Isotopic composition of the precipitations in the central Mediterranean: Origin marks and orographic precipitation effects

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[1]   The isotopic composition of the rainfall in northwestern Sicily (Italy, central Mediterranean) was investigated in the period February 2002 to March 2003. A rain gauge network was installed and sampled monthly. The monthly values of the D and ^{18}O ratios showed a wide range that reflected seasonal climatic variations. Mean weighted values were used to define an isotopic model of precipitation. Temporal variations in deuterium excess were also investigated. Using mean volume weighted values, the Local Meteoric Water Line (LMWL) can be represented by the equation: $\delta D = 4.7\delta^{18}O - 8.2$ ($r^2 = 0.96$). Deuterium excess ($d = \delta D - 8\delta^{18}O$) was found to be strongly related to orography. The coastline samples were characterized by mean weighted deuterium excess values close to 12.5‰; samples from inland areas showed values of 16‰, while samples taken from the main reliefs showed values close to 19‰. In inland areas, isotopic exchange between raindrops and moisture could shift the deuterium excess values slightly. On the higher reliefs, the interaction between falling raindrops and orographic clouds could shift the deuterium excess values significantly. The low slope of the LMWL could be referred to the high deuterium excess values of the higher sites and is related to orographic precipitation rather than to evaporation processes during the fall of the raindrops. The results obtained suggest that local orographic features may significantly change the isotopic composition of precipitation.

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1.   Introduction and Background

[2]   Deuterium and oxygen isotopic ratios are often used as tracers to investigate hydrological paths. A good knowledge of the factors governing isotopic fractionation is helpful in understanding hydrogeological processes. The deuterium-excess parameter d, defined by *Dansgaard* [1964] as $d = \delta D - 8\delta^{18}O$, is one of the most useful isotopic tools in defining the formation site and trajectories of atmospheric moisture that give rise to precipitation. It has been observed to be essentially fixed at the site of sea-air interactions [*Craig and Gordon*, 1965]. *Gat and Carmi* [1970] used data with abundant rainfall in order to minimize the effects resulting from the evaporation of falling drops, and they stressed the role of the interaction between air masses and the Mediterranean Sea in governing the deuterium excess of precipitations. Later *Rindsberger et al.* [1983] showed that the isotopic compositions of precipitations in coastal east Mediterranean areas can serve as an information source regarding air mass origin and trajectories. Using long-term mean monthly values of the stations included in the Global Network for Isotopes in Precipitation (GNIP) database, *Araguás- Araguás et al.* [2000] observed that in the Northern Hemisphere deuterium excess varies seasonally showing lower values than 10‰ during summer months and higher values during winter months. *Cruz-San Julian et al.* [1992] described the correlation between *d*-excess values of precipitation and altitude in southeastern Spain as being the result of the evaporation of raindrops below the cloud base; so that the lower *d*-excess values of precipitation at sea level would be the result of a higher degree of evaporation of raindrops. Recently, the relationships between the isotopic composition of precipitation in the Mediterranean Basin and air circulation patterns and climate have been highlighted by *International Atomic Energy Agency* [2005]. The authors would therefore underline the promising role of the isotopic approach which could be used as an additional parameter when monitoring changes in circulation patterns. In many cases deuterium excess has been used to describe very different phenomena that are, everywhere, related to nonequilibrium fractionation processes.

[3]   When we investigate the isotopic composition of precipitation we should distinguish between the Synoptic and Mesoscale and the convective scales. In fact, while the first two cover phenomena between 20 km, 2,000 km and more, and give us isotopic information regarding air mass trajectories and/or vapor origin, the last one, i.e., the convective scale, covers phenomena between 0.2 and

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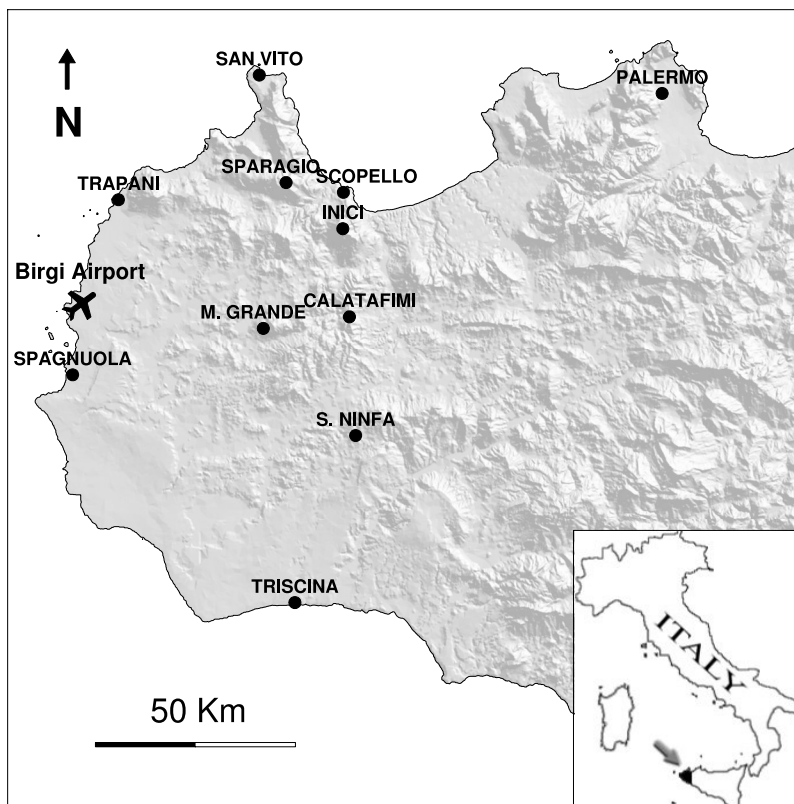[2] Dipartimento di Chimica e Fisica della Terra, Università degli Studi di Palermo, Palermo, Italy.

