

n. 33

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Abstract

The present paper proposes a method to simplify the very complex isotopic fractionation processes occurring during the water cycle. The method is constrained by a relatively small number of variables, with the precision needed in hydrological applications. After a theoretical introduction on the adopted interpolation criteria, two cases in the Mediterranean are presented. In both cases the evaluation of the "geometric complexity" of the systems appears to be the best tool to produce reliable isotopic models. If the complexity is low, it is apparently easier to fit different models; on the contrary the higher the complexity is, more difficult it is to find a reliable model but, at the same time, more difficult it is to find effective alternative models.

1. Introduction

The isotopic signature of natural waters, expressed in terms of δ^{18} O and δ D, is an important information for understanding the complex relationships between meteoric waters and aquifers [*Gonfiantini*, 1978]; in particular, in hydrological applications, the comparative analysis of the average δ^{18} O and δ D values in meteoric precipitations and underground waters allows to identify the actual catchment basins that feed the aquifers.

If contributions from outer hydrogeological structures, and/or re-evaporation of infiltrated waters due to high temperature/low humidity climatic regimes are negligible, the average isotopic composition of underground waters is related to the isotopic signature of precipitation by the following relation:

$$\delta^{uw}_{mrt}$$
 (18O,D) = $\Sigma_{(ss=1,mrt)} \delta^{p}_{ss}$ (18O,D) *(P_{ss}/P_{mrt}); [1]

where δ^{uw}_{mrt} is the average isotopic composition of underground waters calculated on period corresponding to the mean residence time (*mrt*) of the considered aquifers, δ^{p}_{ss} the isotopic composition of precipitations in a single sampling session (*ss*); the weighing factor P_{ss}/P_{mrt} is the ratio between the amount of precipitations occurred in a single sampling session and the heights of the whole *mrt* period.

In a typical hydrogeological application *mrt* is at least 1 year, due to the natural frequency of variations in atmospheric phenomena, and *ss* is typically 1 month, due to practical and economic reasons.

The main question when equation [1] is applied to hydrological models is: how great is the error in extending to the whole catchment area the data collected in a very limited number of sampling points?

In order to answer the previous question it is necessary to consider all the factors that influence the isotopic signature of precipitations, that are:

- i) initial composition of condensing vapour according to the Rayleigh distillation processes [*Craig and Gordon*, 1961];
- ii) factors affecting rainfall event dynamic and thermodynamic, like temperature inside and at the base of clouds [*Yurtsever and Gat*, 1981; *Tzur*, 1971], physical state of precipitation and rainfall rate [*Yurtsever and Gat*, 1981];
- iii) previous condensation history of the air masses, expressed in terms of distance from the sea and/or altitude gradients.

The present paper proposes a method to simplify the very complex isotopic fractionation processes occurring during the water cycle, constraining it with a relatively small number of variables. The precision of the proposed model fits the level needed in hydrological applications.

After a theoretical discussion on the adopted interpolation criteria, two case studies in the Mediterranean area, both located in Sicily (Italy), will be presented: one is the Oreto River Valley, a little watershed in the metropolitan area of Palermo, the other is the karst area of the Madonie Natural Park in Northern Sicily (Figg. 1 and 2).

The Oreto Valley represents a case study completely developed under the logic flowchart presented in this paper; the Madonie area refers to older data previously studied with a classical approach but now reinterpreted using the methodology here discussed.

2.Theoretycal background of proposed spatial modelling procedure

The isotopic signature of meteoric waters has been previously expressed both in terms of δ^{18} O and δ D; as well known from the scientific literature [*Yurtsever and Gat*, 1981], deuterium and oxygen isotopic compositions are not independent variables, but they are related to each other by a strong linear correlation. So, if we assume that deuterium and oxygen isotopic composition are reciprocally dependent, we can also state that spatial modelling of isotopic signature may be performed using only one of these two variables; this simplification has been adopted in the development of the presented method, and in particular all the subsequent cal-



Figure 1 Map of Oreto Valley river, reporting locations of sample points and rain Oxygen-18 contour lines.





5

Independent variables	Regression coefficients	Standard deviation (±δ)
t, P, L, A	0.8	2.82
t, P, L	0.8	2.82
t, P	0.79	2.86
t	0.79	2.84

Table 1 Results of multiple linear regression analyses for monthly weighted mean of δ^{18} O; t is average monthly temperature, P is average monthly rainfall amount, L is latitude, A is altitude.

culations will only deal with $\delta^{18}O$.

