Isotope and geochemical studies on sediment samples of Lake Ohrid/Lake Prespa

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(Photo: curtesy of Bernd Wagner)

Kinds of animals.....



(with the permission of Elonora and Simona)

Remembering that :

- -The instrumental record is not enough long for giving data for exploring the natural variability of the Earth climate;
- -For testing model, instead we need accurate and longer climate record;
- -For doing this we need natural archives able to capture in great detail the past climatic changes;
- -The effect on climatic changes is not only influenced by the global climatic condition but also by the local environment (natural or human-modified);
- -Overall, we need strong integration from different disciplines (geosciences, social sciences, archeology, physics)

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The past is the key to the future*

BRUCE R. DOE

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Abstract-A new major frontier of geological research, which was initiated in the 1970's, involves predicting future geologic trends or events through study of the present and past, rather than trying to understand the past, often using what one knows about the present. Like most scientific frontiers, this one began from practical considerations-environmental concerns. The lack of formal recognition of this frontier results from fragmentation among many Federal agencies and highly focused mission-oriented programs (e.g., earthquake prediction, CO₂, nuclear-energy safety, etc.). Most programs aim to predict only the next 50-100 years, but much longer periods of the past need to be studied to do this. Nuclear-waste disposal has sometimes been considered in terms of the next million years, a period of time permitting significant and broad geologic changes. Decreasing public interest in environmental concerns relegates many questions from the realm of applied research back to that of basic research. Most of these questions are so fascinating, however, that the frontier is still worth pursuing. Such questions include whether a phenomenon will or will not take place and the rates at which it can develop (e.g., how fast do rifts form, how fast can a caldera event begin, and how quickly can a glacial maximum arrive?). Common elements of all studies include the historic record, trends in the Quaternary, analogues in various periods of the geologic time scale, and allowance for phenomena never experienced before. Other examples of studies include the Cretaceous as a period of a climatic extreme, an especially interesting time period; establishing the amount of paleocloudiness, a particularly challenging and important research area; acid rain as a possible new phenomenon. Geochemistry has much to contribute to this frontier science.

"Normally in geology, we try to understand the past, often making use of the *low of uniformitarianism* i.e. – <u>the present is the key to the past</u>. in the new frontier, <u>the present and the past are used to forecast future</u> <u>geologic trends or event</u>" (Doe, 1983). Then we need "proxy records*" able to reconstruct past climate like temperature and change hydrological conditions.

Moreover, we need to have "proxy material" relatively abundant, which can trace the aforementioned climatic information.

The oxygen isotopic composition has many advantages:

-Oxygen is one of the most abundant element on the crust;

-It is part of many minerals (particularly carbonate minerals);

-Once acquired the isotopic composition of a certain mineral is relatively stable;

-The oxygen isotopic composition of a precipitate is often related to temperature and the isotopic composition of the "substrate";

-Then can trace both the "story" of the substrate as well.

**Proxies* are parameters that can be measured in an *archive* (e.g. ice cores, speleothems) and which stand in, or substitute for, an environmental parameter (e.g. temperature, precipitation, vegetation type).

DEFINITION, STANDARD AND NOTATION

Isotopes are atoms whose nuclei contain the same number of protons (Z) but a different number of neutrons (N). The term *isotopes* is derived from Greek (meaning equal places) and indicates that isotopes occupy the same position in the periodic table.

Isotopes have the same atomic number Z (Z = number of protons)

But different Mass number = Z + N (N=neutrons)

We denote isotopes in the form ^mE, here the superscript *m* denotes the mass number (i.e., sum of the number of protons and neutrons in the nucleus).



Isotope fractionation may be either equilibrium or kinetic. Equilibrium system are characterized by a minimum in the free energy. Where a reaction has not gone to completion, where there is a barrier (e.g. removal of reaction product) ect, the fractionation is often kinetic: many biological processes are characterized by kinetic isotopes fractionation.

The stable isotope composition of a compound and its variation (specifically for stable isotopes i.e. ¹⁸O and ¹⁶O) are measured by a mass spectrometer relative to a standard, and operatively expressed in "delta" (δ) per mill notation

 $\delta = [(Rsample-Rstandard)/Rstandard]x1000$

 $\delta^{18}O = [({}^{18}O/{}^{16}Osample - {}^{18}O/{}^{16}Ostandard)/{}^{18}O/{}^{16}Osample]x1000$

By "delta" definition δ_{standard} is "0".

It obvious that isotopic composition expressed with delta is a number, which depends on the standard used.

