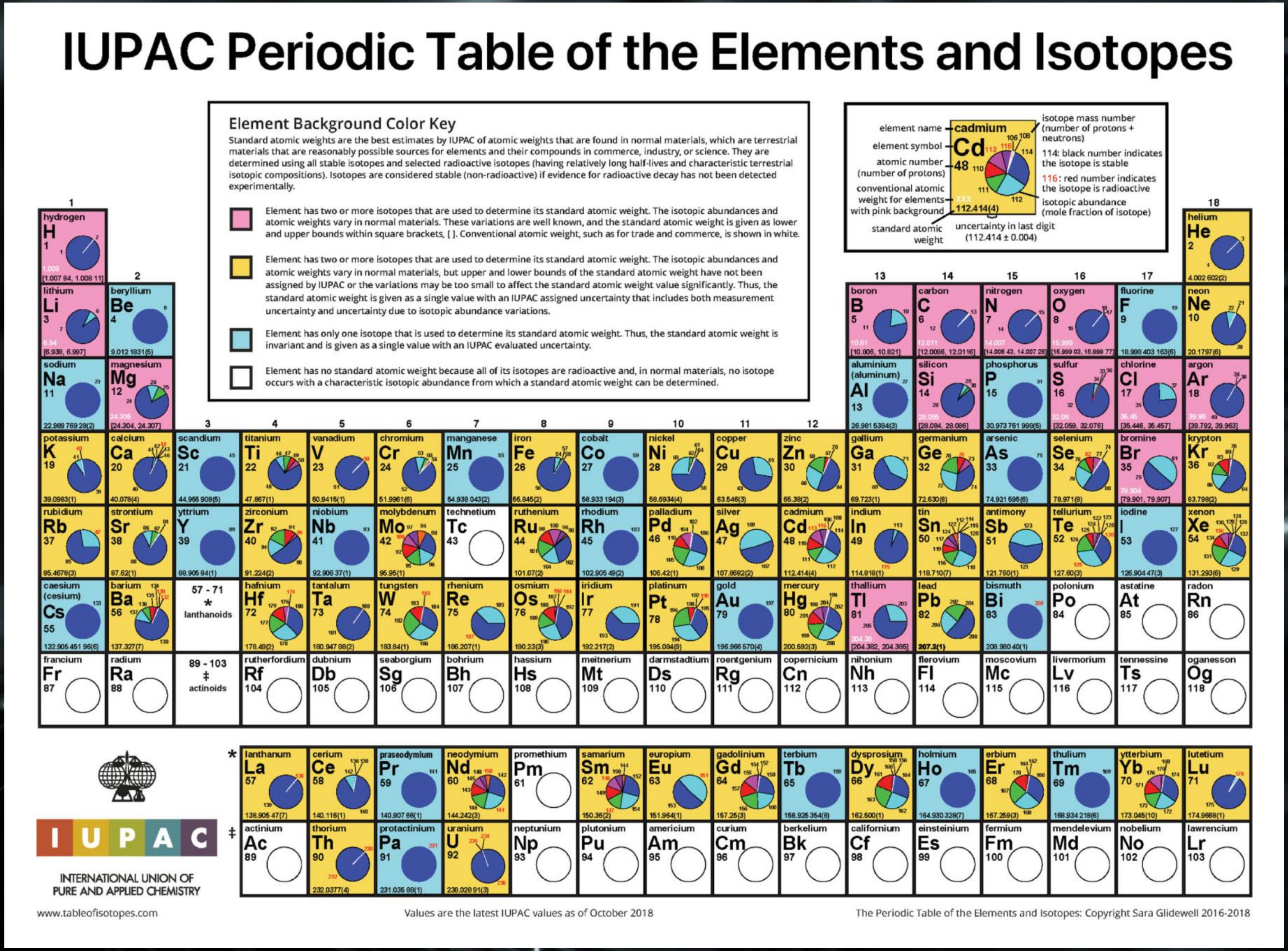
$$\delta_{(‰\ \text{or ppt})} = \frac{R_{(\text{sample})} - R_{(\text{standard})}}{R_{(\text{standard})}} \times 1000$$

R = $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{34}S/^{32}S$, $^{2}H/^{1}H$ (D/H)

Selected stable isotopes

δ value	R value	Standard
$\delta^{2}H$	$^{2}H/^{1}H$	V-SMOW
$\delta^{3}He$	$^{3}He/^{4}He$	Atmospheric He
$\delta^{6}Li$	$^{6}Li/^{7}Li$	L-SVEC
$\delta^{11}B$	$^{11}B/^{10}B$	NBS 951
$\delta^{13}C$	$^{13}C/^{12}C$	V-PDB
$\delta^{15}N$	$^{15}N/^{14}N$	Atmospheric N_2
$\delta^{18}O$	$^{18}O/^{16}O$	V-SMOV
$\delta^{34}S$	$^{34}S/^{32}S$	CDT
$\delta^{37}Cl$	$^{37}Cl/^{35}Cl$	SMOC

V-SMOW – Standard Mean Ocean Water (artificially prepared in the International Atomic Energy Agency in Vienna)
SMOC – Standard Mean Ocean Chloride
V-PDB – Pee Dee Belemnite (artificially prepared in the International Atomic Energy Agency in Vienna)
V-CDT – Canyon Diablo Troilite (artificially prepared in the International Atomic Energy Agency in Vienna)



Number of stable isotopes

Number of elements in the periodic table

118

Number of stable isotopes

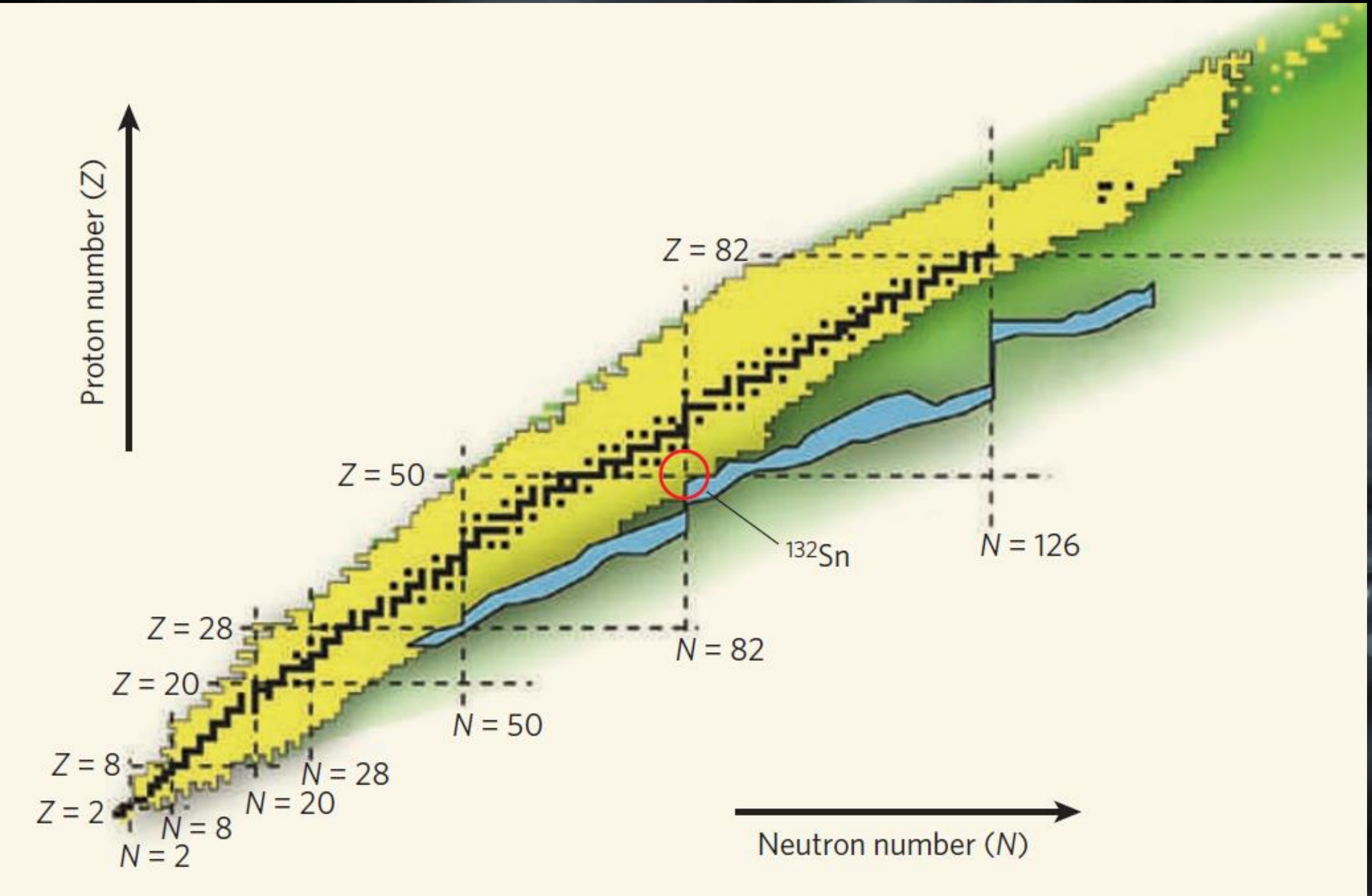
~300

Number of radioisotopes

~3000 (~3000-6000 unknown radionuclides)

N. E. Holden *Pure Appl. Chem.* 2018, 90, 1833–2092

Stability of nuclei



Nuclides of even atomic numbers are more abundant (>3) than those with odd numbers (1-2), except for He, Be and C

The doubly magic stable isotopes:

^{4}He: 2 protons + 2 neutrons

^{16}O: 8 protons + 8 neutrons

^{40}Ca: 20 protons + 20 neutrons

^{48}Ca: 20 protons + 28 neutrons

^{208}Pb: 82 protons + 126 neutrons

The number of protons (*Z*) against the number of neutrons (*N*) for stable isotopes (black), radioactive isotopes that have been produced (yellow), radioactive isotopes that may exist but have not yet been observed (green), and isotopes that are thought to be produced in a succession of nucleosynthesis reactions called the r-process (blue)

Cottle, P. (2010). Doubly magic tin. *Nature*, *465*(7297), 430-431.

Fractionation process

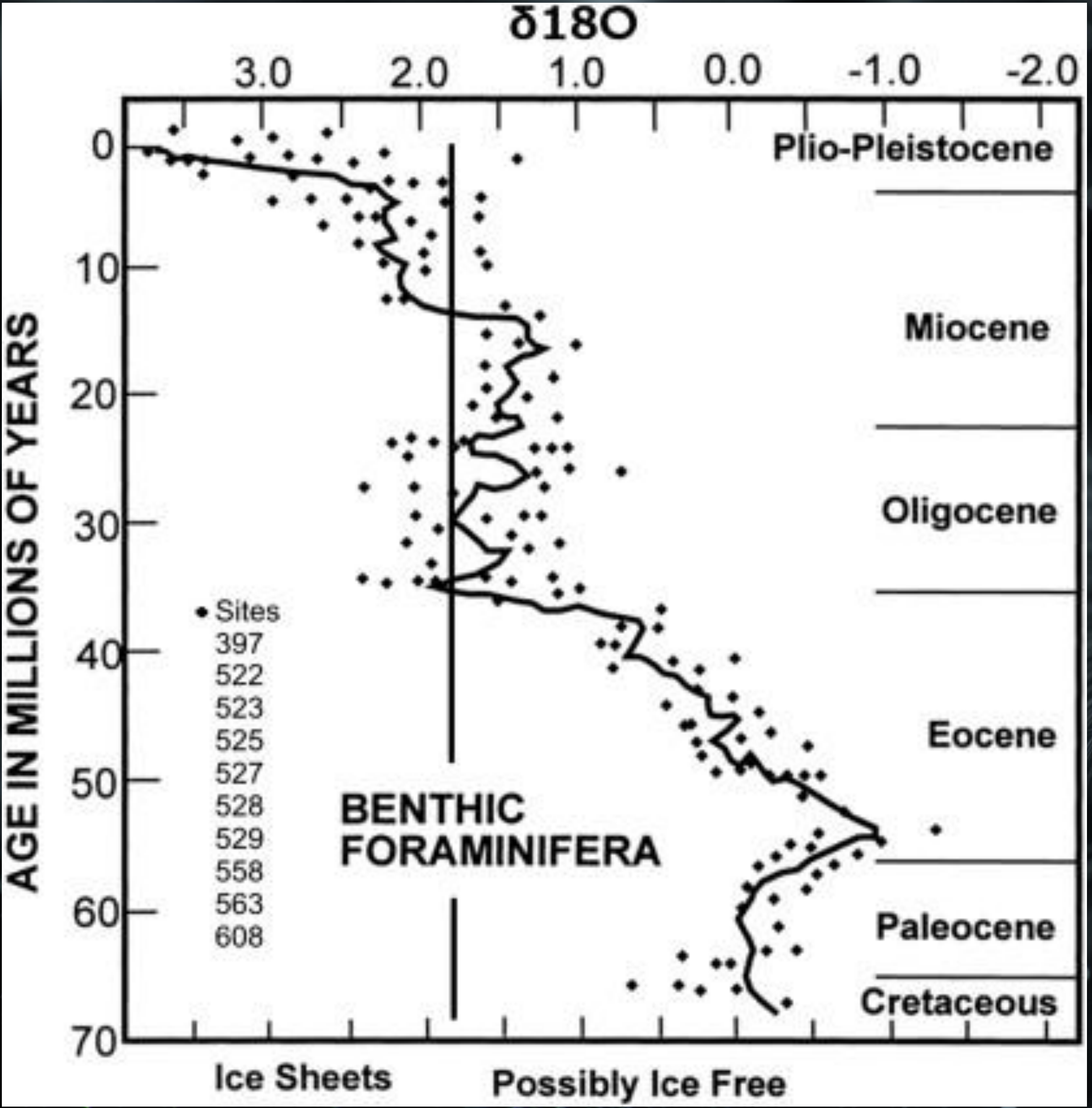
Isotope fractionation is the partitioning of isotopes between two substances /two phases of the same substance with different isotope ratios

This process occurs as:

1. Isotope exchange reactions (equilibrium isotope distribution) e.g. evaporation-condensation processes
2. Kinetic processes, which depend primarily on differences in reaction rates of isotopic molecules (incomplete and unidirectional processes like evaporation, dissociation reactions, biologically mediated reactions, and diffusion)

Application of stable isotopes in geology

- Thanks to the study of the isotopic composition of rocks, it is possible to determine their origin (genesis)
- The isotopes He, Hf, Ne, Pb and O are used to study the source of magma in the Earth's mantle
- Isotopic composition of H, C, O, S can be helpful in reconstructing the crystallization of minerals occurring in paragenesis and their crystallization temperatures
- Reconstruction of paleotemperatures – during glacials the values of $\delta^{18}O$ are lower than during periods with higher temperature (e.g. interglacials)
- Studies $\delta^{11}B$ in marine carbonates were used to reconstruct the pH of sedimentary basins, as the fractionation of $^{11}B/^{10}B$ depends on pH



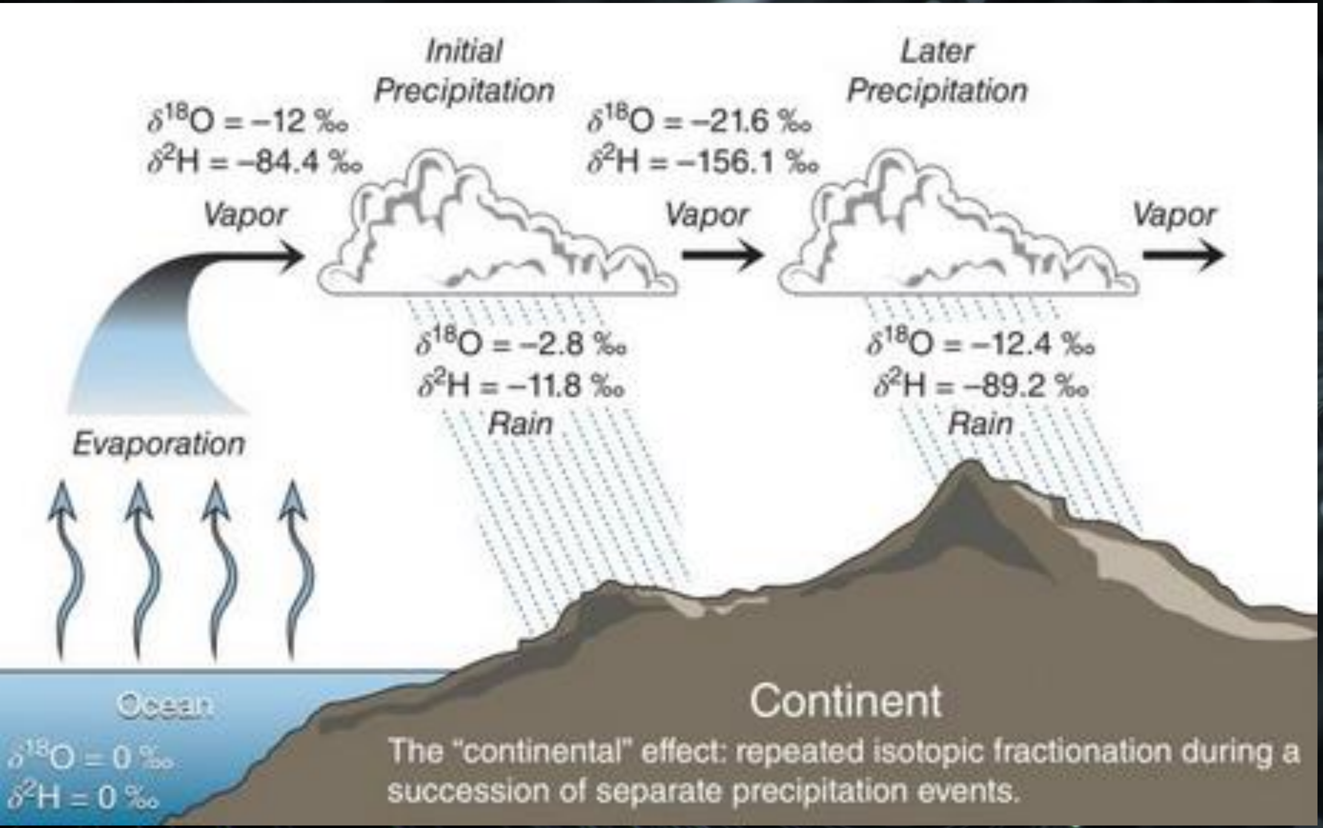
Trends in the Cenozoic oxygen isotopic record

Ishman, S. E., Karlsen, A. W., Cronin, T. M., Cronin, T. M., Wagner, R. S., & Slattery, M. (1999). Chesapeake Bay benthic foraminifera. *Microfossils from Chesapeake Bay sediments: illustrations and species database*, *10*(25), 99-45.