Figure 1. Scheme map of the studied area. Rain gauge grid is shown by solid circles.

20 km [*Houze*, 1993] and gives us information about local effects.

[4] The main objective of this work is to define an isotopic composition model of precipitation in the central Mediterranean, capable of distinguishing between large-scale processes and local ones. To reach this aim a high-density network of rain gauges has been used.

2. Methods

[5] A rain gauge network was installed in northwestern Sicily (Figure 1). The sites were chosen with the aim of accurately investigating the relationship between the isotopic composition of rainwater and the local morphological features. All the stations were sampled monthly and about 350cc of Vaseline oil were added in order to avoid evaporation processes. The amount of precipitation was also registered and air temperature data were collected at the climatic station located at Trapani-Birgi Airport. To relate storm trajectories to isotopic marks of precipitation, infrared satellite images and synoptic charts were obtained and analyzed (images from EUMETSAT dissemination service, synoptic charts from © British Crown copyright 2006, published by the Met Office UK).

[6] D/H water measurements were carried out using the *Kendall and Coplen* [1985] technique (reaction with zinc at 450°) and a mass spectrometer Finnigan Mat Delta Plus, while $^{18}O/^{16}O$ measurements were carried out by means of the CO_2-water equilibration technique [*Epstein and Mayeda*, 1953] using a mass spectrometer Analytical Precision AP2003. The analyses were performed at the Istituto

Nazionale di Geofisica e Vulcanologia (INGV), Palermo Department. The isotope ratios are expressed as deviation per mil (δ in ‰) from reference V-SMOW. The uncertainties are ± 0.1‰ and ± 1‰ for $\delta^{18}O$ and δD respectively.

3. Climatic Setting

[7] The Sicilian climate is a typically Mediterranean one. The Mediterranean climate is a special type of climate characterized by hot summer droughts and winter rain in the midlatitudes, north of the subtropical climate zone. In summer, the subtropical high-pressure cells drift toward the Northern Hemisphere (from May to August). This coincides with substantially higher temperatures than in winter and little rainfall (Figure 2). During the winter, the high-pressure cells drift back toward the equator, and the weather is dominated by cyclonic storms [*Bolle*, 2003]. Perturbations, generated prevalently in winter-spring in the west, move along northwest trajectories when the fronts are cold, and along southwest trajectories when the perturbations are hot. At ground level the mean monthly relative humidity is always higher than 70% and close to 80% during the rainy season (Figure 2). Climatic features and calcareous soil are responsible for the poor vegetation coverage of the studied area.

4. Results

[8] The Mediterranean climate is characterized by a cold rainy season and a hot dry one. Therefore, when all the monthly values are used to define a local meteoric water
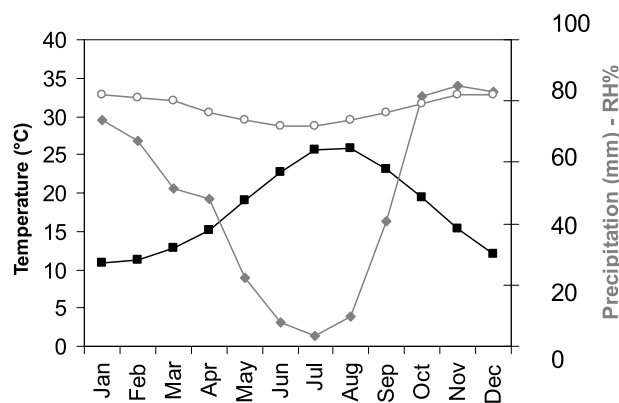
Figure 2. Mean values of air temperature (right axis), precipitation and relative humidity (left axis) at Trapani Birgi Airport.

line, said line will be strongly influenced by extreme values. (Figure 3). In fact, during the hot months only small amounts of rain fall and their isotopic abundances are very different from those of the other months. Sometimes these abundances reflect effects such as caused by the evaporation of raindrops during the fall itself (e.g., July 2002 samples from S. Vito and Triscina, see Table 1). On the other hand, some samples taken during the cold months show very negative values that may be ascribed to cold air masses coming from the north (e.g., December 2002 samples). We have therefore preferred to use volume weighted values that reflect the main processes involved.