Oxygen isotopic composition is influenced by many factors, depending on the kinetic and thermodynamics of the condensation processes involved in rain, hail and snow formation and/or on the interactions between these condensed particles, atmosphere and orographic structures.

Data from I.A.E.A. network [*Yurtsever* and Gat, 1981], have been compared with a series of geographical and meteorological parameters by multiple linear regression analyses (Table 1).

Discussing the results, the authors highlight that on a global scale only temperature seems to play a fundamental role in determining isotopic composition, whereas on a regional scale factors such as amount of precipitation and evaporation may assume a great importance. The standard deviation of the cited relationships, generally higher than 2 δ ‰, is too great for hydrogeological applications.

The same happens in the Mediterranean area, if δ^{18} O values are plotted vs. temperature and rainfall amount. Standard deviations of measured monthly isotopic data, collected in two stations of the Madonie area during the year 1978 [*Hauser et al.*, 1980], showed values ranging from 2.4 to 1.7 δ ‰, whereas the residuals of the model that links these to monthly values of air temperature and rainfall amount [*Madonia et al.*, 1997] are of the same order (2.1-1.3 δ ‰). In other words, the model unfits the hydrological system involved because its error is equal to the observed natural variations.

The high dispersion of the modelled data is probably due to the complex dynamic of meteoric events in this sector of the Mediterranean Sea. In Northern Sicily rainfalls are related to three different conditions:

i) incoming of Atlantic perturbances from NW;

- ii) incoming of African perturbances from all the southern quadrants;
- iii) local evaporation/condensation phenomena driven by orography.

For each rainfall event, the initial isotopic composition of the clouds, and the progressive depletion in heavy isotopes that occurs between the initial and final separation of condensed water droplets from the same cloud, are completely different in each of the three conditions previously described.

In the first one we have humid air masses generated by evaporation processes occurred at colder temperatures with respect to the local ones (more negative initial isotopic composition), and progressively depleted in heavy oxygen isotopes from NW to SE.

In the second situation evaporation occurs at higher temperatures (more positive initial isotopic composition) and the depletion of heavy isotopes goes from S to N.

In the last case evaporation happens at local temperature and the first rainfall is separated from a water vapour that preserves the initial isotopic composition, determined by the Rayleigh distillation processes.

Water vapour is then suddenly uplifted by the coastal mountain chain, until it reaches the thermodynamic conditions for condensation: depletion in heavy isotopes is then a vector with the same versus and direction of altitude gradient.

Under these conditions it is practically impossible to develop a model that predicts the initial isotopic composition of a meteoric event, because there are too much variables involved and interacting with each other. On the other hand, in an ordinary hydrological study, the choice of sampling each rainfall is of no practical appliance.

Such as complex dynamics impose some constraints in hydrogeologic isotopic models:

- i) The minimum reference time to develop a model should be a complete hydrological year, due to the partial statistical compensation between the various meteoric events related to perturbances incoming from different directions; for shorter time periods, i.e. a single month, the predominant winds may cause strong variations in the initial isotopic composition of rain, that is reflected in high dispersion of the modelled data.
- ii) The traditional procedures of isotopic modelling, like vertical gradient or distance from the sea, seems to be ineffective due to the

excessive simplification of the model respect to the natural systems. As an example, in a watershed where rainfall events are driven by orography, the altitude gradient may coincide or not, for the whole or only in part, with the vector representing the so called "continentality effect"; so, it is necessary to take into account both horizontal (distance from the sea) and vertical (successions of valleys and mountain chains) variations, which reciprocally interact in all the possible combinations.

The implementation of a more reliable modelling procedure must then be based on the numerical conversion of the "geometric factor", this term defining the interaction of all the orographic elements that influence isotopic composition of precipitations.

The so defined "geometric factor" verifies the influence of geographic parameters, like altitude, distance from the sea or direction of perturbance propagation, in driving rainfall phenomena, with the aim of designing a correct isotopic sampling network. As shown in Figure 3, if two or more mechanisms of isotopic composition variations are interacting, a wrongly designed sampling network may preclude the separation of the single effects, leading to an ineffective model.

If no correlation is found between rainfall amounts and geographic variables, a diffused wildcat network represents the only way to proceed. If correlation is verified, it is then possible to distribute sampling points taking into account the expected isotopic variations.