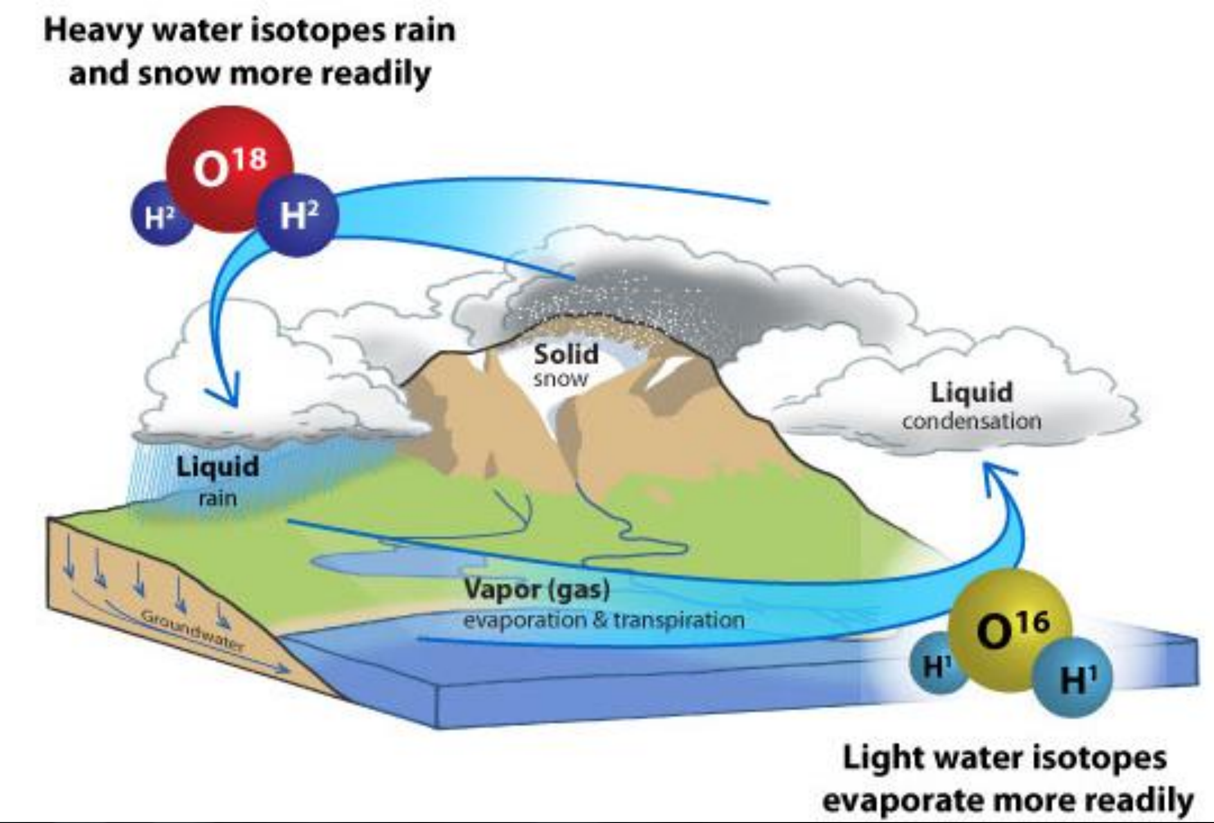
During glacial interval ^{18}O is enriched in ocean waters and depleted in glacial ice. The foraminifera calcifying their test in isotopic equilibrium with sea water during glacial times are thus enriched in ^{18}O as compared to those calcifying during interglacial intervals

Tiwari, M., Singh, A. K., & Sinha, D. K. (2015). Stable isotopes: Tools for understanding past climatic conditions and their applications in chemostratigraphy. In *Chemostratigraphy* (pp. 65-92). Elsevier.

Changing hydrogen and oxygen isotope composition of meteoric water



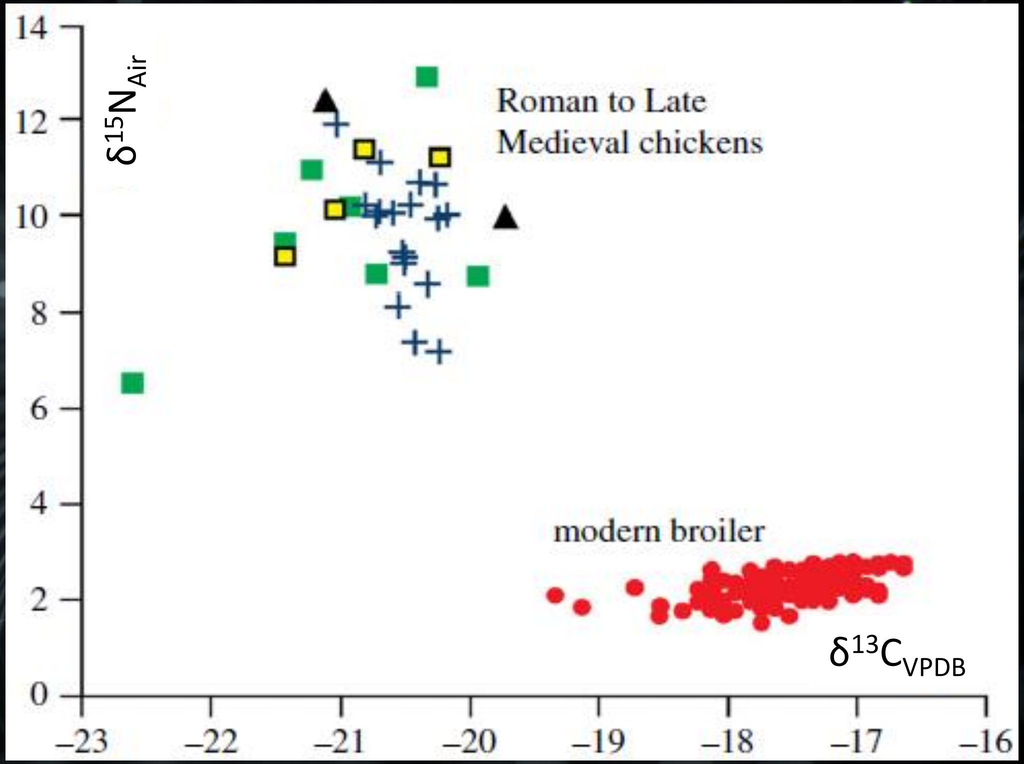
Meier-Augenstein, W. and *Kemp*, H. F. *2012*. Stable Isotope Analysis: General Principles and Limitations. Wiley Encyclopedia of Forensic Science



https://www.usgs.gov/media/images/water-cycle-and-water-isotopes

The broiler chicken as a biostratigraphic marker of the Anthropocene

"Modern broiler chickens are morphologically, genetically and isotopically distinct from domestic chickens prior to the mid-twentieth century. The global range of modern broilers and biomass dominance over all other bird species is a product of human intervention"



Carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope values of chicken bone collagen

Bennett, C. E., Thomas, R., Williams, M., Zalasiewicz, J., Edgeworth, M., Miller, H., ... & Marume, U. (2018). The broiler chicken as a signal of a human reconfigured biosphere. *Royal Society Open Science*, *5*(12), 180325.

Stable isotopes in hydrology

$\delta^{13}C$, $\delta^{2}H$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$, $\delta^{34}S$, Pb	Origin of groundwater
$\delta^{34}S$, $\delta^{11}B$, $^{87}Sr/^{86}Sr$, $\delta^{37}Cl$	Origin of salinity
$\delta^{2}H$, $\delta^{18}O$	Source of groundwater

Le Bot B., Oulhote Y, Deguen S., Glorennec P. Using and interpreting isotope data for source identification. *Trends in Analytical Chemistry* 30(2), 2011.

Stable isotopes in ecology

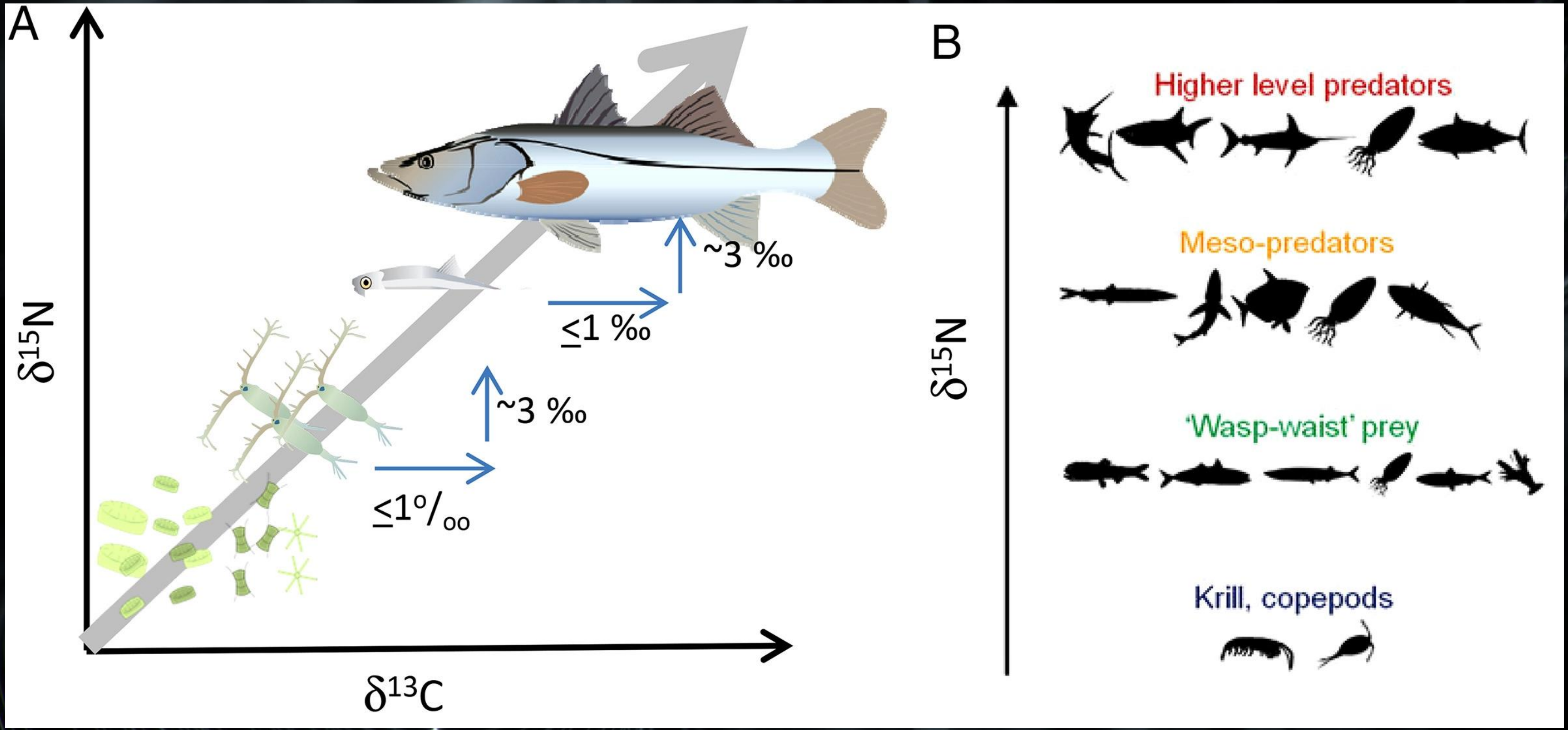
- Stable isotopes H, C, N and O are used to study trophic relationships in ecosystems, mainly marine ecosystems
- The isotopic ratios of carbon in the diet of herbivores are used to study what plants animals feed on
- Nitrogen isotopes are used to study the trophic level of animals
- Isotopes of hydrogen and oxygen are used to study the migration routes and origin of animals (the isotopic composition of hydrogen and oxygen tissues depends on the isotopic composition of the environment during their formation)

Stable isotopes in ecology

$\delta^{13}C$, $\delta^{15}N$	Fish migrations
$\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$	Bird migrations
$\delta^{13}C$, $\delta^{2}H$	Origin of pest insects
$\delta^{13}C$, $\delta^{15}N$	Position in a food chain

Le Bot B., Oulhote Y, Deguen S., Glorennec P. Using and interpreting isotope data for source identification. *Trends in Analytical Chemistry* 30(2), 2011.

Changes in stable nitrogen isotope at trophic levels of the ecosystem



Food web relationships based on $\delta^{13}C$ and $\delta^{15}N$

Glibert, P. M., Middelburg, J. J., McClelland, J. W., & Jake Vander Zanden, M. (2019). Stable isotope tracers: Enriching our perspectives and questions on sources, fates, rates, and pathways of major elements in aquatic systems. *Limnology and Oceanography*, *64*(3), 950-981.