Two different δ -scales are in use:

 $\delta^{18}O(v \le 0.05)$ and $\delta^{18}O(v \ge 0.05)$, because of two different categories of users, who have traditionally been engaged in O-isotope studies.

The VPDB scale is used in low-temperature studies of carbonate. PDB is a Cretaceous belemnite from the Pee Dee Formation and was the laboratory Working standard used at the university of Chicago in the early 1950's when the paleotemperature scale was developed. The original supply of this standard has long been exhausted, therefore secondary standards have been introduced (see Table), whose isotopic compositions have been calibrated relative to PDB.

All other oxygen isotope analyses (waters, silicates, phosphates, sulfates, high-temperature carbonates) are given relative to VSMOW (Mean Ocean Water).

 $\delta^{18}O(VSMOW) = 1.03091x\delta^{18}O(VPDB) + 30.91$

and

 $\delta^{18}O(PDB) = 0.97002x\delta^{18}O(VSMOW) - 29.98$

Standard	Material	PDB scale	VSMOW scale
NBS-19	Marble	-2.20	(28.64)
NBS-20	Limestone	-4.14	(26.64)
NBS-18	Carbonatite	-23.00	(7.20)
NBS-28	Quartz	(-20.67)	9.60
NBS-30	Biotite	(-25.30)	5.10
GISP	Water	(-53.99)	-24.75
SLAP	Water	(-83.82)	-55.50

 δ^{18} O-values of commonly used oxygen isotope standards on VPDB and VSMOW scale (parenthesis denote calculated values)

The variation of the ¹⁸O/¹⁶O ratio of natural compounds in the terrestrial environment can be used as a tracer for climatic and hydrological changes on land



The most common material can be carbonate minerals which may occurs in different polymorph (e.g. calcite-aragonite) and in different environments.



Pedogenic carbonate (Bk horizon, over raised beach deposit, Patagonia)



Marl lake deposits (Sulmona basin, Central Italy, Middle Pleistocene)



Land snail shells (Various localities)



Cave chemical deposits (speleothems) Tana che Urla (Central Italy)



Travertine and Tufa



Foraminifera





Marine Molluscs (bivalvi e/o gasteropodi)

Corals

In natural waters carbonate dissolution/precipitation is dominated by the chemical equilibrium between CO2-H2CO3-H2O

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CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^- + HCO_3^-
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CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^{-}
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If the solution looses CO_2 (degassing) $CaCO_3$ precipitation may occurs (in nature this can be driven by differences in pressure between the solution and the external environment of by, for instance, biological CO_2 uptake by photosynthesis).

 Ω calcite= (mCa²⁺x mCO₃²⁻) / Kcalcite

If $\Omega_{calcite}=1$, the solid and solution are in equilibrium; if $\Omega_{calcite}<1$, the solution is undersaturated and mineral dissolution can occur; if $\Omega_{calcite}>1$ the solution is supersaturated and precipitation should occurs.

How does change the ¹⁸O/¹⁶O ratio in carbonates?

 $T^{\circ}C = 16.0 - 4.14(\delta^{18}O_{calcite} - \delta^{18}O_{water}) + 0.13(\delta^{18}O_{calcite} - \delta^{18}O_{water})^{2*}$

1000lna $\approx \delta^{18}$ Ocalcite – δ^{18} Owater

For the past: One equation two unknowns!

 $\delta^{18}O_{calcite}$: "what we measure"

 $\delta^{18}O_{water}$: "unknown"

Temperature: "unknown"

Rate of change with temperature: ca. -0.2‰/°C



A) Equilibrium δ^{18} O fractionation between water and CaCO₃ (1000ln α) as a function of temperature. Under equilibrium conditions, aragonite will be precipitated with δ^{18} O values ~0.7 to 0.8‰ higher than calcite. B) Gradient of δ^{18} O equilibrium fractionation as a function of temperature, units of ‰^PC; for calcite (Kim and O'Neil, 1997) and aragonite (Patterson et al., 1993; Kim et al., 2007), the gradients vary from -0.18‰^PC at 35 °C to -0.23‰^J°C at 5 °C for calcite.

*This equation is valid for calcite. Sometime called Craig equation.

For a general introduction on stable isotope geochemistry

Stable Isotope Geochemistry 6th Edition

Deringer

Hoefs

For the topic of the lectures e.g. M.J. Leng (ed): Isotopes in Palaeoenvironmental research. Developments in Palaeoenvironmental Research Series, n°10.