After sampling and isotopic measurements, for a period of at least a complete hydrologic year, average oxygen isotopic values, weighted by rainfall amounts, are plotted vs. the same variables previously used for rainfall distribution modelling.

If no correlation is found, only classical interpolation methodologies are to be used, either deterministic (like T.I.N., Triangulated Irregular Network) either stochastic (like kriging).

In the opposite case, after a statistical calculation of the equations linking oxygen isotopic composition to the selected geographic variables, it is then possible to derive a spatial distribution of $\delta^{18}O$.

3. Discussion of the selected cases

3.1 The Oreto River Valley

The Oreto River Valley is located in northern Sicily, just southwest of the city of Palermo (Figure 1). The river flows for about 20 km, from the source at 786 m of altitude to the Gulf of Palermo; its watershed has a surface of about 116 km², a SW-NE orientation and is surrounded by mountains with a maximum eleva-



Figure 3 Expected variations in Oxygen-18 content of precipitation due to increasing distance from the sea and topographic profile.

Independent variable(s)	a	b	c	r ²	σ
$R.A.=a^*x+b^*y+c$ - All data					
Altitude (A, m a.s.l.)	0.86	-	525	0.61	158
Distance from the sea (D, km)	39.87	-	445	0.53	173
A, D	0.70	8.79	493	0.23	169
R.A.=a*x+b*v+c - Oreto Vallev				1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	
Altitude (A, m a.s.l.)	1.49	-	357	0.92	126
Distance from the sea (D, km)	69.34	-	202	0.98	67
A, D	0.13	63.87	209	0.91	82

Table 2 Oreto River Valley: linear regression equation for values of yearly amounts of precipitations plotted versus altitude and distance from the sea of the selected rain gages (Hydrographic Service network).

tion of about 1400 m.

Yearly rainfall amounts, both for the whole stations and for these located within the Oreto Valley, were correlated with altitude and distance from the sea (Table 2); as clearly shown in the table, relationships are much more evident within the valley (r^2 0.92 and 0.98 respectively) than for whole stations (r^2 ranging from 0.23 to 0.61).

This situation perfectly reflects the different geometry of the two sub-systems: in the previous case vectors of altitude gradient and distance from the sea have same direction and versus along a unique valley, with a single aspect, open towards the sea on one side and completely closed on the opposite by high mountains almost continuous in space. In the second situation we have different valleys with different aspects and very variable altitude gradient, opened towards the coast in two different directions (SE and NW), separated by articulated and discontinuous divides.

Within the Oreto Valley the best correlation is observed between rainfall amount and distance from the sea but also the other parameters show a good relationship. It has to be stressed that in this case, since the vectors of distance from the sea and altitude gradient have the same direction and versus, the two effect are perfectly superimposed and not separable. As a direct consequence, if we plot rainfall amount versus altitude we are also considering distance from the sea and vice versa: the little differences in the values of correlation coefficients are probably caused only by the little model instability due to the reduced data population.

A sampling network of five stations, operating between August 1995 and July 1996, was then realized taking into account expected isotopic variations in rain waters affected by the same mechanisms of rainfall amounts. Data on network characteristics and on the collected samples are reported in Table 3. The reliability of the rain propagation model is confirmed by the data of Table 4, which agree with those obtained from historical time series.

Oxygen isotopic composition of rain collected in the network was plotted vs. the same geographic parameters used in rainfall amount model (Table 5). In this case, the results of linear regressions of δ^{18} O values indicate altitude as the parameter best correlated, but the difference is so small (r² 0.97 and 0.98), having no physical significance. Also for isotopic composition we can state that the very simple geometry of the studied system allows the development of a very reliable spatial model.

Although vertical gradients are generally described by a linear relationship, while distance from the sea effect by a decay-type polynomial curve, in this specific case the decay type curve approaches a straight line, due to short distances from the sea,.

In order to extend isotopic data collected in the network to the whole valley, the first linear equation reported in Table 5 was used to attribute values of δ^{18} O to a series of fictitious rain gages (about twenty), located along the watershed; the δ^{18} O contour map presented in Figure 1 was finally derived from both measured and calculated values, using a kriging interpolation procedure.