[9] Weighted isotopic composition data of the monthly rain samples were computed for the period April 2002 to March 2003 (Table 2). The deuterium excess parameter d was computed according to *Dansgaard* [1964] definition $d = \delta D - 8\,\delta^{18}O$. Coastal sites show similar isotope ratios; close to -6.3 for oxygen and $-38\,\delta‰$ for hydrogen. These values are more negative with respect to the weighted mean value found by *Celle-Jeanton et al.* [2001] for the western Mediterranean region during the period 1985–1991 ($-4.45\delta^{18}O$ and $-25.96\delta‰$ at Tunis). Such differences could be explained by taking the long-term relation between isotopic composition of precipitation and climate into account. As shown by *Rozanski et al.* [1992], the weighted mean value significantly increased (more than 1 $\delta‰$) between 1986 and 1990 in response to the temperature increase, as compared with the 1970 to 1990 average.

[10] The altitude effect was estimated by plotting weighted isotopic composition versus the altitude of the rain gauges (Figure 4a). The linear regression equation is:

$$\delta^{18}O/‰ = -(0.0018 \pm 0.0001)H - (6.27 \pm 0.07) \quad r^2 = 0.96$$

where H is the altitude in m.

[11] The vertical oxygen isotopic gradient is $-0.18‰/100$ m; this value is close to that estimated by *Hauser et al.* [1980] ($-0.20‰/100$ m) and that estimated by *Favara et al.* [1998] ($0.21‰/100$ m) in different areas in Sicily. A vertical oxygen isotopic gradient value, close to that observed in Sicily, was also found using the data obtained from stations located in several sites in Europe ($-0.21‰/100$ m) [*Poage*

and Chamberlain, 2001]. This suggests that it is not strongly dependent on local features. δD is also well related to altitude (Figure 4b) in accordance with the equation:

$$\delta D/‰ = -(0.0085 \pm 0.0009)H - (37.68 \pm 0.50) \quad r^2 = 0.90$$

from which a vertical hydrogen isotope gradient of $-0.85‰/100$ m can be deduced.

[12] By plotting d versus altitude (Figure 5), a good correlation was found. As shown in Figure 5 the correlation between d and altitude is given by the equation:

$$d/‰ = (0.0061 \pm 0.0007)H + (12.5 \pm 0.3) \quad r^2 = 0.90$$

Nevertheless we can distinguish three different groups: the six samples collected at an altitude of <100 m a.s.l., fall in group A; they are located at random in a small range of d. The three samples with 400 m < altitude < 700 m a.s.l., fall in group B; they hardly ever show any d variation. The two samples collected at an altitude $\approx$ 1,000 m a.s.l., fall in group C; they are located in the main reliefs of the studied area: M. Sparagio and M. Inici. These samples are characterized by comparatively very high values of d. As regards the samples belonging to group C we must take into account the contribution of the local orographic clouds. In fact, wherever a layer of air is subjected to an upward motion as a result of topographically induced wave motions and is sufficiently moist, a cloud will form [*Houze*, 1993]. Even in flows over small hills, orographic clouds can enhance local precipitations. Under these conditions, there is insufficient time for precipitation to form solely within the cloud. However, if there are small droplets falling from higher-level clouds, they will grow rapidly as they pass through the saturated air within the orographic cloud, producing bigger drops at the ground (by coalescence). This process is known as the seeder-feeder mechanism [*Klemp*, 1992; *Houze*, 1993].
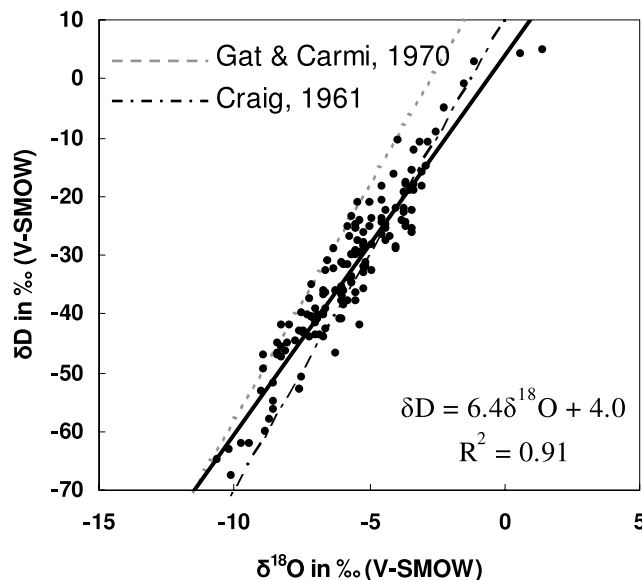

Figure 3. $\delta D‰$ versus $\delta^{18}O‰$ diagram. Monthly values of the period February 2002 to March 2003 are shown.