Stable isotope research in forensic sciences: the authenticity of food products

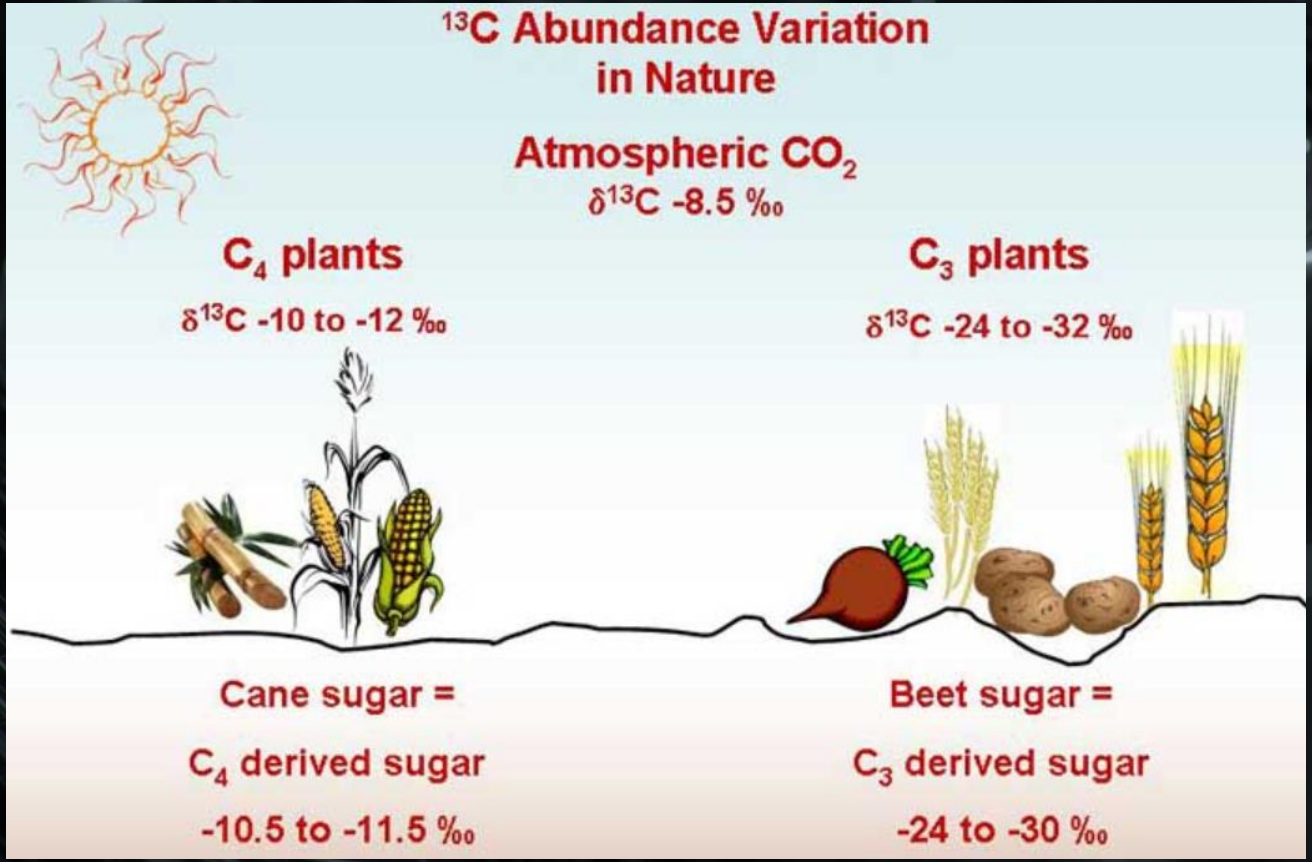
- For the first time, stable isotopes were used to establish the authenticity of wine in the European Union (origin and year of production)
- Currently, this method is used to check the authenticity of other products: milk, honey, juices, spices
- Carbon stable isotopes allow to determine the origin of plant products (isotope composition reflects the type of photosynthesis)

Stable isotope research in forensic sciences: the origin of food products

- Stable oxygen isotopes in food containing water indicate the place of origin (isotopic composition of food reflects the isotopic composition of local rainwater)
- Nitrogen and sulfur isotopes can be used to determine the place of origin of the product ($\delta^{34}S$ values indicate distance from the sea, $\delta^{15}N$ inform about cultivation practices, which vary from country to country)
- Stable strontium isotopes can be used as an indicator of place of origin because they reflect the isotopic composition of the bedrock

$\delta^{13}C$ values in C3 and C4 plants

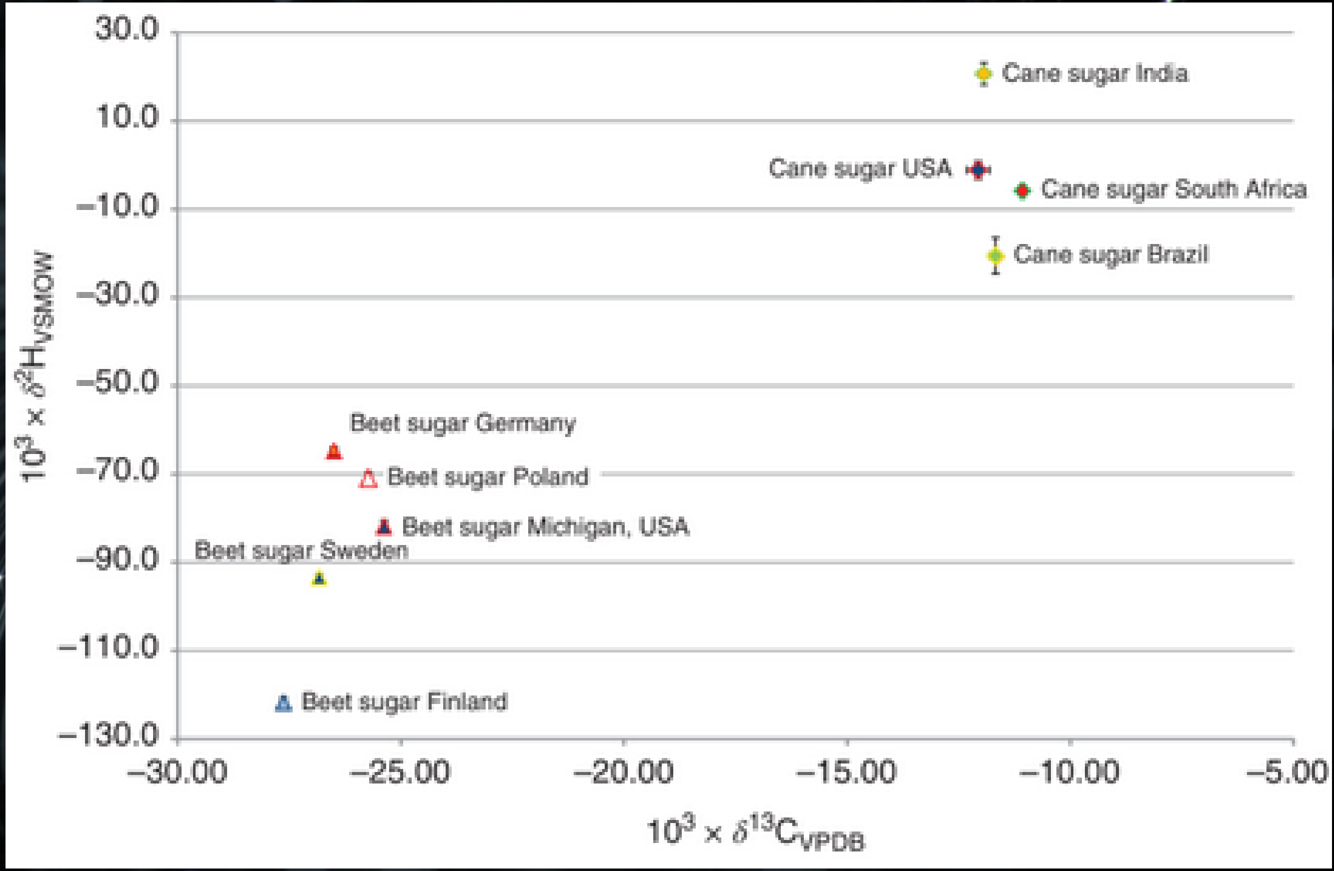
C3 plants – the first product of CO_2 assimilation is 3-phosphoglyceric acid (three-carbon compound)
C4 plants – the first stable product of CO_2 assimilation is a compound with four carbon atoms – oxaloacetate (e.g. corn, sugar cane, millet)



https://www.hutton.ac.uk/research/departments/environmental-and-biochemical-sciences/isotope-applications

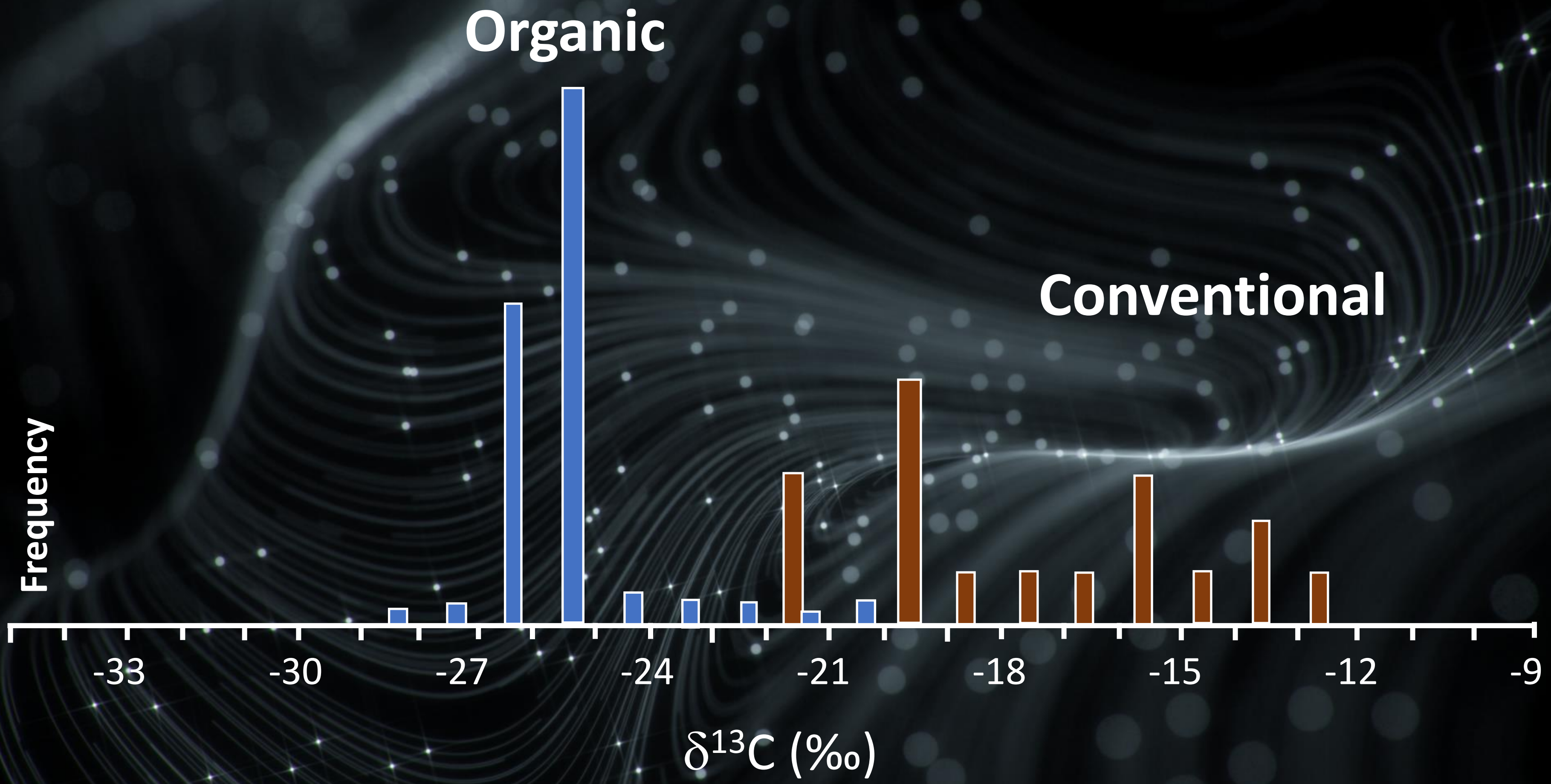
Carbon and hydrogen isotopes in sugar from different regions of the world

SUGAR TYPE	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{2}H_{VSMOW}$ (‰)
Beet sugar, Poland	-25.42	-71.0
Beet sugar, Sweden	-26.84	-93.4
Cane sugar, Brazil	-11.76	-21.4
Cane sugar, S Africa	-11.10	-6.7



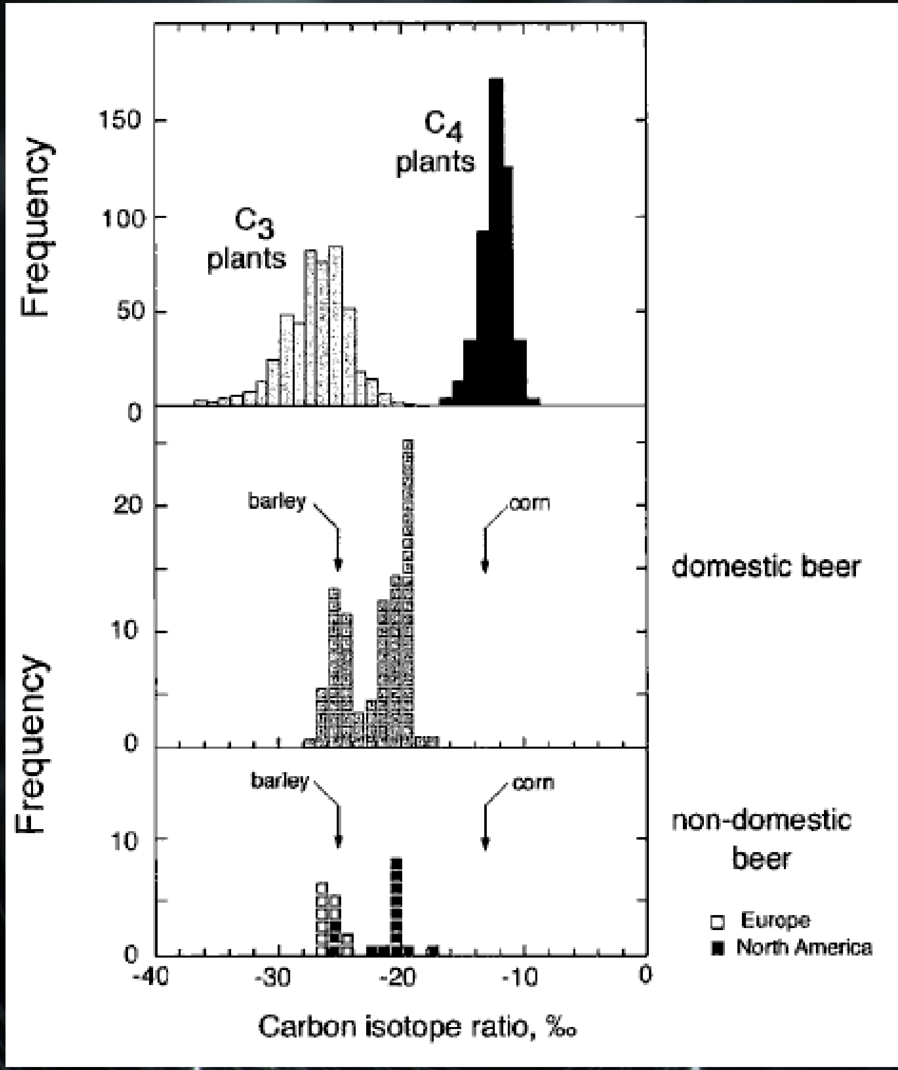
Meier-Augenstein, W. (2017). Stable isotope forensics: methods and forensic applications of stable isotope analysis. John Wiley & Sons.