3.2 The Madonie Natural Regional Park

The regional Park of the Madonie is situated 50 km east from Palermo, on the northern coast of Sicily (Figure 2). The area is characterized by a karst massif with a maximum elevation of about 2000 m and an articulated orographic structure; its slopes vary all the way around with a recurrence of peaks and deep valleys.

Due to the greater range of distances from the sea, with respect to the previous case study, when we relate rain heights with this variable we have to use the decay-type polynomial equation instead of the linear one. The results shown

	Alto	fonte	Mon	reale	Pale	rmo	Pizz	zuta	Stra	isatto
Altitude (m a.s.l.)	450		370		10		1030		850	
Dist. f. the sea (km)		10.5		9		0.5		16.5		16
MONTH	δ ^{is} O	R.A.	δ ¹⁸ O	R.A.	δ ^{is} O	R.A.	δ ¹⁸ O	R.A.	δ ^{is} O	R.A.
08/95	-3.2	56	-3.4	73	-3.4	53	-4.0	55	-4.0	48
09/95	-6.5	55	-6.7	185	-5.1	95	-8.0	55	-7.9	58
10/95		0		0		0		0		0
11/95	-5.9	199	-5.5	214	-5.2	151	-6.9	280	-6.6	229
12/95	-6.3	208	-7.3	191	-5.2	106	-7.5	251	-7.4	248
01/96	-6.1	167	-5.8	109	-4.1	62	-6.8	151	-7.0	152
02/96	-8.4	233	-8.8	205	-7.3	134	-9.8	261	-9.7	264
03/96	-7.8	165	-7.7	145	-6.6	145	-9.2	248	-9.3	233
04/96	-4.5	82	-3.9	96	-2.9	39	-6.0	105	-5.5	106
05/96	-5.4	69	-6.1	70	-5.9	44	-7.3	126	-7.1	117
06/96	-3.9	66	-3.1	58	-2.2	39	-3.0	30	-2.8	32
07/96		0		0		0		0		0
Year	-6.39	1300	-6.39	1346	-5.35	868	-7.66	1562	-7.59	1487

Table 3 Altitude, distance from the sea, δ^{18} O and rainfall amount (R.A., mm) for the Oreto River Valley sampling network.

Independent variable(s)	a	b	c	r ²	σ
$R.A.=a^{*}x^{+}b^{*}y^{+}c$	second?		and the second second		1-37.53
Altitude (A, m a.s.l.)	0.623	-	975	0.87	112
Distance from the sea (D, km)	40.66	-	886	0.96	66
A, D	-0.202	52.87	867	0.92	76

Table 4 Oreto River Valley: linear regression equation for values of yearly amounts of precipitations plotted versus altitude and distance from the sea of the selected rain gages (sampling network operating in the hydrological year 1995/1996).

in Table 6 highlight how the relative best correlation is obtained plotting rainfall amount versus altitude and distance from the sea (r^2 equal to 0.68).

The r² value for this relationship is sensibly lower respect the Oreto case, due to the major geometric complexity of the natural system. The rainfall dynamics seems to be controlled on one hand by the uplifting and consequent condensation of humid air masses, coming from the sea, due to the presence of a continuous mountain chain parallel to the coast. On the other hand, the anti correlation with the distance of the sea expresses the loss of water vapour charge in the atmosphere that occurs as the rainfall events proceed from the sea to the interior. If we think to this phenomenon in terms of δ^{18} O variations, we would have a parallel progressive depletion in heavy isotopes governed by a Rayleigh-type fractionation process.

The general framework just presented has been adopted for the reinterpretation of isotopic data collected in a sampling network of 5 pluviometers, that operated in the Madonie area between June 1992 and August 1993 (Table 7); the geometric arrangement of the sampling points was designed only to verify the existence of variations in oxygen isotopic composition of rain due to classical parameters (altitude gradient and/or distance from the sea).

Despite the minor number of sampling points and the short time interval (only one year), the correlation between rain heights and territorial variables it is not very different respect to the Hydrographic Service data: (best $r^2=0.655$, Table 8).

If we plot rainfall amounts versus altitude and distance from the sea in two different graphs (Figure 4), and trace the best fitting curves (linear and polynomial of the second degree respectively), we can derive the same useful information for improving our model. When we consider the variations of rain heights with the altitude we note that three points lie close to the best fit line (Cefalù, Mongerrati and Piano Battaglia), one below (Petralia) and another above (Isnello).