Table 1. Monthly Isotopic Composition of Rainwater at Each Site[a]

Month	SN (470 m a.s.l)				TR (13 m a.s.l)				SG (15 m a.s.l)				TP (12 m a.s.l)				SP (1100 m a.s.l)				IN (980 m a.s.l)			
	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d
Feb 2002	25	−5.4	−21.0	22	21	−4.5	−24.5	12	8	−3.6	−17.7	11	4	−1.5	−0.8	11	43	−6.3	−28.9	22	22	−5.6	−23.5	21
Mar 2002	15	−3.4	−15.6	12	12	−3.3	−18.1	8	15	−2.8	−10.8	12	10	−1.1	2.8	12	60	−4.5	−18.3	18	36	−5.5	−24.9	19
Apr 2002	32	−5.7	−26.9	19	23	−4.5	−26.5	10	26	−4.9	−28.4	11	23	−5.9	−31.6	16	18	−7.4	−43.2	16	23	−8.5	−51.8	16
May 2002	73	−3.7	−19.5	10	53	−3.1	−11.0	14	33	−3.0	−18.3	6	33	−3.3	−19.0	7	76	−5.3	−24.3	18	65	−5.4	−29.5	14
Jun 2002	5	n.a.	n.a.		8	−4.0	−29.0	3	7	−3.6	−24.7	4	5	−3.4	−25.4	2	7	−6.2	−46.6	3	18	−7.6	−53.0	8
Jul 2002	8	1.4	4.8	−6	28	0.6	4.3	−1	3	n.a.	n.a.		6	−3.7	−22.1	8	4	−7.0	−41.5	15	8	−7.2	−43.9	14
Aug 2002	37	−5.2	−28.4	13	13	−4.0	−28.5	4	27	−3.4	−22.6	5	27	−4.9	−32.9	6	65	−6.7	−40.1	14	89	−5.6	−33.9	11
Sep 2002	11	−5.1	−32.1	9	14	−3.8	−24.2	6	20	−6.9	−40.8	14	27	−5.6	−30.1	15	41	−7.1	−35.2	22	68	−7.9	−42.0	21
Oct 2002	89	−8.2	−45.8	20	58	−5.4	−28.2	15	96	−5.5	−25.6	18	56	−5.6	−30.0	15	104	−8.4	−44.8	22	95	−9.0	−53.4	19
Nov 2002	141	−6.6	−36.4	16	120	−5.3	−29.5	13	100	−6.6	−32.7	20	113	−6.6	−39.4	13	168	−8.0	−45.2	19	184	−7.6	−43.0	18
Dec 2002	119	−11.4	−74.2	17	154	−10.1	−67.7	13	118	−9.4	−62.1	13	91	−8.7	−58.0	12	193	−10.2	−63.0	19	187	−10.6	−64.9	20
Jan 2003	102	−7.1	−40.5	16	86	−5.1	−31.2	10	96	−5.6	−34.8	16	71	−6.6	−42.5	10	184	−8.4	−47.8	19	150	−7.5	−39.8	20
Feb 2003	57	−8.2	−42.4	23	74	−7.1	−40.7	16	71	−7.4	−42.9	16	53	−7.2	−37.5	20	93	−8.9	−47.1	24	96	−8.9	−49.4	22
Mar 2003	33	−4.5	−20.8	15	24	−2.5	−9.2	11	26	−3.6	−18.0	11	18	−7.0	−43.6	12	22	−6.2	−36.0	14	25	−7.7	−44.6	17