Stable isotopes in hydrology: Clark, I., and P. Fritz, *Environmental Isotopes in Hydrogeology*, Lewis Publishers, Boca Raton, 1997. The observed variations of deuterium and oxygen-180 content in natural waters are closely related to isotopic fractionation occurring during the evaporation and condensation "freezing" of water\ when the heavy water molecules H_2 ¹⁸O and ¹H²H¹⁶O preferentially remain in or pass into the liquid/solid respectively.



Globally precipitation defined a clear relation in the $\delta D - \delta 180$ space (firstly defined by Craig, 1961) and called GLOBAL METEORIC WATER LINE



Gridded global maps interpolating δ^{18} Ovalues





Observing the two maps it is apparent that:

-There is a relation with latitude;

-This suggests a relation with temperature;

- This suggests that the main moisture source for the rainfall are lower latitude and this moisture is transported latitudinally.

Because climate is (in a very broad sense) the necessity to reduces the imbalance of incoming radiation between N and S latitudes, it is clear that isotopes are effective tracers of climate.

In this paper Dansgaard defined several isotopes effect

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Stable isotopes in precipitation

By W. DANSGAARD, Phys. Lab. 11, H. C. Ørsted Institute, University of Copenhagen

(Manuscript received April 28, 1964)

ABSTRACT

In chapter 2 the isotopic fractionation of water in some simple condensation-evaporation processes are considered quantitatively on the basis of the fractionation factors given in section 1.2. The condensation temperature is an important parameter, which has got some glaciological applications. The temperature effect (the δ 's decreasing with temperature) together with varying evaporation and exchange appear in the "amount effect" as high δ 's in sparse rain. The relative deuterium-oxygen-18 fractionation is not quite simple. If the relative deviations from the standard water (S.M.O.W.) are called δ_D and δ_{18} , the best linear approximation is $\delta_D = 8 \delta_{18}$.

Chapter 3 gives some qualitative considerations on non-equilibrium (fast) processes. Kinetic effects have heavy bearings upon the effective fractionation factors. Such effects have only been demonstrated clearly in evaporation processes, but may also influence condensation processes. The quantity $d = \delta_D - 8 \, \delta_{13}$ is used as an index for non-equilibrium conditions.

The stable isotope data from the world wide I.A.E.A.-W.M.O. precipitation survey are discussed in chapter 4. The unweighted mean annual composition of rain at tropical island stations fits the line $\delta_D = 4.6 \ \delta_{18}$ indicating a first stage equilibrium condensation from vapour evaporated in a non-equilibrium process. Regional characteristics appear in the weighted means.

The Northern hemisphere continental stations, except African and Near East, fit the line $\delta_D - 8.0 \, \delta_{14} + 10$ as far as the weighted means are concerned ($\delta_D = 8.1 \, \delta_{14} + 11$ for the unweighted) corresponding to an equilibrium Rayleigh condensation from vapour, evaporated in a non-equilibrium process from S.M.O.W. The departure from equilibrium vapour seems even higher in the rest of the investigated part of the world.

At most stations the δ_D and varies linearily with δ_{18} with a slope close to 8, only at two stations higher than 8, at several lower than 8 (mainly connected with relatively dry climates).

Considerable variations in the isotopic composition of monthly precipitation occur at most stations. At low latitudes the amount effect accounts for the variations, whereas seasonal variation at high latitudes is ascribed to the temperature effect. Tokyo is an example of a mid latitude station influenced by both effects.

Some possible hydrological applications are outlined in chapter 5.

Empirically established dependence of δp on various environmental factors, in fact measuring the degree of rain-out of the air parcel:

- Latitude

- Altitude
- Distance to the coast ,
 - Surface air temperature (t_{sur}),
 - Amount of rainfall (R in mm),

Tellus XVI (1964), 4

Isotope "effects"

- SEASONAL EFFECT winter rains are depleted in heavy isotopes with respect to summer rains. This effect is pronounced at mid and high latitudes
- LATITUDE EFFECT precipitation at high latitudes is generally depleted in heavy isotopes when compared to precipitation at low latitudes
- ALTITUDE EFFECT rains collected at high elevation (mountains) are depleted in heavy isotopes with respect to rains collected at low elevation (lowland).
- CONTINENTAL EFFECT rains become depleted in heavy isotopes with increasing distance from the coast
- AMOUNT EFFECT heavy rains are depleted in heavy isotopes with respect to light rains. This effect is seen mostly in tropical regions.
- EVAPORATION EFFECT light rains in arid or semi-arid regions are often enriched in heavy isotopes due to partial evaporation during fall

Spatial relation



 $\delta^{18}O/T$ (‰/°C)

Slope changes from high latitudes to tropical areas.