δ^{13}C in conventional and organic beef



Boner M, H Förstel. 2004. Stable isotope variation as a tool to trace the authenticity of beef. *Analytical and Bioanalytical Chemistry* 378: 301-310

Beer adulteration



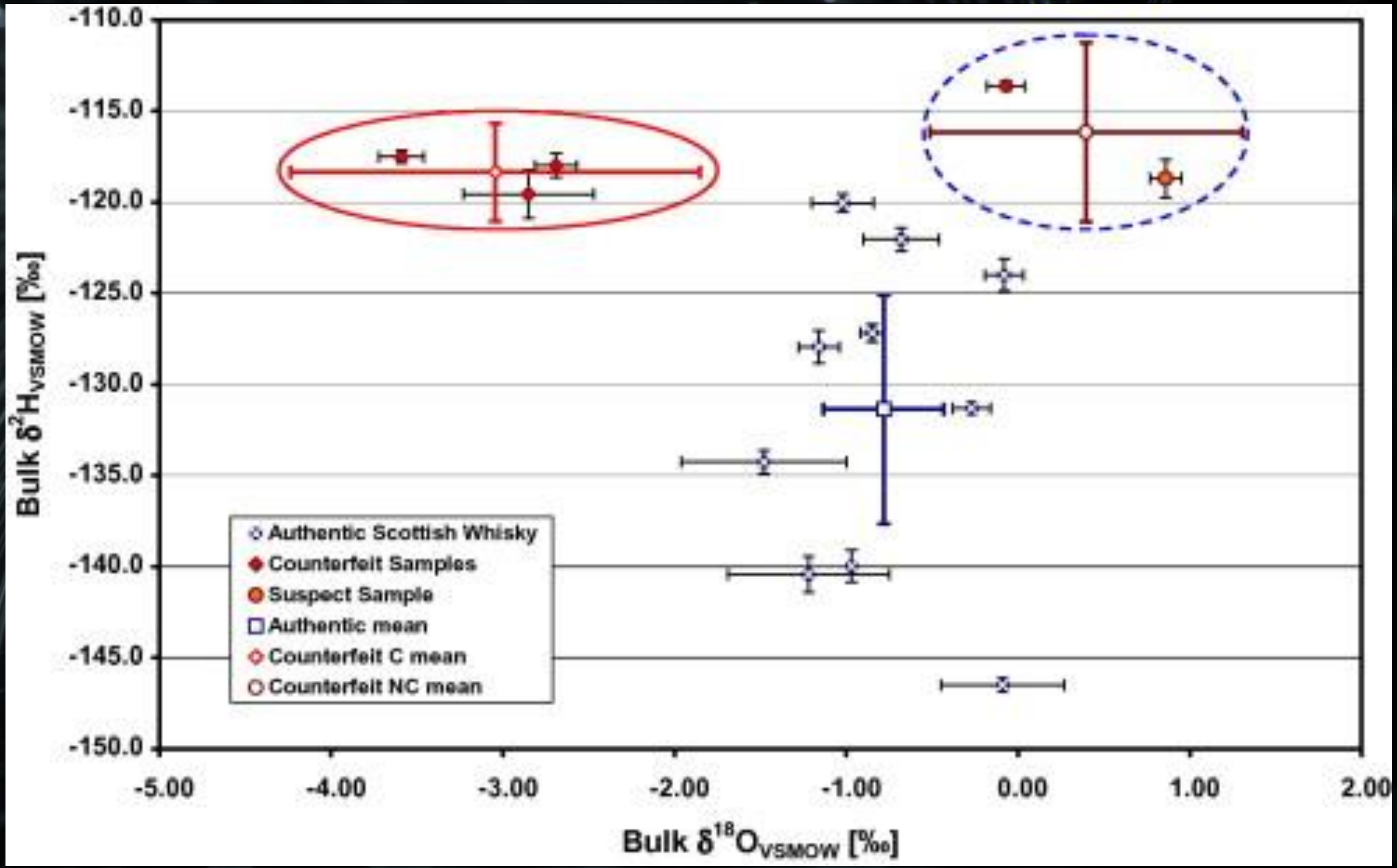
Beer = barley or wheat grain + hops + water

Barley is a C3 plant and corn is a C4 plant. Some samples of American beer have higher values of $\delta^{13}C$ (addition of 50% corn+50% barley) than European beer (addition of 100% barley)

Ehleringer J.R., Cerling T.E., West J.B., 2007. Forensic science applications of stable isotope ratio analysis. In: Blackledge RD, editor. Forensic analysis on the cutting edge: new methods for trace evidence analysis. Hoboken, NJ: John Wiley & Sons, Inc. 399–422.

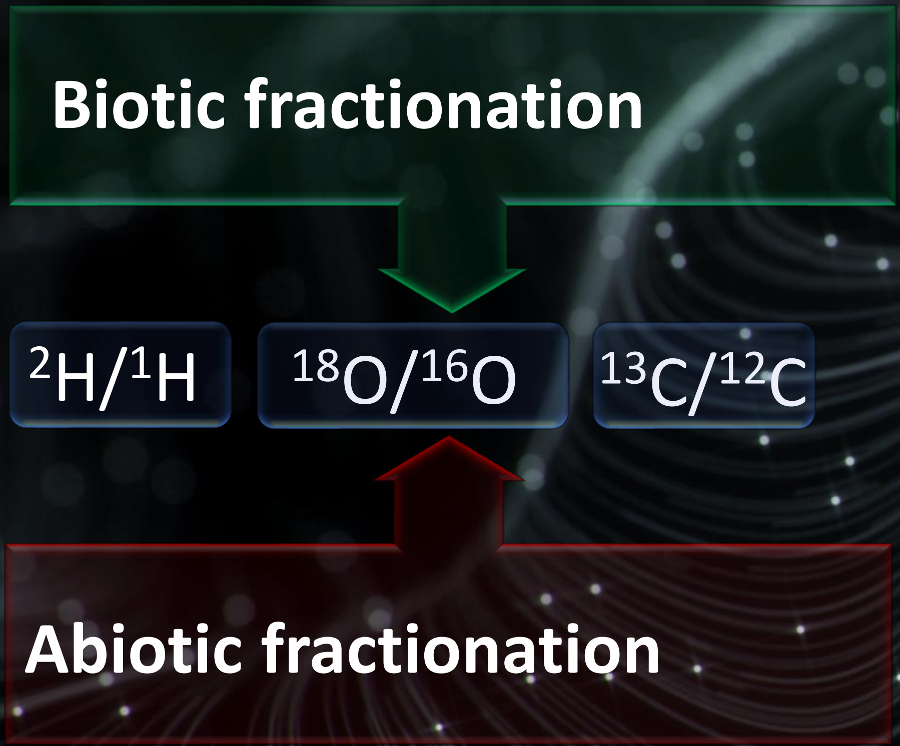
Application of ^{2}H and ^{18}O stable isotopes for detection of counterfeit scotch whisky

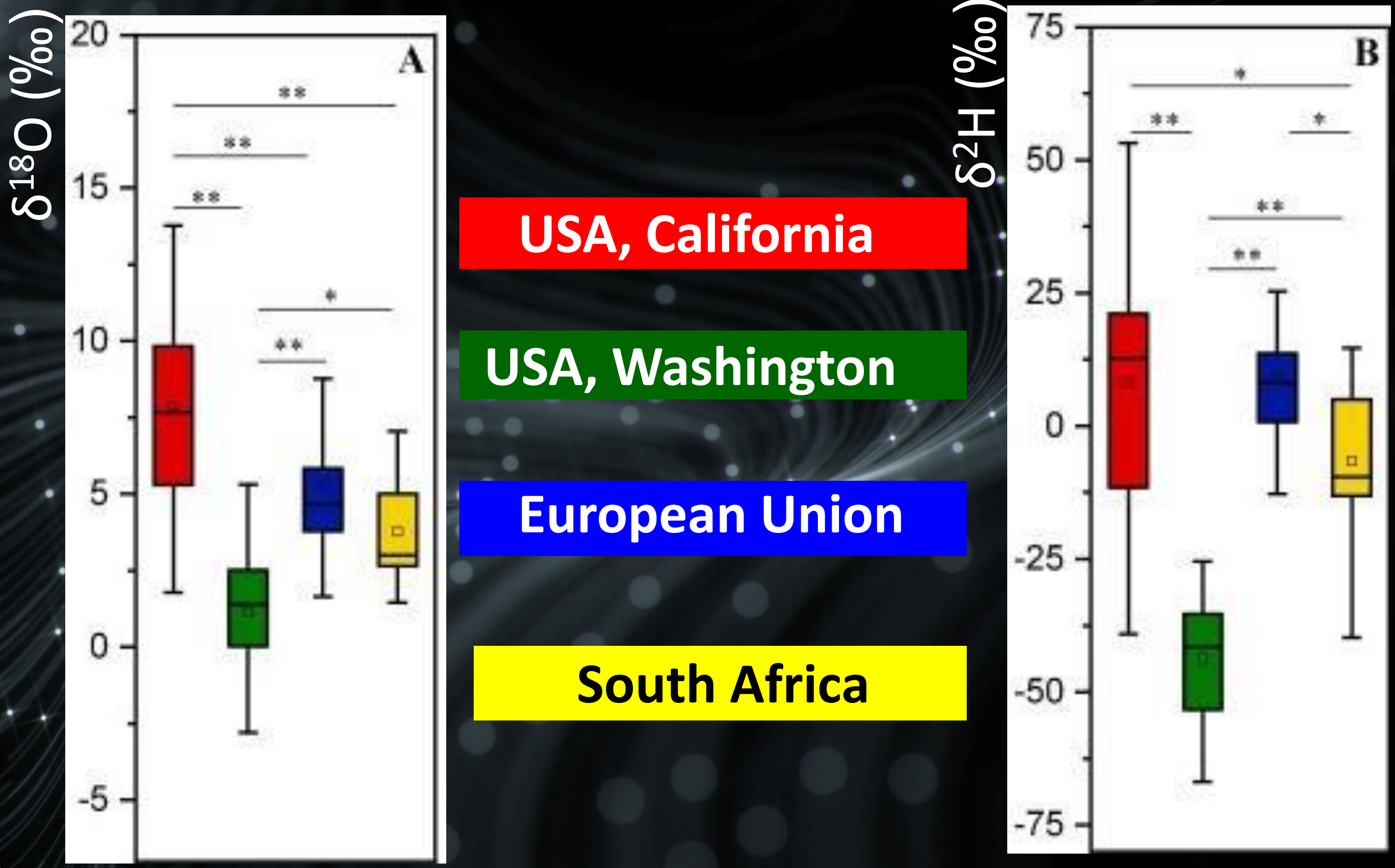
Bulk $\delta^{2}H$ and corresponding bulk $\delta^{18}O$ values from genuine whiskies, counterfeit whiskies and a whisky suspected to be counterfeit



Meier-Augenstein, W., Kemp, H. F., & Hardie, S. M. L. (2012). Detection of counterfeit scotch whisky by 2H and 18O stable isotope analysis. *Food Chemistry*, *133*(3), 1070-1074.

Wine authentication with stable isotopes





Christoph, N., Hermann, A., & Wachter, H. (2015). 25 Years authentication of wine with stable isotope analysis in the European Union–Review and outlook. In *BIO Web of Conferences* (Vol. 5, p. 02020). EDP Sciences.

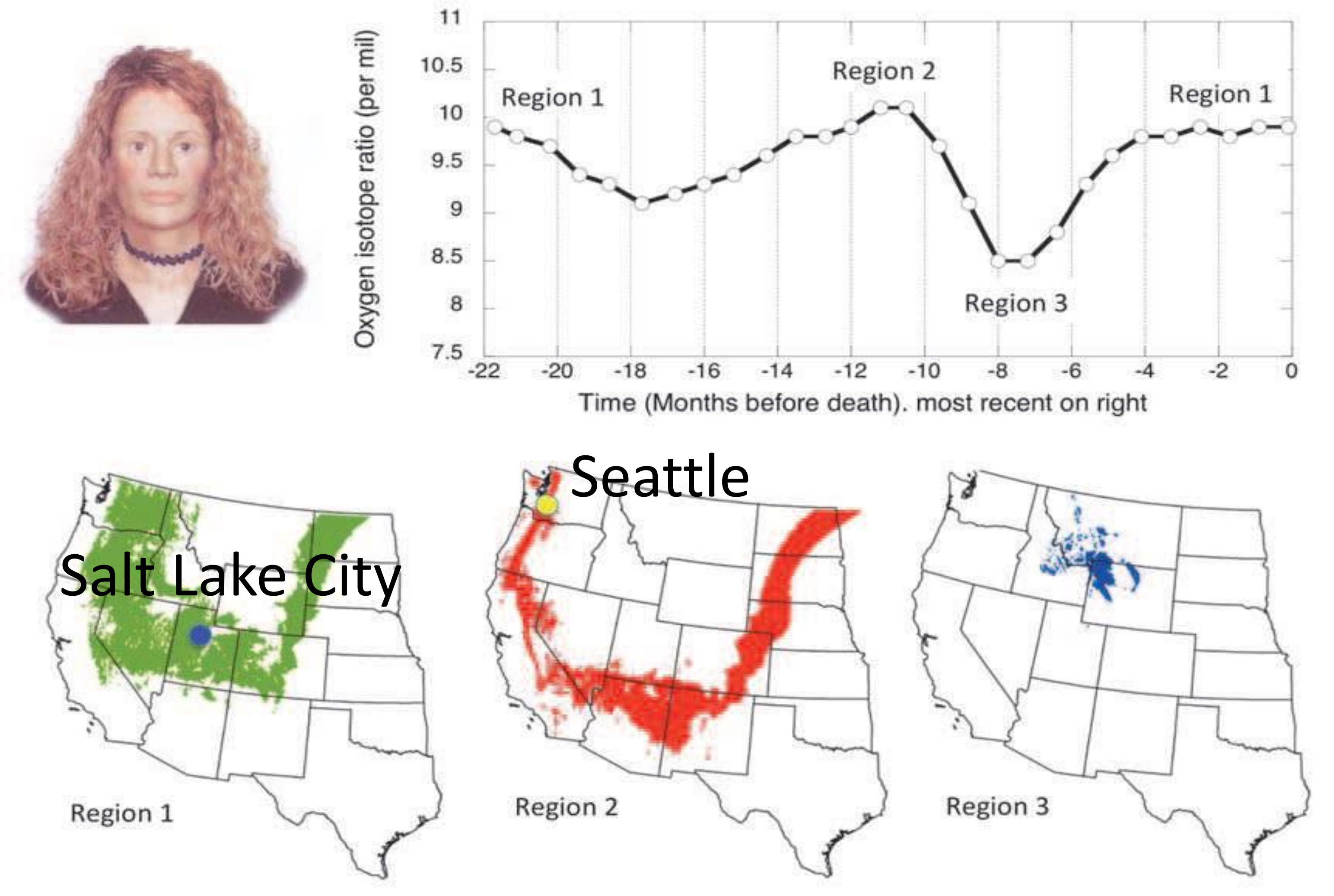
Orellana, S., Johansen, A. M., & Gazis, C. (2019). Geographic classification of US Washington State wines using elemental and water isotope composition. *Food Chemistry: X, 1*, 100007.

Isotopes in determining food authenticity

$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$	▪ Mineral water
$\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{34}S$, $^{87}Sr/^{86}Sr$, $\delta^{2}H$	▪ Milk ▪ Meat
$\delta^{13}C$, $\delta^{15}N$, $\delta^{16}O$	▪ Rice
$\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$	▪ Tea
$\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, $^{87}Sr/^{86}Sr$	▪ Orange juice

Le Bot B., Oulhote Y, Deguen S., Glorennec P. Using and interpreting isotope data for source identification. *Trends in Analytical Chemistry* 30(2), 2011.

Stable isotope research in forensic sciences: identification of unknown murder victims



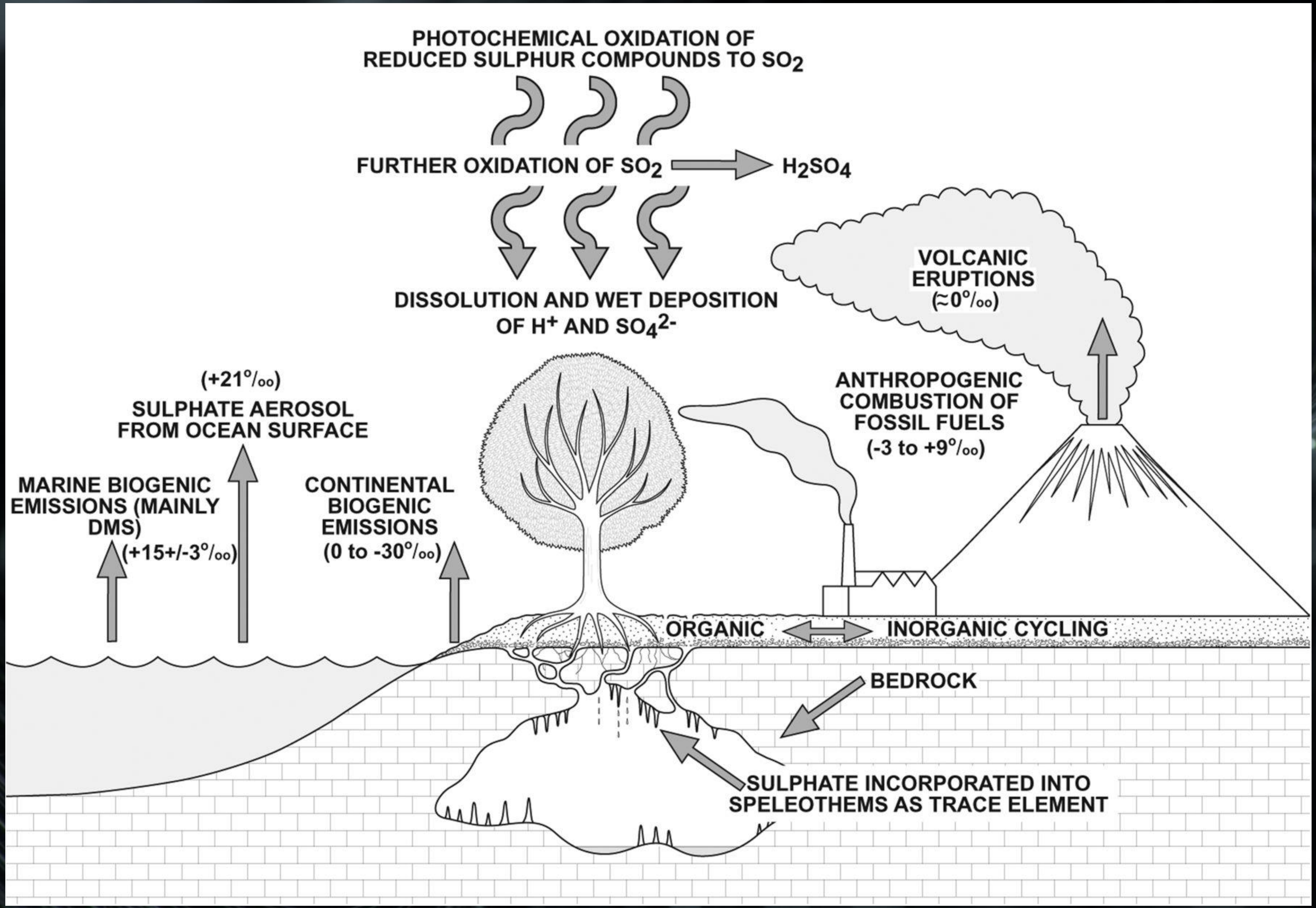
Ehleringer, J. R., Chesson, L. A., Valenzuela, L. O., Tipple, B. J., & Martinelli, L. A. (2015). Stable isotopes trace the truth: from adulterated foods to crime scenes. *Elements*, *11*(4), 259-264.