Month	MG (675 m a.s.l)				CA (400 m a.s.l)				SV (15 m a.s.l)				SC (60 m a.s.l)				IP (85 m a.s.l)				Rainy Days	Mean Temperature
	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d	mm	$\delta^{18}O$	δD	d		
Feb 2002	28	−5.8	−25.3	21	13	−4.1	−16.4	16	n.a.	n.a.	n.a.		n.a.	n.a.	n.a.		n.a.	n.a.	n.a.		2	14.0
Mar 2002	23	−3.9	−10.4	21	21	−5.2	−26.3	15	17	−2.2	−4.9	13	28	−3.3	−12.1	14	20	−5.5	−29.2	15	1	15.5
Apr 2002	6	−4.4	−25.4	10	20	−5.2	−28.8	13	37	−5.9	−38.5	9	20	−6.1	−40.9	8	46	−6.8	−43.6	11	4	16.0
May 2002	64	−3.7	−22.9	7	53	−4.5	−23.7	12	35	−3.5	−18.9	9	59	−2.9	−14.9	8	61	−4.0	−22.1	10	5	19.8
Jun 2002	6	−5.5	−38.0	6	15	−5.2	−35.7	6	6	−3.4	−26.2	1	6	−3.6	−25.3	4	11	−5.3	−41.9	1	1	22.8
Jul 2002	6	−6.0	−40.9	7	7	−4.4	−27.7	8	8	−6.0	−36.9	11	4	n.a.	n.a.		10	−5.8	−37.8	9	2	25.6
Aug 2002	51	−5.6	−34.8	10	49	−6.0	−35.3	13	65	−6.0	−37.8	10	54	−4.2	−26.8	7	56	−4.4	−24.8	10	1	25.3
Sep 2002	11	−5.0	−21.0	19	23	−5.1	−28.5	12	13	−3.0	−15.9	8	21	−4.4	−22.5	13	33	−5.0	−25.2	15	3	23.0
Oct 2002	39	−6.3	−32.3	18	93	−7.1	−40.7	16	49	−6.7	−39.9	14	84	−6.9	−40.4	15	29	−5.7	−34.1	12	6	19.7
Nov 2002	97	−6.7	−36.7	17	148	−6.5	−31.0	21	93	−6.0	−31.5	17	153	−5.8	−31.6	15	73	−5.2	−27.9	14	10	17.5
Dec 2002	136	−11.6	−72.2	21	145	−9.7	−62.3	15	100	−8.5	−55.0	13	143	−8.5	−56.2	12	100	−8.8	−60.0	10	12	13.4
Jan 2003	110	−7.0	−39.1	17	128	−7.0	−41.2	15	84	−7.5	−50.8	9	121	−5.9	−36.1	11	127	−6.7	−44.1	10	13	12.2
Feb 2003	41	−8.2	−47.3	18	75	−8.4	−46.7	21	55	−6.7	−36.2	17	81	−8.1	−46.4	18	98	−7.3	−40.4	18	11	9.1
Mar 2003	22	−4.9	−24.0	15	19	−5.5	−30.0	14	12	−5.5	−36.6	7	8	−5.2	−32.0	10	12	−5.2	−33.2	8	5	11.2

[a]Rainy days and mean temperature (°C) at Birgi Airport are also given. SN, S. Ninfa; TR, Triscina; SG, Spagnola; TP, Trapani; SP, Sparagio; IN, Inici; MG, M. Grande; CA, Calatafimi; SV, S. Vito; SC, Scopello; IP, INGV-PA.

Table 2. Volume Weighted Average Annual Isotopic Composition and Computed d-Excess[a]

			April 2002 to March 2003				
Rain Gauge	Latitude	Longitude	Altitude, m asl	mm	δD	$\delta^{18}O$	d-Excess
S. Ninfa	37°46′	12°53′	470	708	−40.9	−7.1	16.2
Triscina	37°35′	12°48′	13	657	−35.9	−6.0	11.9
Spagnuola	37°50′	12°28′	15	626	−36.7	−6.3	13.9
Trapani	38°01′	12°32′	12	524	−39.2	−6.5	12.7
Sparagio	38°03′	12°46′	1100	976	−46.7	−8.2	19.2
Inici	38°00′	12°51′	980	1008	−46.9	−8.1	18.1
M. Grande	37°53′	12°44′	675	590	−43.2	−7.4	15.9
Calatafimi	37°52′	12°52′	400	775	−40.9	−7.1	16.1
San Vito	38°10′	12°44′	15	555	−40.0	−6.5	12.3
Scopello	38°02′	12°51′	60	752	−37.7	−6.3	12.5
Palermo	38°09′	13°18′	85	657	−38.7	−6.3	11.7

[a]Coordinates of each site are also given.

[13] In the studied areas cap clouds can be seen all year round on the main reliefs, while several kinds of orographic clouds can be seen occasionally over inland areas.