For continental Europe we have a values of ca. 0.58‰/°C

For Mediterranean is lower Not well defined: ca. 0.2-0.3 %o/°C

Important: the temperature is the station temperature.

This relation is (mostly) spatial (different stations)

Multi-annual temp and isotope fluctuations

(single station)



"Amount effect" It is the empirical relation of inverse correlation between δ^{18} O and Precipitation (mm)



The initial definition was related to tropical island. However, other areas can show a strong negative relation between rainfall amount and isotopic composition of precipitation).

For instance some region dominated by monsoon can have significant relation with precipitation amount (but in other temperature may be more dominant eg. Johnson & Ingram, 2004 EPSL)

WESTERN MEDITERRANEAN



 The δ¹⁸Op‰/°C ratio is usually rather low (ca +0.2‰/°C);

-The so called "amount effect" is quite pronounced (for many stations, but complex in the details);

-"North Atlantic" precipitation are usually more "negative" than "Mediterranean" precipitations (e.g. Celle-Jeanton et al., 2001, JGR).

(Bard et al., 2002 EPSL)



This would be a reason of curios isotopic effect.....

Before any others consideration the peculiar regime in the mediterranean compared to, for instance to central and N. Euorpe give rise at two different set of paleoclimatic reconstruction (or at least accordign to the «Pisa School»)

Regattieri et al., 2015

As rain falls on the ground, a number of processes take place that modify the isotope composition of the incoming precipitation. Details of these processes depend on the nature of the terrain and on the characteristics of the rain, such as its amount and duration, intensity, and intermittency.



Once water has penetrated deep into the ground\ below the unsaturated zone\ its isotopic composition remains practically unchanged during subsurface movement and storage "except at high temperature\ where isotopic exchange of oxygen with the rock matrix can occur.

EVAPORATION IS ONE OF THE MOST IMPORTANT ISOTOPIC EFFECT AFFECTING CONTINENTAL WATER AFTER RAINFALL PRECIPITATION



EVAPORATED WATERS DEFINES A TREND IN THE δD-δ¹⁸O WITH LOWER SLOPE COMPARED TO LMWL

John Gibson's web page, University of Waterloo

For instance, rivers in humid regions (Amazon) show little deviation form the GMWL; those flowing in arid lands (Rio Grande in the southwestern U.S. and the Darling River in Australia) do.

However, the hydrological cycle can be affected by climatic changes



The most obvious change is between glacials to interglacials periods when significant exchange of water mass occur between land (ice cap) and ocean. As seen before ice caps must tends to be depleted in heavy isotopes (when they growth leaving ocean enriched in heavy isotopes. So the isotopic composition of rainfall and the source of rainfall varies in concert.

Solving the Graig's equation



Map showing the distribution of sites used in this study. Symbol shape denotes SST proxy type (circle =Mg/Ca, square =UK37), symbol color represents how much time the record spans (see scale bar), and symbol outline color signifies age model type (black= δ^{18} Ob, white= δ^{18} Op).

In the marine environment is possible to solve the equation and obtaining the isotopic composition of water knowning T using other proxies. In this slide the example the concerns planktonic foraminera and then superficial waters.

Shakun et al., 2015 EPSL, 426.



Ice volume and temperature components of marine δ^{18} Oc. (**a**) The LR04 benthic δ^{18} Ostack, which records both global ice volume and deep ocean temperature (Lisiecki and Raymo, 2005). (**b**) Global SST (red) and δ^{18} Osw(blue) stacks calcu-lated in this study showing the temperature and ice volume components of marine δ^{18} Oc. (**c**) Ice-rafted debris concentration at Ocean Drilling Program site 980 in the North Atlantic (McManus et al., 1999). The δ^{18} Obthreshold for ice-rafting (4.14) is demarcated by the horizontal black dashed line and vertical shading.

Components in lake sediment useful for δ^{18} O studies

1. Carbonates

Fine

fraction/marl/bulk/authigenic/endogenic (<63 microns)

Ostracod shells

Snail shells

(Chara-type encrustations)

2. Biogenic silica Diatoms

They can represent different conditions!!!









Lake hydrological budget:

dV = P + Si + Gi - E - So - Go

V= volume

P= precipitation on the lake surface

Si= surface inflow from rivers and/or overland flow Gi= groundwater inflows E= evaporation

- So = Surface outflow
- Go= groundwater outflow.