Stable isotopes in environmental studies

Lead stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb	Pollution with Pb compounds
$\delta^{15}N$, $\delta^{18}O$, $\delta^{13}C$,	Pollution with nitrates
Lead stable isotopes, $\delta^{34}S$	Coal combustion emissions
Lead stable isotopes, $^{87}Sr/^{86}Sr$	Particulate pollution
$\delta^{13}C$, $\delta^{15}N$, $\delta^{37}Cl$	Pollution with organic compounds
$\delta^{18}O$, $\delta^{34}S$	Pollution with sulfur compounds

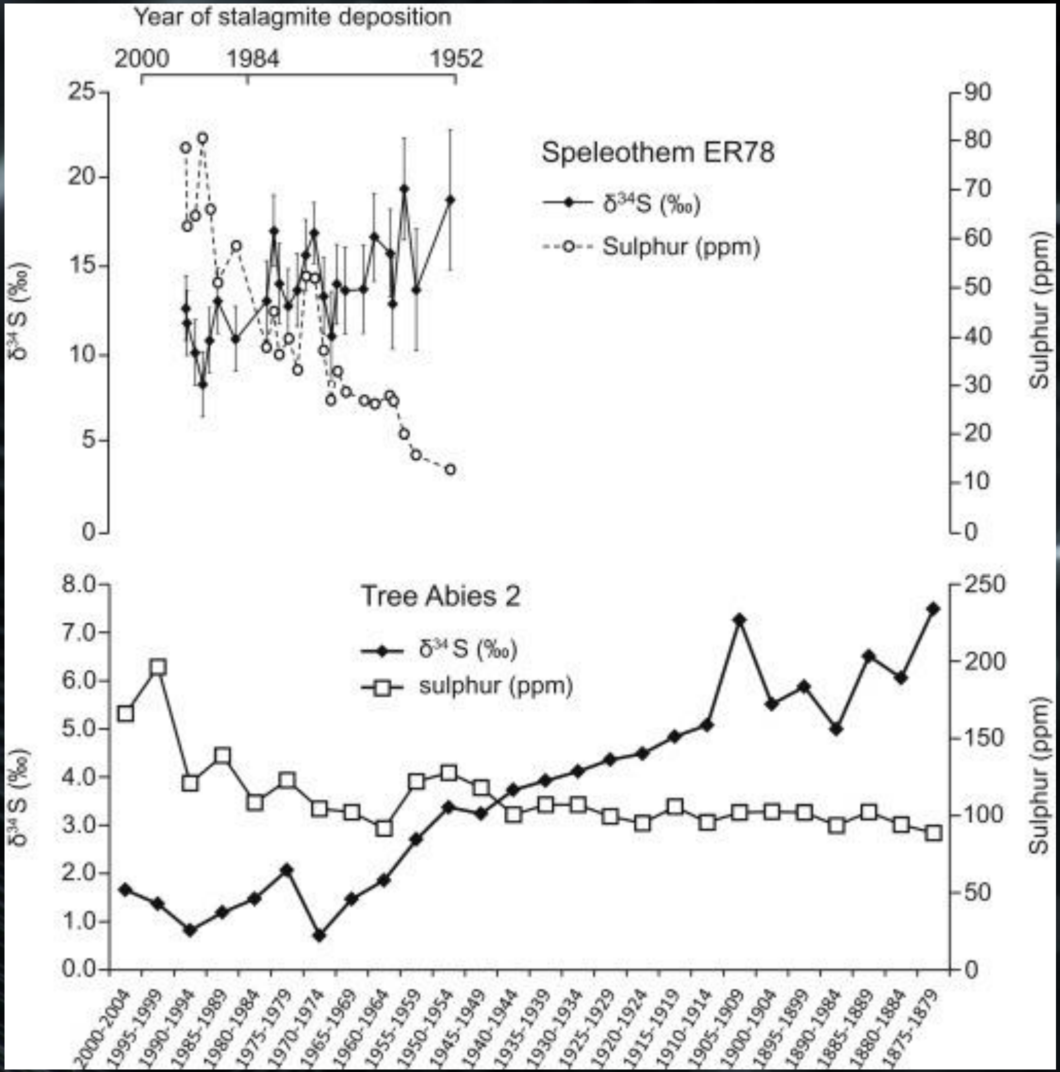
Le Bot B., Oulhote Y, Deguen S., Glorennec P. Using and interpreting isotope data for source identification. *Trends in Analytical Chemistry* 30(2), 2011.

Environmental paleoreconstruction

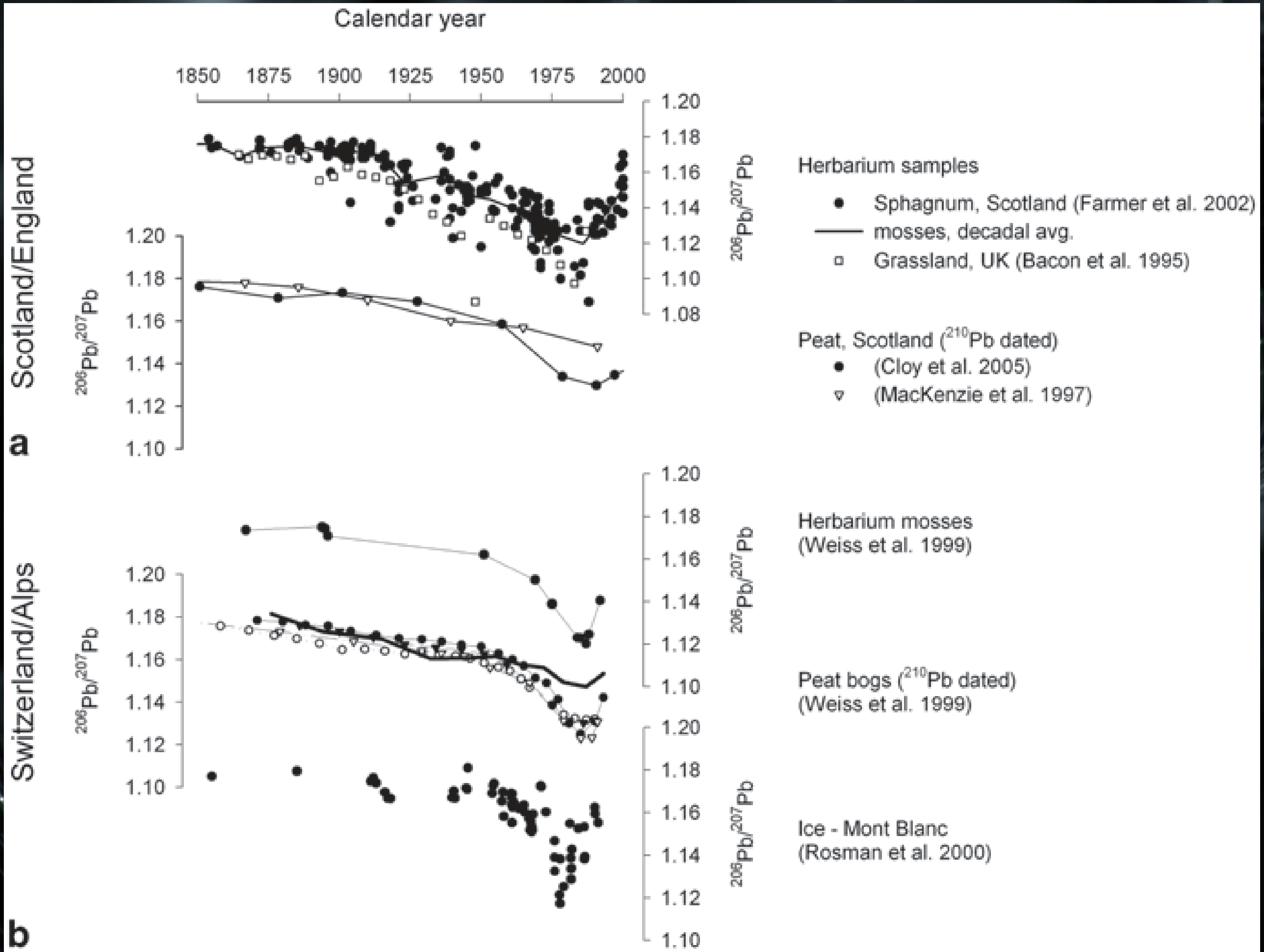


Wynn, P. M., Fairchild, I. J., Baker, A., Baldini, J. U., McDermott, F. (2008). Isotopic archives of sulphate in speleothems. *Geochimica et Cosmochimica Acta*, *72*(10), 2465-2477.

Records of sulfur loading to speleothem ER78 and tree ring archives (fir) of environmental change collected from Ernesto cave in NE Italy

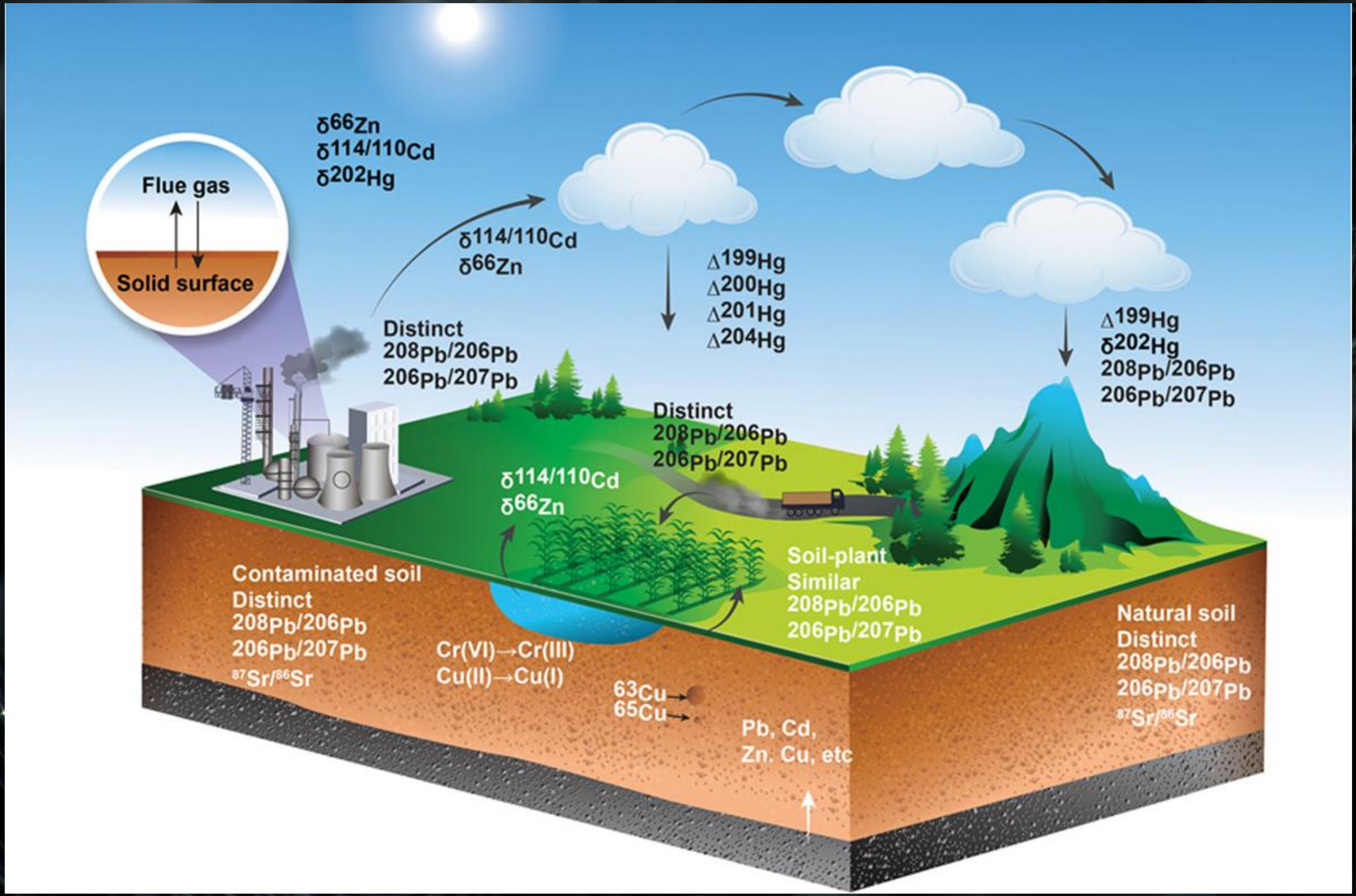


Wynn, P. M., Loader, N. J., Fairchild, I. J. (2014). Interrogating trees for isotopic archives of atmospheric sulphur deposition and comparison to speleothem records. *Environmental Pollution*, *187*, 98-105.



Hansson, S. V., Bindler, R., De Vleeschouwer, F. (2015). Using peat records as natural archives of past atmospheric metal deposition. In *Environmental Contaminants* (pp. 323-354). Springer, Dordrecht.