[14] Because of the location of western Sicily's main reliefs, the main source of moisture is direct evaporation from the Mediterranean Sea. In fact, the poor vegetation coverage and the lack of significant evaporating water bodies in the inland area, have lead us to believe that recycled moisture is negligible with respect to maritime moisture. Orographic clouds form locally and we know that the Mediterranean Sea is a classic example of a reservoir producing water vapor characterized by high deuterium excess [Gat and Carmi, 1970; Gat et al., 2003]. Thus reasonably high values of d should be found in orographic clouds. As far as the isotopic abundances are concerned, the process that enhances the size of the droplets may be approximately considered as being a mixing between two amounts of water having different isotopic compositions. In this hypothesis, if the relative fractions of seeder clouds and feeder clouds are known and the isotopic composition of the precipitation at the ground is given, the hypothetical deuterium excess of orographic clouds can be computed. A schematic illustration of the process is shown in Figure 6a in which the d plotted values are of Scopello (d = 12.5, 60 m a.s.l.) and M. Inici (d = 18.1; 980 m a.s.l.) sites. Since a very good correlation was found between the precipitation amounts of the two sites ($P_{Scopello} = P_{M.Inici}*0.83$, $r^2 = 0.95$; where P is the amount of rain, Figure 6b), and as they are very close (horizontal distance = 6 Km, Figure 6c), we assume that the contribution of the higher clouds (generally with base altitude > 1,000 m a.s.l.) is the same for the two sites. We therefore estimated the orographic fraction of the precipitation to be about 17% of the total collected rain. Using these values an approximate mean value of d close to 45 was computed for orographic clouds.

[15] This value is higher than that found by Gat et al. [2003] (ranging between 9.2 and 34.5‰) for Mediterranean vapor, so that the origin of air masses cannot be considered the only factor producing deuterium enrichment. Moreover, rain samples showing deuterium excess values up to 40‰ have been found at Cheju Island (Korea) [Lee et al., 1999]. On this island the formation of cap clouds is a frequent process and for this reason it has been chosen for the ACE-ASIA aerosol-cloud interaction experiment [Bower et al., 2001].

[16] We cannot model the mean isotopic composition of the precipitation by analyzing only the monthly data because they strongly reflect seasonal variations. Furthermore the monthly samples often represent mixing between several rain events having different origins. Nevertheless, twice the monthly isotopic composition of the precipitation was in good agreement with the processes previously described. In fact, samples taken in February 2002 and
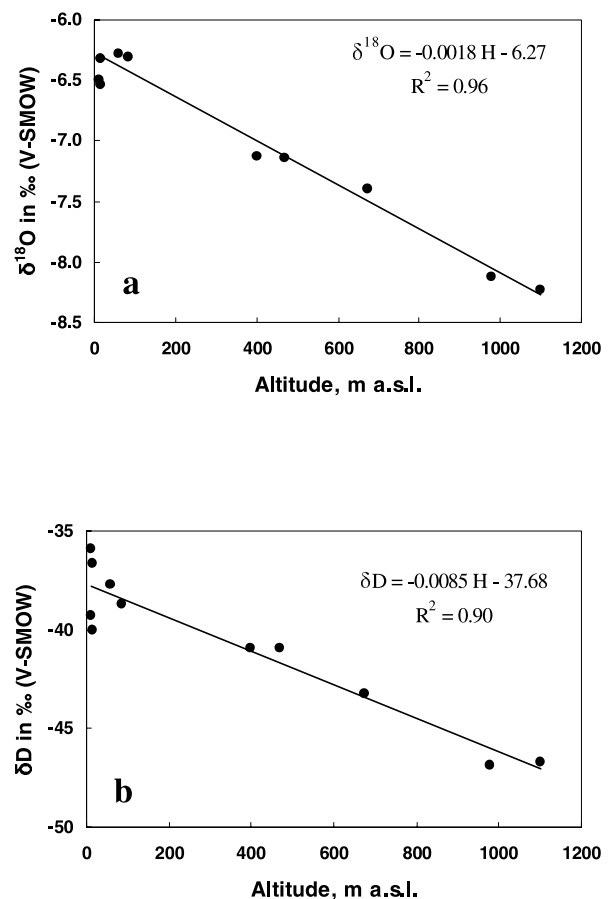

Figure 4. (a) Weighted $\delta^{18}O$‰ values versus altitude (February 2002 to March 2003). (b) Weighted δD‰ values versus altitude (February 2002 to March 2003).
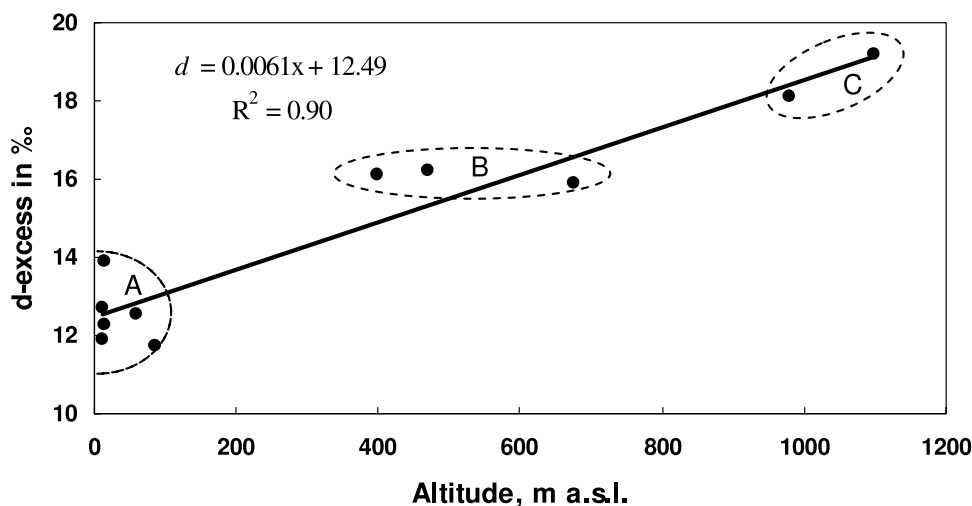
Figure 5. Weighted d ‰ values versus altitude (February 2002 to March 2003).