If we calculate for this point, using the best fit equation, the expected altitude corresponding to the observed rainfall amounts, we found the theoretical values of 1300 m; this value is exactly that of the Dipilo Mount, immediately seaward respect to the deep valley where the Isnello sampling point is located (Figure 5). In order to correctly explain the Petralia case, we have to consider the whole rainfall varia-

Independent variable(s)	a	b	c	r ²	σ
$\delta^{is}O=a^*x+b^*y+c$	Second and Second				
Altitude (A, m a.s.l.)	-0.0024	-	-5.39	0.98	0.17
Dist. from the sea (D, km)	-0.1463	-	-5.14	0.97	0.21
A, D	-0.0014	-0.059	-5.27	0.97	0.16

Table 5 Oreto River Valley: linear regression equation for values of yearly δ^{18} O values plotted versus altitude and distance from the sea of the selected rain gages (sampling network operating in the hydrological year 1995/1996).

Independent variable(s)	a	b	c	d	e	r ²	σ
$R.A.=a^*A+b^*D+c^*D^2+d^*D$) ³ +e	1					
A						0.404	
D, D ²	1					0.422	
D, D ² , D ³						0.427	
A, D ²	· · · · · · · · · · · · · · · · · · ·					0.587	
A, D, D ²	0.2114	12.61	-0.6617		662	0.684	44
A, D, D ² , D ³	0.1911	-2.57	1.2749	-0.0549	671	0.676	44

Table 6 Madonie area: linear regression equation for values of yearly amounts of precipitations plotted versus altitude and distance from the sea of the selected rain gages (Hydrographic Service network). D is distance from the sea (km), A altitude (m a.s.l.).



Figure 4 Variations of rain heights due to increasing distance from the sea and altitude in the Madonie Mounts area.

	Cefa	lù(1)	Isnel	lo(2)	P.Batt	aglia(3)	Monge	errati(4)	Petral	ia(5)
Altitude (m a.s.l.)	1	25	585		1	650	7	40	94	0
Distance from the sea (km)	(0.0		10.0	1	8,8	1	0.9	23	.8
Month	δ ¹⁸ O	R.A.	δ ¹⁸ O	R.A.	δ ¹⁸ O	R.A.	δ ¹⁸ O	R.A.	δ ¹⁸ O	R.A.
9/92		0	S	0		0	- 1	0		0
10/92	-4.4	125	-5.9	73	-7.3	72	-6.4	59	-6.0	50
11/92	-6.4	22	-7.8	81	-7.1	92	-7.6	61	-7.4	73
12/92	-7.4	129	-8.6	212	-9.3	117	-9.7	212	-10.2	198
1-2/93	-6.4	110	-7.7	224	-8.0	337	-8.4	210	-8.7	188
3/93	-8.2	56	-10.8	153	-9.8	236	-9.8	86	-10.5	52
4/93	-3.9	78	-5.6	57	-8.5	84	-6.3	53	-5.8	44
5/93	-5.6	48	-6.0	58	-9.2	49	-7.1	35	-7.3	49
6/93		0		0		0		0		0
7/93		0	-	0		0		0	· · · · · · · · · · · · · · · · · · ·	0
8/93		0		0		0		0		0
Year	-5.9	568	-8.1	858	-8.6	987	-8.5	716	-8.6	654

Table 7 Values of δ^{18} O and rainfall amount (R.A., mm) for the Madonie area sampling network operating in the year 1992/93.

tions. As already discussed, we have a rising of rainfall amounts, due to vertical gradient, partially compensated by the lowering effect due to the increase of the distance from the sea.

The expected values will be higher just at the main divide between northern (seaward) and southern watersheds; on the southernward flank the combination of increasing distance from the sea and decreasing altitude will lower the total heights of precipitations (see also Figure 5). The focal point is that the lowering of rainfall amounts, in the southern quadrants, cannott be of the same order of the northern ones, because the clouds are depleted of all the water vapour condensed during the precipitation events already occurred. So, in absence of further information (other rain gages on the southern flank at different altitude and distance from the sea) we cannot express in a numeric code this fact. As a consequence, a correction factor can be applied only to the Isnello point, and in particular it consists in changing the real altitude of the sampling point (585 m) with fictitious value of 1300 m (Dipilo Mount maximum altitude). In

other words, the rainfall amount in a certain X,Y position reflect the height of the nearest elevation of the topographic surface able to influence the mean cloud altitude.