Lake isotopic hydrological budget

dVδlake=Pδp + Si δi + Gi δi - E δe - So δo -Go δo

where δ lake, δp , δi are the isotopic values of the different fraction (either $\delta^{18}O$ or δD)





Surface inflow

Groundwater inflow

Groundwater outflow



Evaporation



(after Leng et al. 2010 Biogescience)

Skutary lake (Albania-Montenegro) Residence time: 120 days!



Isotopic composition of lake water is variable but lies on the local Meteoric Water line (LMWL).

Zanchetta et al., 2012 JQS.

Ohrid and Prespa are sister lakes



after Albrecht & Wilke 2008

They are connected by a series of impressive karst springs

Differential lake responses to common water balance forcing (hypothetical) The ISOMED view



East Mediterranean δ^{18} O lake records, Last Glacial Maximum to Present (Roberts et al., 2008 QSR)



BACK TO OHRID

During «warmer period» (Generically interglacial) the dominant carbonate phase is calcite $(CaCO_3)$ which precipitate during period of maximum phytolankton axctivity.



SEM photos of bulk sediment from the centre of Lake Ohrid indicating (a) diatoms and their fragments and (b) autigenous carbonates (after Wagner et al., 2009).

During Glacials siderite $(FeCO_3)$ is the main carbonate phase.

Siderite is generally formed under anoxic and reducing conditions, which typically have a high CO_2 partial pressure, elevated Fe/Ca and a low sulphide concentration.

Siderite is probably forming during early diagenesis, therefore its formation is different from direct precipitation from lake water column.



Individual siderite crystals amalgamating to form a larger siderite crystal 30 cluster (After Lacey et al., 2015 BGD).

Ohrid and Prespa



Lacey et al., 2014.

This general trend would be the effect of change in seasonal pattern of insolation during the Holocene, which may have affected seasonal precipitation regime and the hydrological budget of the lake(s).



Data after Berger, 1991.

In detail this change is quite complex at different latitudes



Changes in orbital forcing during the (12000 yr BP to 3000 yr in future) for June (a) and December (b). The figures show clear trends depending on the latitude.



4.2 (4.2-3.8) cal BP:

If you have «it» your are «lower latitude controlled (Monsoon-Mediterranean)»

If you have «it» not you are N. Atlantic contolled (e.g. NAO)

In any case:

Please, check chronology.

In a few words: seasonality and regional climate is important.

Zanchetta et al. 2015 In press AMQ



The record is discontinuous. Partially filled by siderite.

Calculation of past lake water is limited by T assumption (not-independently calculated but assumed on present day conditions).

> Present day lake isotopic values

Lacey et al. Submitted BGD





Shackleton et al., 2003 GPC

- The beginning of the Eemian coincides with a rapid rise in sea-surface temperature. The onset of Eemian is significantly later than the attainment of the MIS 5e plateau in benthic.

- This implies that in contrast to the base of the Holocene, the major ice sheets had completely melted before the beginning of interglacial climatic conditions in Northwest Europe.

- The end of the Eemian occurs after the end of MIS5e, with a strong cooling corresponding to C24 event in N. Atlantic.

Marine and continental records of the last interglacial in core MD95-2042 on a time scale based on radiometric dates for uplifted corals. From the top: Sedimentation rate implied by the age controls marked; benthic δ^{18} O record (replicates averaged); planktonic δ^{18} O record (replicates averaged); sea surface temperature based on U³⁷ k alkenones; major groups of pollen taxa.

HOW TO LINK ALL RECORDS AT REGIONAL SCALE?

We need a common time scale obtained by radiometric methods!





Marine and terrestrial were linked using using radiometrically dated spleothems (U/Th).

(Marino et al., 2015, Nature; Grant et al., 2012)

Surface sea waters, speleothems and lake carbonates are linked by hydrological cycle......





HOW TO LINK IT TO DEEP CORE IN OHRID?

We tuned the succession with «particular» points in the oxygen isotopes time-series with additional point obtained from tephra layers. Approch very conservative (used very few clear points other could be used but....)

Different stories from different proxies.....obvious but Synchronized at regional scale.



TIC % from Ohrid DEEP site plotted on original (grey dashed line, after Franke et al. 2015) and new age model (red line) compared to alkenone SST from core ODP-975 (Martrat et al., 2014 on Marino et al., 2015 chronology).

this Using approach that seems oxygen isotopes (in the termination at least) is partially affected by effect» (rapid «source melting of Nothern Hemisphere melting of ice sheet). Whereas other proxies would be more affect by temperature.

ANY CONCLUSION? NO READY FOR BETTER REGIONAL UNDERSTANDING!





FUCINO RECORD: HIGH PROBABILITY TO FIND SAME TEPHRAS LIKE OHRID.....