January 2003 from the rain gauges situated along the coast, fit well with the Global Meteoric Water Line (GMWL) described first by *Craig* [1961], while the other samples show higher values of d (Figure 7).

[17] In January 2003 group A samples fitted very well with GMWL ($R^2 = 0.99$); group B samples had intermediate d values while group C samples had d values about 10 units ‰ higher than those of group A. If the different d values were due to evaporation of rain during the fall, the group A samples should have been evaporated and, as a consequence, should have been enriched. Moreover, evaporated rain samples usually lie along low-slope lines [*Yurtsever and Gat*, 1981]. Since in this case these requirements were not verified, we assume that significant evaporation of rain during the fall did not occur. In addition, according to *Stewart* [1975], drops evaporating in atmospheres at intermediate and high relative humidity gradually attain equilibrium with the atmospheric vapor. Since relative humidity of the atmosphere column below 1,200 m a.s.l. is usually higher than 70% (Figure 7), evaporation, and consequently kinetic fractionation, is believed unlikely. Even though the isotopic effects, due to evaporation of rain, are believed negligible; further studies could supply additional tools to quantitatively estimate such effects.

[18] Storms generating precipitations in January 2003 came from the Atlantic Ocean (Figure 8). This particular case of samples fitting the GMWL suggests that general circulation processes and local fractionation phenomena didn't change the isotopic composition of the water vapor that generated precipitations.

5. Local Meteoric Water Line

[19] Having described the processes governing the isotopic composition of precipitations, we will now define the equation describing the Local Meteoric Water Line (LMWL):

$$\delta D = (4.70 \pm 0.32)\delta^{18}O - (8.2 \pm 2.2) \quad r^2 = 0.96 \quad (1)$$

The slope of the LMWL (Figure 9) is lower than that of the GMWL and of that defined in the same area by *Favara et*

al. [1998]. As a result of the low value of the slope, the intercept is a negative number. Since stations at an altitude higher than 400 m a.s.l. are affected by local orographic clouds we also defined the LMWL* using data taken only from the coastline stations (Figure 9).

[20] The LMWL* equation is therefore:

$$\delta D = (7.00 \pm 1.84)\delta^{18}O + (6.2 \pm 11.6) \quad r^2 = 0.78 \quad (2)$$

The LMWL* may be considered representative of mesoscale processes. That's to say that coastline sites are not influenced by local features. High values of d in sites situated at elevations higher than 400 m a.s.l. (i.e., groups B and C), produce a "lever effect" that rotates the LMWL around the area of dots, which refer to the coastline sites (group A), that acts as a fulcrum (Figure 9).

[21] Most of the local groundwater [*Liotta*, 2004] fell within the GMWL and the MMWL (Mediterranean Meteoric Water Line) [*Gat and Carmi*, 1970]. However, they fell above the LMWL (Figure 10), which suggests that the groundwater is generally characterized by higher deuterium excess. The explanation of this comes from the spatial distribution of the rain. As well known, mountains represent the main recharge area of aquifers; the largest amount of precipitation in the area under study can be found at M. Sparagio and M. Inici, where high values of d have been measured. This leads to high values of d in the groundwater.