If we recalculate expected rainfall amounts (RA) using this new value for Isnello we will found a better correlation ($r^2=0.909$, $\sigma=50$) for the equation of the type:

$$RA = 0.2974 \text{ x } A - 0.2502 \text{ x } D + 537$$
[2]

where A and D are altitude in m a.s.l. and distance from the sea in km respectively. Values of measured rainfall amounts are plotted in Figure 5 with the rain heights calculated using both the real and fictitious altitude for the Isnello station.

In the next step, the rain propagation model was applied to the interpretation of isotopic data: the results are reported in Table 9.

As clearly shown in the table the isotopic signature seems to be driven only by the increasing distance from the sea, i.e. a typical Rayleigh distillation process, correctly sampled

Independent variable(s)	a	b	c	d	e	r ²	σ
Rainfall amount=a*A+b*D+c*D2-	$+d^*D^3+e$						
A						0.486	
D, D ²						0.161	
D, D ² , D ³						0.392	
A, D ²	0.3404		-0.4537		592	0.655	98
A, D, D ²				NAME OF		0.398	
A, D, D ² , D ³	No	physica	1 significance	of the pa	rameters (e is negativ	c)

Table 8 Madonie area: linear regression equation for values of yearly amounts of precipitations plotted versus altitude and distance from the sea of the selected rain gages (network 1992/93) D is distance from the sea (km), A altitude (m a.s.l.).

Independent variable(s)	a	b	c	d	е	r ²	σ		
$\delta^{Ib}O = a^*A + b^*D + c^*D^2 + d^*$	D^{i+a}	2		1					
A						0.506			
D, D ²		-0.3237	0.0092	· · · · · · · · · · · · · · · · · · ·	-5.9	0.959	0.23		
D, D ² , D ³		-0.3936	0.0178	-0.00025	-5.9	0.937	0.29		
A, D ²						0.388			
A, D, D ²		No physical significance of the parameters (a is positive)							
A. D. D ² , D ³		No	physical sig	nificance of t	he param	eters (a is po	ositive)		

Table 9 Madonie area: linear regression equation for values of yearly δ^{18} O values plotted versus altitude and distance from the sea of the rain gages (sampling network operating in the hydrological year 1992/1993).

and described by the decay-type curve illustrated in Figure 5. We can observe strong variations in δ^{18} O values only between the most northern stations (Cefalù and Isnello), while for the other sampling points oxygen isotopic composition is quite similar. The asymptotic value of -8.5/-8.6is rapidly reached on the northern flank of the massif. This means that amount and isotopic signature of precipitations obbey to different dynamics: the former is driven by the complex orographic structures involved, the latter by a more simple mechanism of separation at equilibrium (progressive depletion in heavy isotopes from the same cloud). In other words, exactly the opposite of the the Oreto case, where the two considered parameters showed the same kind of variations.

The related $\delta^{18}O$ contour map of Figure 2 has been obtained with the method already discussed.

4. Conclusions

In the two cases here discussed the relationships between rainfall amounts, oxygen isotopic composition of precipitations and geographic variables, as altitude, distance from the sea or geometry of the mountain chains, show an high variability.



Figure 5 Measured and modelled rain heights and Oxygen-18 contents in the Madonie Mounts area.

In the Oreto case a very simple geometric system is reflected in both the spatial distribution of rain heights and isotopic composition, that seem to obbey to the same mechanisms.

In the Madonie case a more complex geometry is reflected in rainfall amounts distributions, while δ^{18} O values depend on a more simple decay-type process (Rayleigh distillation).

In the first situation classical approaches, like vertical or distance from the sea gradients, may be both used in order to produce a reliable spatial distribution model of δ^{18} O in precipitations.

In the Madonie case only the distance from the sea influences isotopic signature.

In both cases the evaluation of the "geometric complexity" of the systems represents an useful tool to produce reliable isotopic models.

If the complexity is low, it is apparently easier to fit different models (Oreto case)

On the contrary the higher the complexity is, more difficult it is to find a reliable model but, at the same time, more difficult it is to find effective alternative models.

In other words, the complexity and uniqueness of the natural systems involved in isotopic fractionation processes represent the main constraints to the implementation of a modeling procedure universally appliable; each application must be consequently considered as a unique case that needs a specific calibration of interpretative models.

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