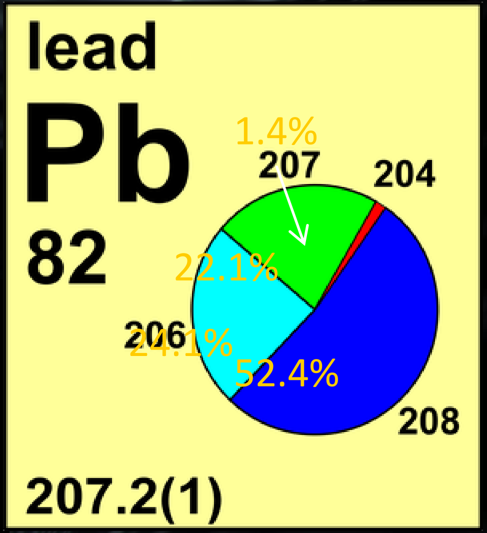
Identification of metal sources in soils



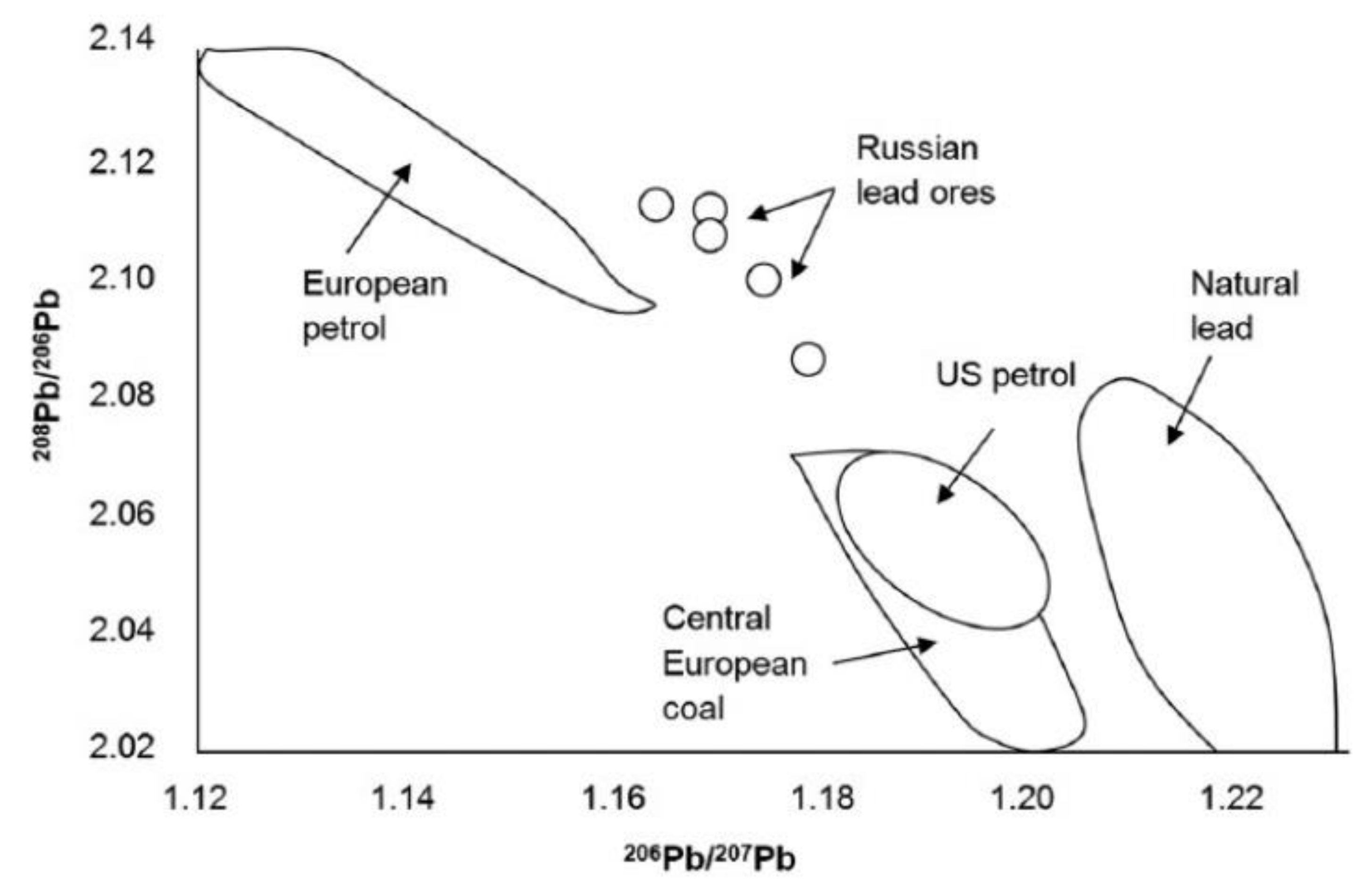
Wang, L., Jin, Y., Weiss, D. J., Schleicher, N. J., Wilcke, W., Wu, L., ... & Hou, D. (2021). Possible application of stable isotope compositions for the identification of metal sources in soil. *Journal of Hazardous Materials*, *407*, 124812.

Lead stable isotopes

- Lead stable isotope ratios are widely used for apportionment of pollution sources and for tracking pollution pathways in the environment because, as opposed to isotopes of copper and zinc, they do not undergo fractionation
- The values of $^{206}Pb/^{207}Pb$ ratio in lead emitted from anthropogenic sources are in the range of 1.15-1.19 whereas in lead from natural sources, the $^{206}Pb/^{207}Pb$ ratio is approximately 1.5
- Higher Pb concentrations in natural archives are accompanied by a decrease in $^{206}Pb/^{207}Pb$ ratio



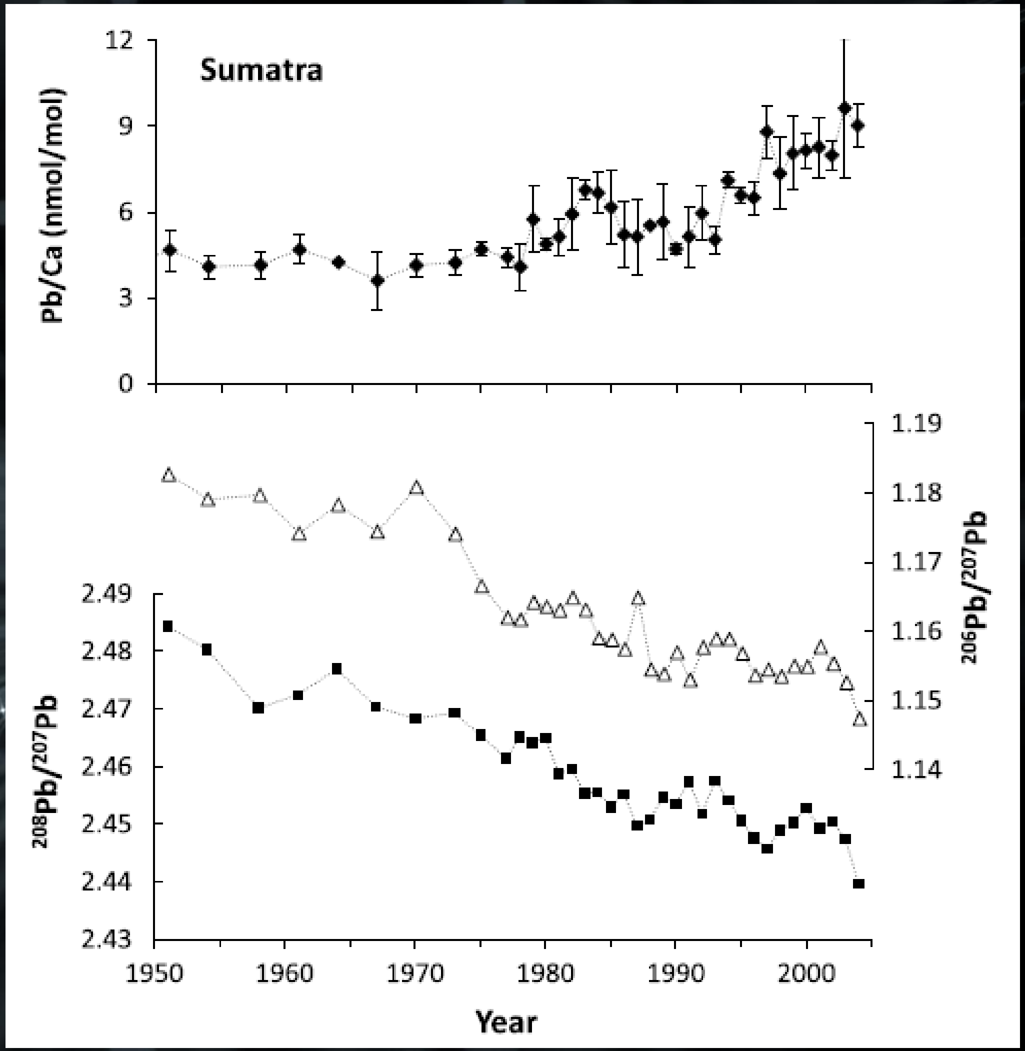
A $^{206}Pb/^{207}Pb$ versus $^{208}Pb/^{206}Pb$ plot showing the different isotopic compositions of selected lead sources



Dean, J. R., Leng, M. J., & Mackay, A. W. (2014). Is there an isotopic signature of the Anthropocene?. *The Anthropocene Review*, *1*(3), 276-287.

Pb/Ca ratios and Pb stable isotopes in corals from western Sumatra

Significant Pb contamination started in the western Sumatra region around the mid-1970s given the increasing Pb/Ca ratios and decreasing $^{206/207}Pb$ and $^{208/207}Pb$ ratios around that time

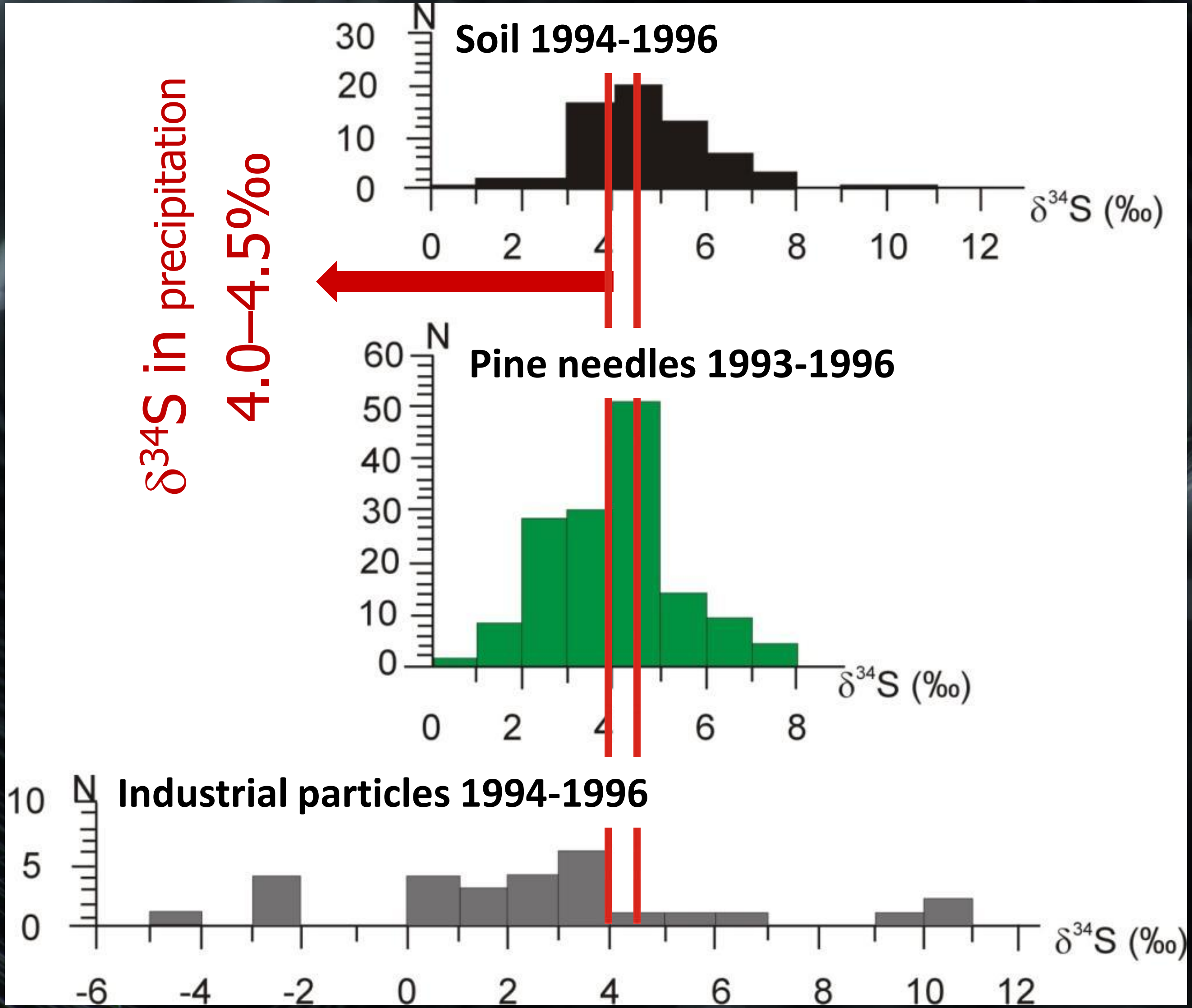


Time series of Pb/Ca (◆), $^{206/207}Pb$ (△), and $^{208/207}Pb$ (■) ratios in the western Sumatra coral

LEE, Jong-Mi, et al. Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. *Earth and Planetary Science Letters*, 2014, 398: 37-47.

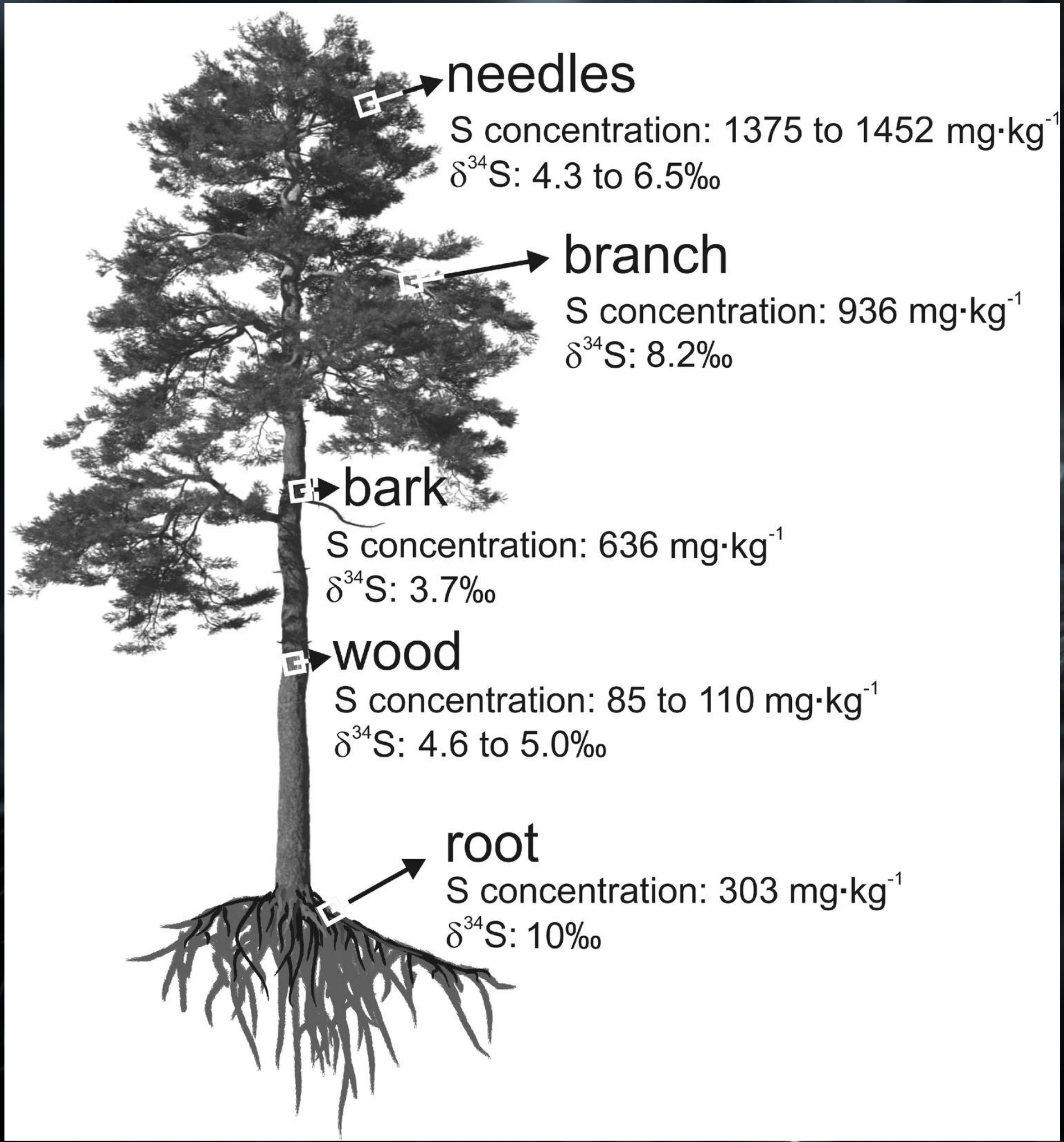
Selected stable isotope research at the Institute of Chemistry, Jan Kochanowski University in Kielce

Anthropogenic impact assessment: isotopic fingerprint



Migaszewski, Z. M., & Pasławski, P. (1996). Trace element and sulphur stable isotope ratios in soils and vegetation of the Holy Cross Mountains. *Geological Quarterly*, *40*(4), 575-594.

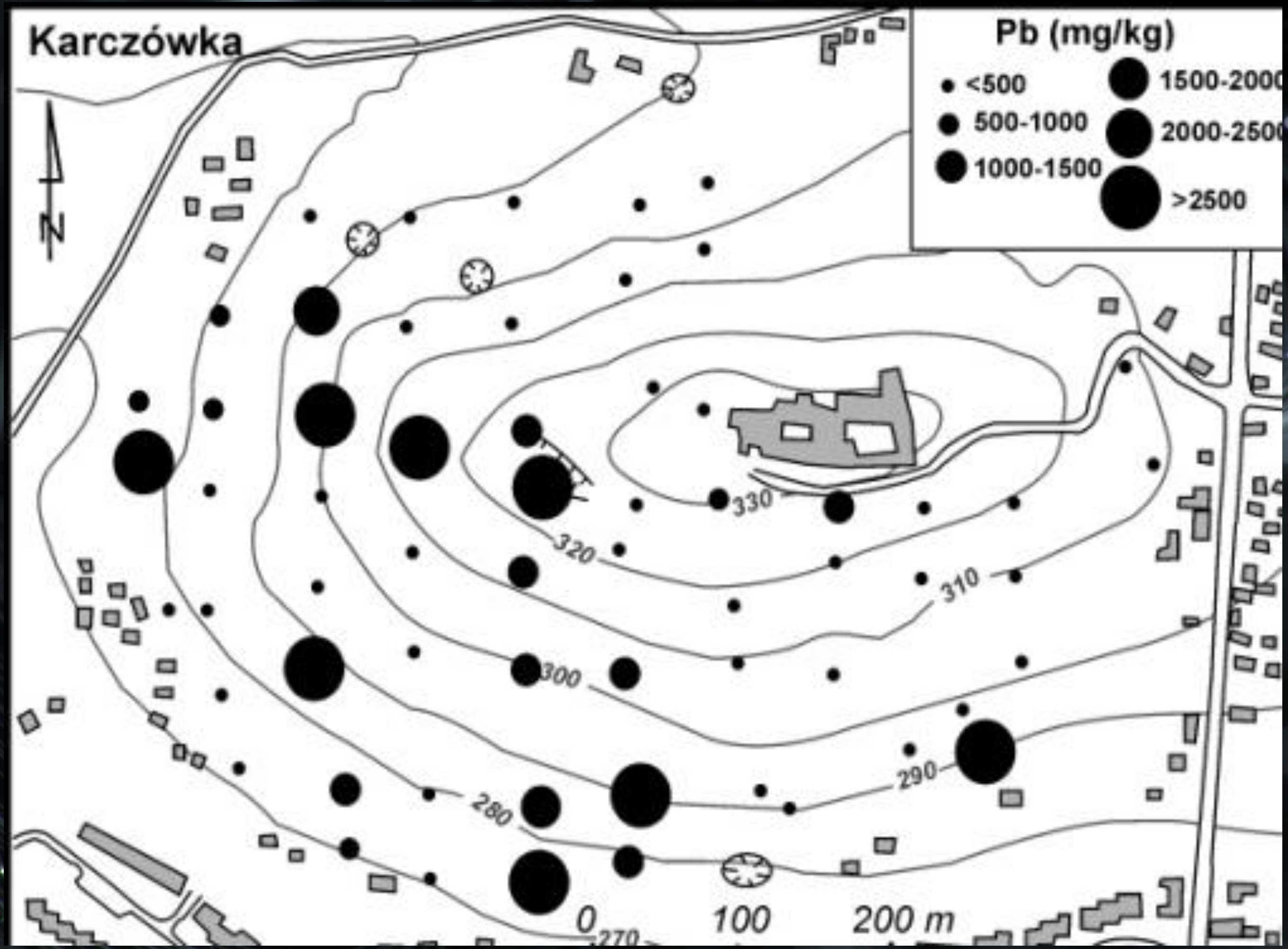
Concentrations of sulfur and $\delta^{34}S$ values in different samples from a single Scots pine (*P. sylvestris*) tree



Dołęgowska, S., Gałuszka, A., & Migaszewski, Z. M. (2021). Significance of the long-term biomonitoring studies for understanding the impact of pollutants on the environment based on a synthesis of 25-year biomonitoring in the Holy Cross Mountains, Poland. *Environmental Science and Pollution Research*, *28*, 10413-10435.

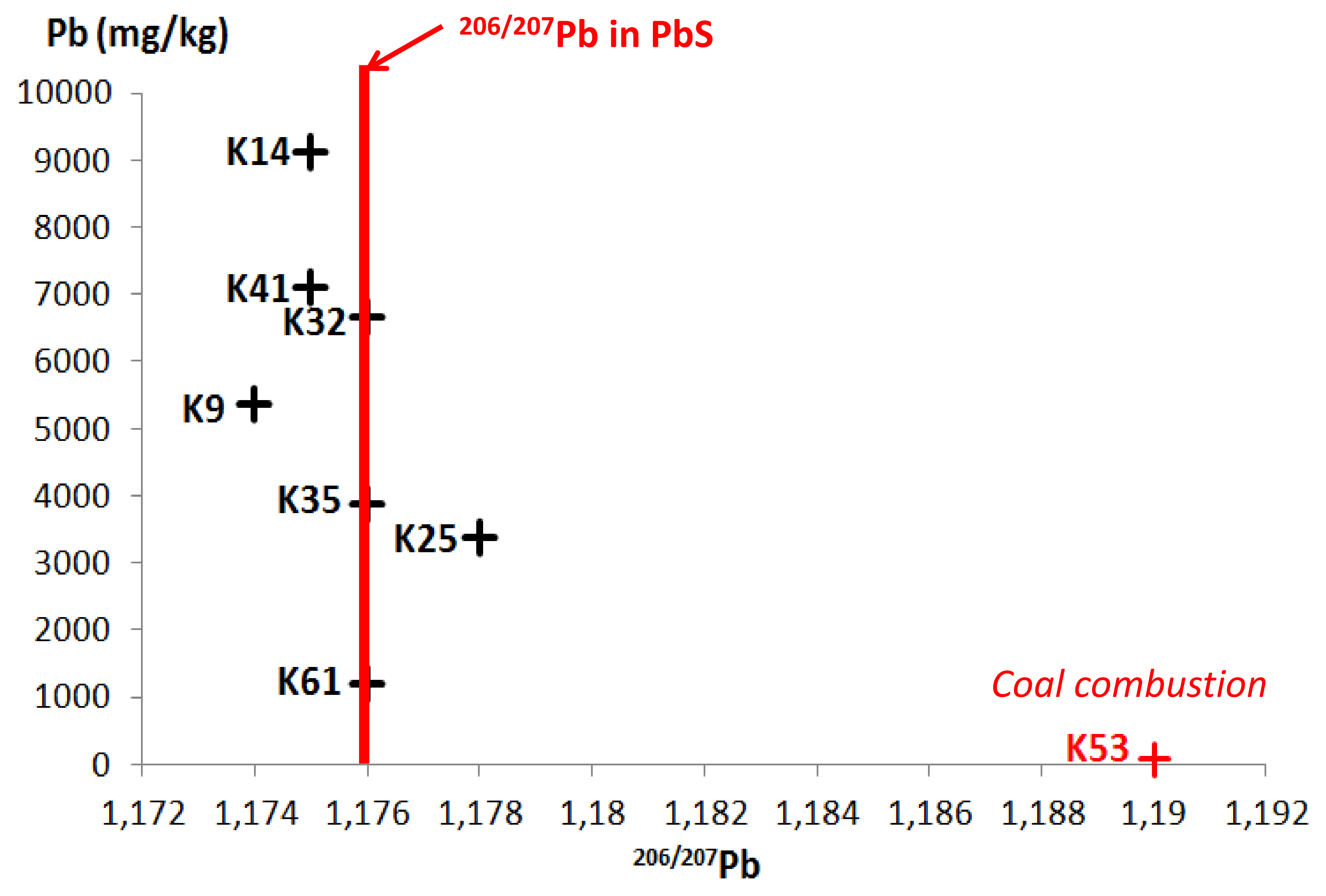
Lead isotopes of galena (PbS) in historic mining site in Kielce

Pb concentrations in soil: 41-9114 mg/kg
(mean value of 1027 mg/kg)



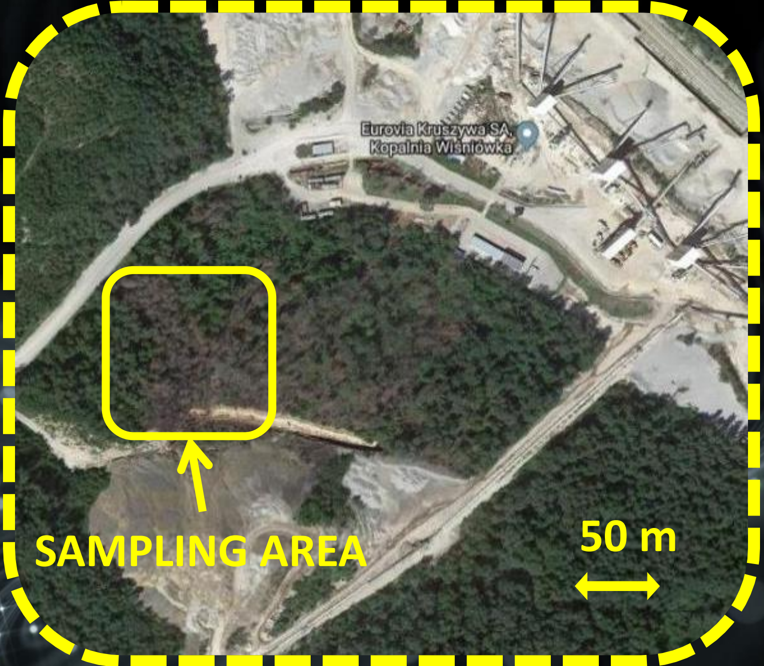
Gałuszka, A., Migaszewski, Z. M., Dołęgowska, S., & Michalik, A. (2018). Geochemical anomalies of trace elements in unremediated soils of Mt. Karczówka, a historic lead mining area in the city of Kielce, Poland. *Science of the total environment*, *639*, 397-405.

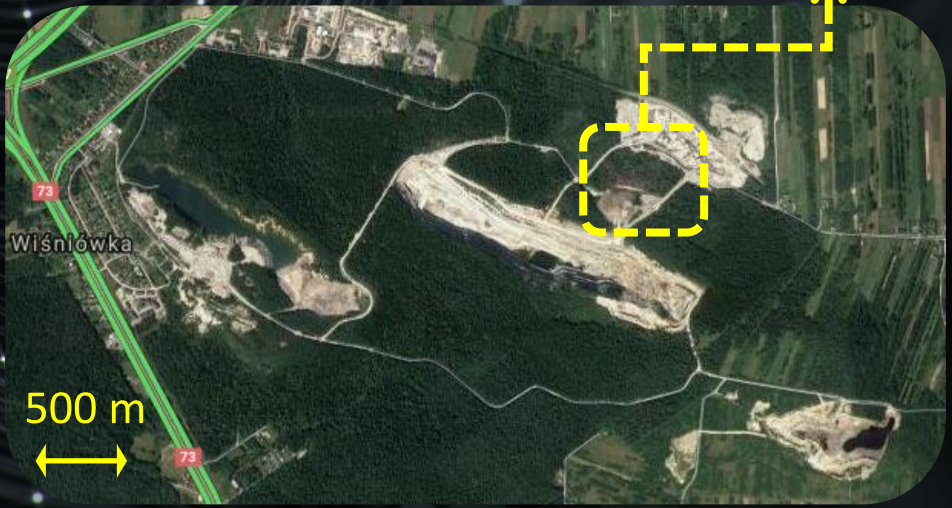
Lead concentration in soil vs. $^{206/207}Pb$



Gałuszka, A., Migaszewski, Z. M., Dołęgowska, S., & Michalik, A. (2018). Geochemical anomalies of trace elements in unremediated soils of Mt. Karczówka, a historic lead mining area in the city of Kielce, Poland. *Science of the total environment*, *639*, 397-405.

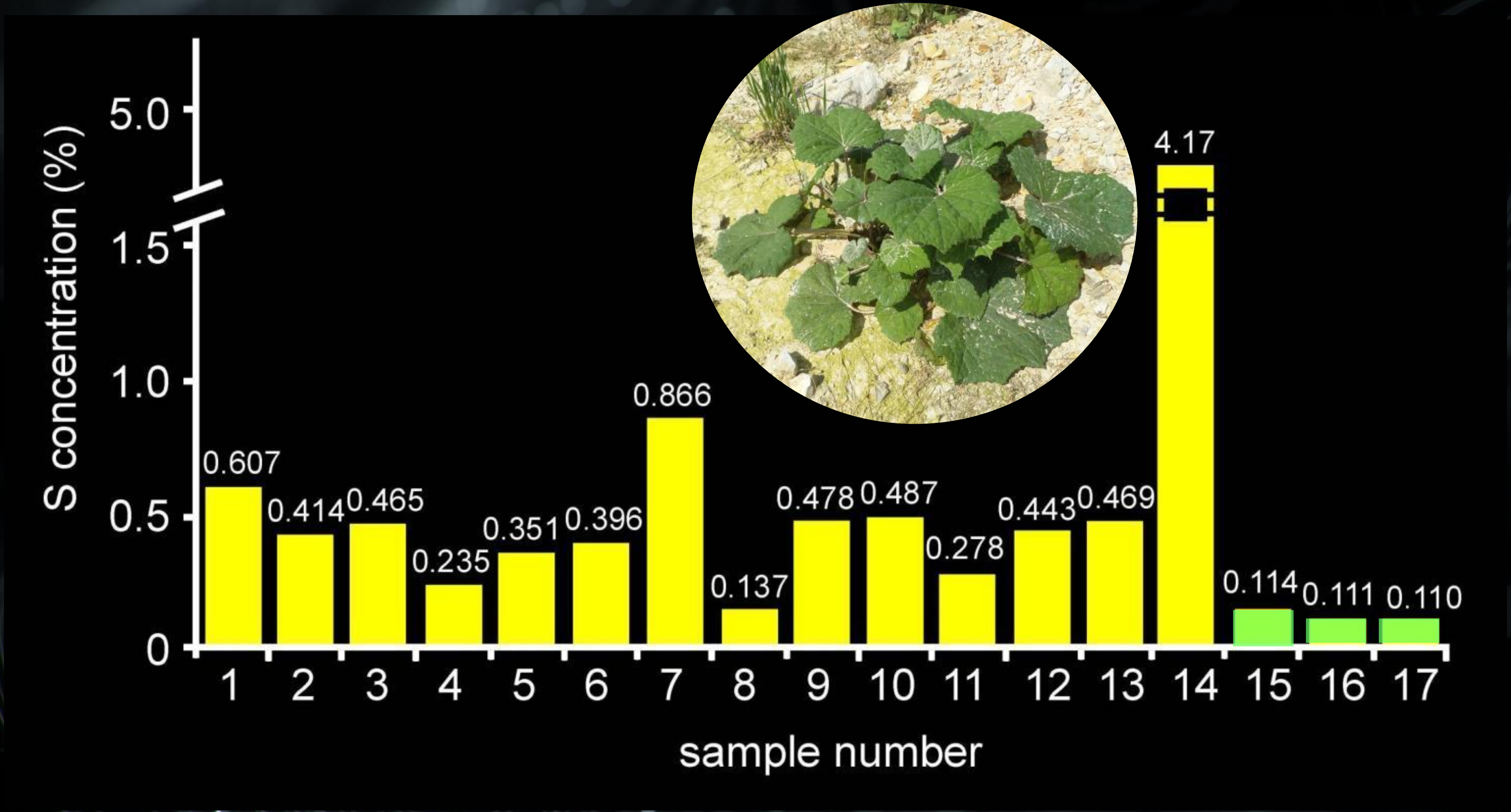
Sulfur isotopes in plants





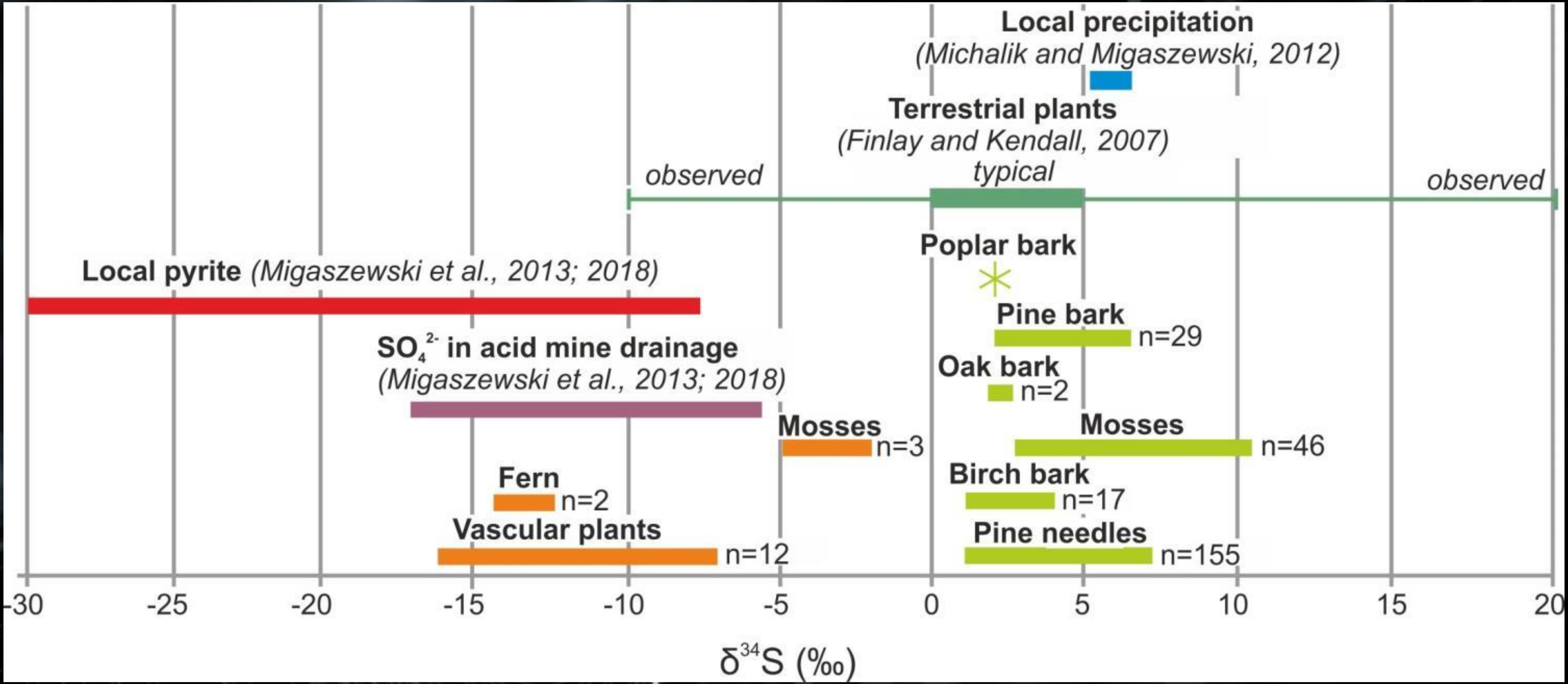
Sample no.	Plant species	Sample no.	Plant species
1	*Pteridium aquilinum*	10	*Juncus effusus*
2	*Betula pendula*	11	*Quercus petraea*
3	*Salix cinerea*	12	*Chamaenerion angustifolium*
4	*Sorbus aucuparia*	13	*Oxalis acetosella*
5	*Pteridium aquilinum*	14	*Tussilago farfara*
6	*Populus tremula*	15	*Drepanocladus aduncus*
7	*Vaccinium myrtillus*	16	*Mnium affine*
8	*Pinus sylvestris*	17	*Pleurozium schreberi*
9	*Frangula alnus*		

Sulfur in plant samples



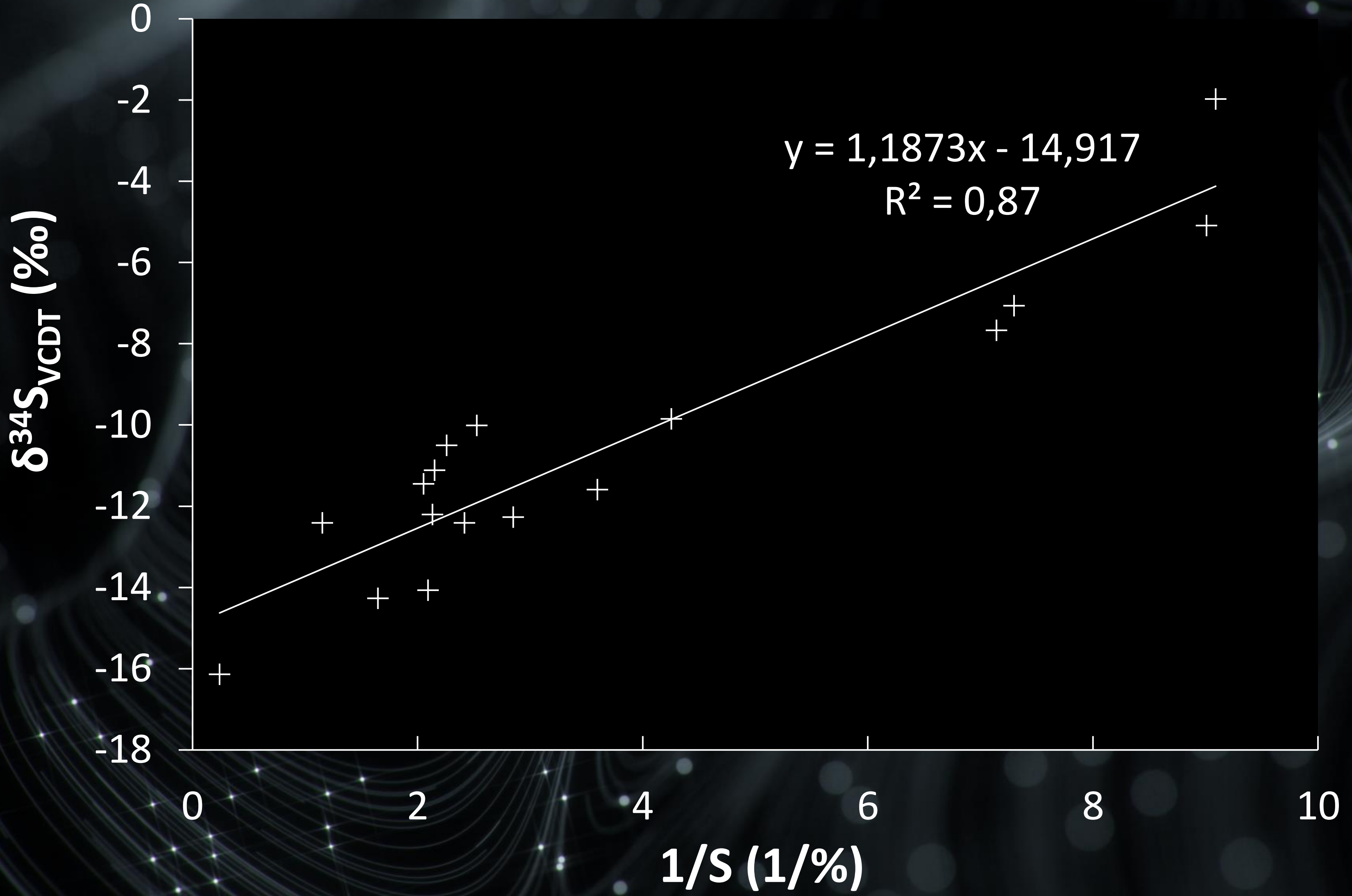
Gałuszka, A., Migaszewski, Z. M., Pelc, A., Trembaczowski, A., Dołęgowska, S., & Michalik, A. (2020). Trace elements and stable sulfur isotopes in plants of acid mine drainage area: Implications for revegetation of degraded land. *Journal of Environmental Sciences*, *94*, 128-136.

Stable sulfur isotopes in the Holy Cross Mts.



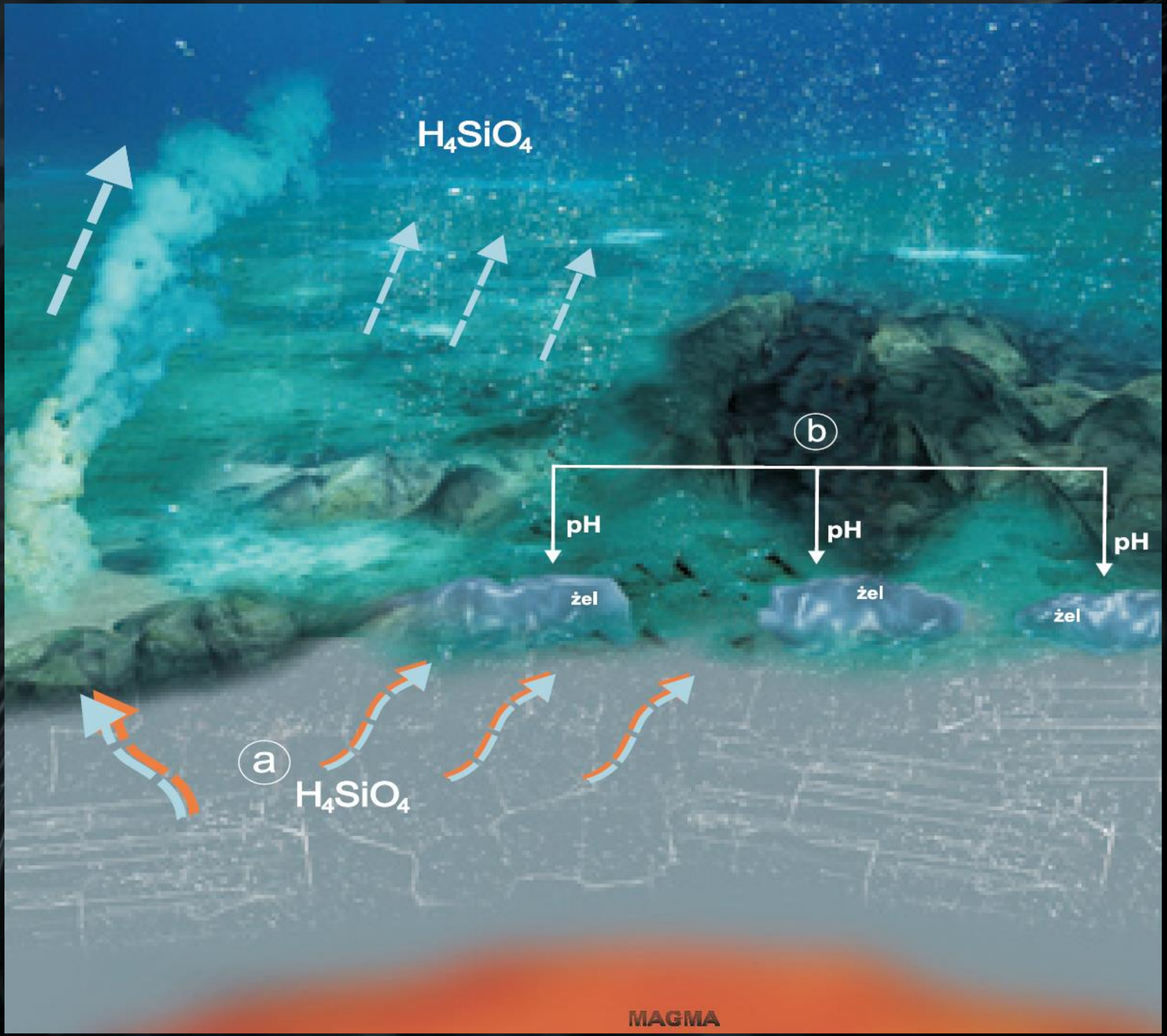
Gałuszka, A., Migaszewski, Z. M., Pelc, A., Trembaczowski, A., Dołęgowska, S., & Michalik, A. (2020). Trace elements and stable sulfur isotopes in plants of acid mine drainage area: Implications for revegetation of degraded land. *Journal of Environmental Sciences*, *94*, 128-136.

Variation in $\delta^{34}S$ versus reciprocal S concentrations in plant samples



Gałuszka, A., Migaszewski, Z. M., Pelc, A., Trembaczowski, A., Dołęgowska, S., & Michalik, A. (2020). Trace elements and stable sulfur isotopes in plants of acid mine drainage area: Implications for revegetation of degraded land. *Journal of Environmental Sciences*, *94*, 128-136.

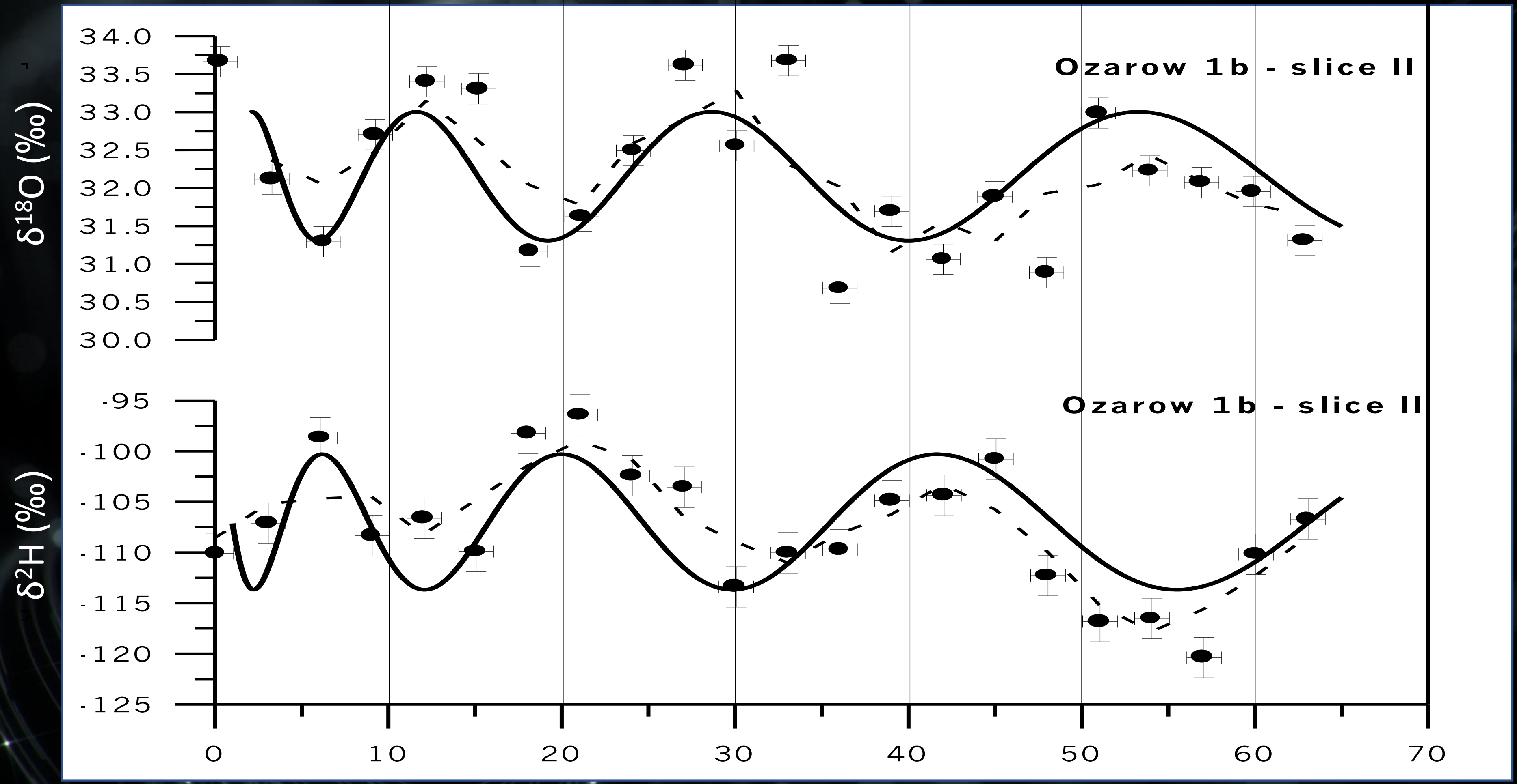
Striped chert genesis



Król, P., & Migaszewski, Z. M. (2009). Rodzaje, występowanie i geneza krzemieni. Zarys problematyki. *Historia krzemienia*, Muzeum Narodowe w Kielcach.

Migaszewski, Z. M., Gałuszka, A., Durakiewicz, T., & Starnawska, E. (2006). Middle Oxfordian–Lower Kimmeridgian chert nodules in the Holy Cross Mountains, south-central Poland. *Sedimentary Geology*, *187*(1-2), 11-28.

Results of stable oxygen and hydrogen isotope determinations in striped chert from Ożarów



Distance from the central part of the sample (mm)

Sharp, Z. D., Durakiewicz, T., Migaszewski, Z. M., & Atudorei, V. N. (2002). Antiphase hydrogen and oxygen isotope periodicity in chert nodules. *Geochimica et Cosmochimica Acta*, *66*(16), 2865-2873.

In memory of late Professor Stanisław Hałas