6. What Can Enhance Deuterium Excess of Orographic Cloud Droplets?

[22] Condensation processes have not been isotopically studied enough, whereas evaporation processes have been modeled by several authors [*Craig and Gordon*, 1965; *Merlivat*, 1970; *Stewart*, 1975; *Merlivat*, 1978; *Cappa et al.*, 2003]. Diffusive transport leads to greater fractionation of the light isotopomers during nonequilibrium processes when molecular diffusion is important [*Cappa et al.*, 2003]. As a result of the different diffusion rates of molecules $^1H_2^{16}O$ $^1H^2H^{16}O$ $^1H_2^{18}O$, kinetic fractionation processes could produce an excess of deuterium in the forming phase,
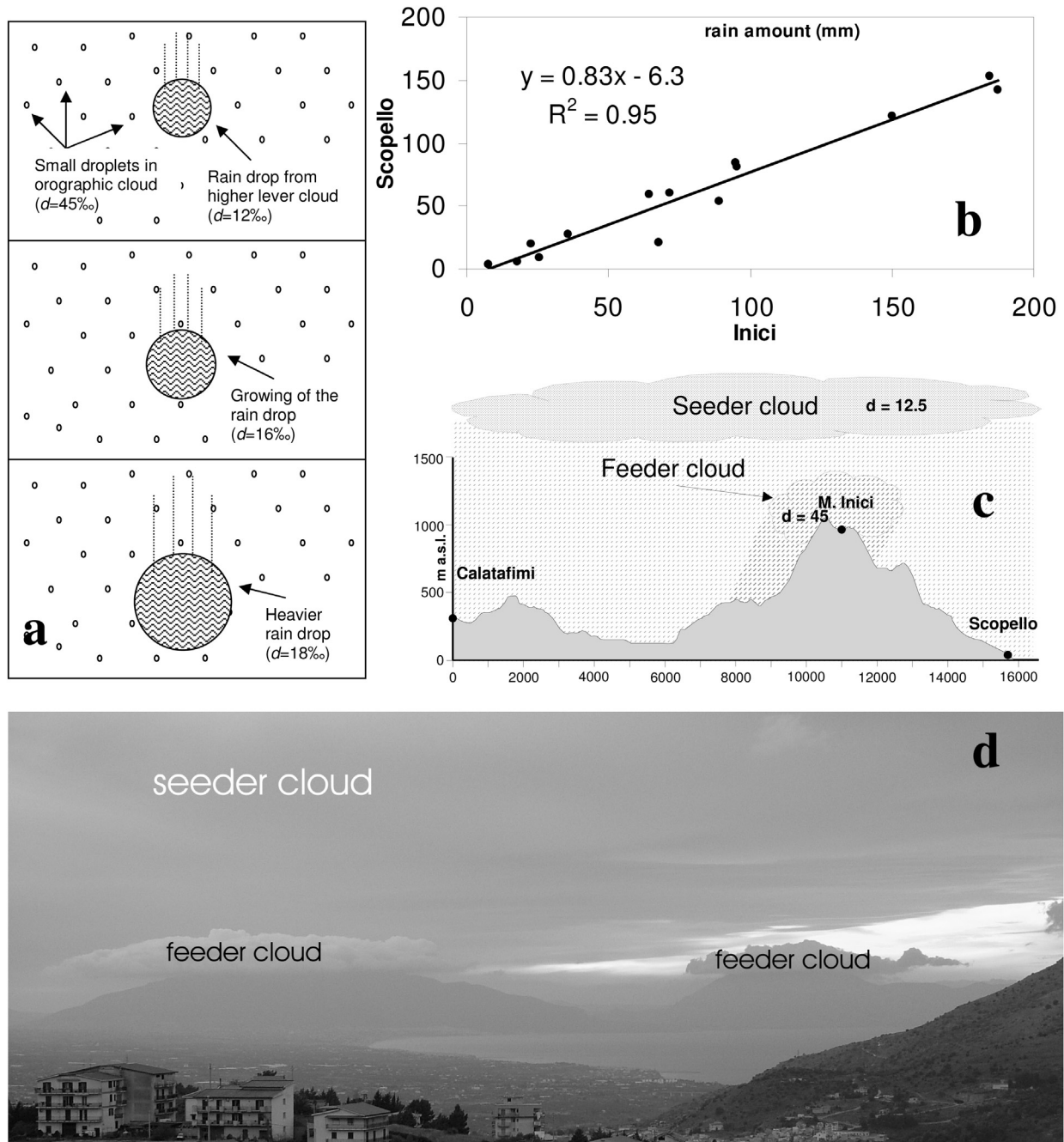
Figure 6. Isotopic effect of the seeder feeder mechanism: (a) growth of the drops coming from seeder clouds during their fall through orographic clouds (not in scale), (b) scattering diagram of monthly rain amounts collected at the Inici and Scopello sites, (c) schematic illustration of the seeder-feeder mechanism at Mount Inici, and (d) picture of Mount Inici (on the left) and Mount Sparagio (on the right) taken during a rainy day.

with respect to the content coming from equilibrium processes.

[23] The d-excess parameter is thought to be the most useful stable-isotope property for the characterization of vapor origin; it is essentially fixed at the site of sea-air interactions by the nonequilibrium transport processes involved [*Craig and Gordon*, 1965]. However, if local kinetic condensation processes do occur, the d-excess parameter may change. In fact solid precipitations often show higher d-values due to nonequilibrium rapid condensation during the growth of ice particles [*Jouzel and Merlivat*, 1984].

[24] The existence of an isotopic kinetic effect at vapor condensation was theoretically predicted by *Stewart* [1975]. According to *Stewart* [1975], condensation of drops in supersaturated atmospheres is the identically opposite process to drop evaporation in undersaturated atmospheres; so
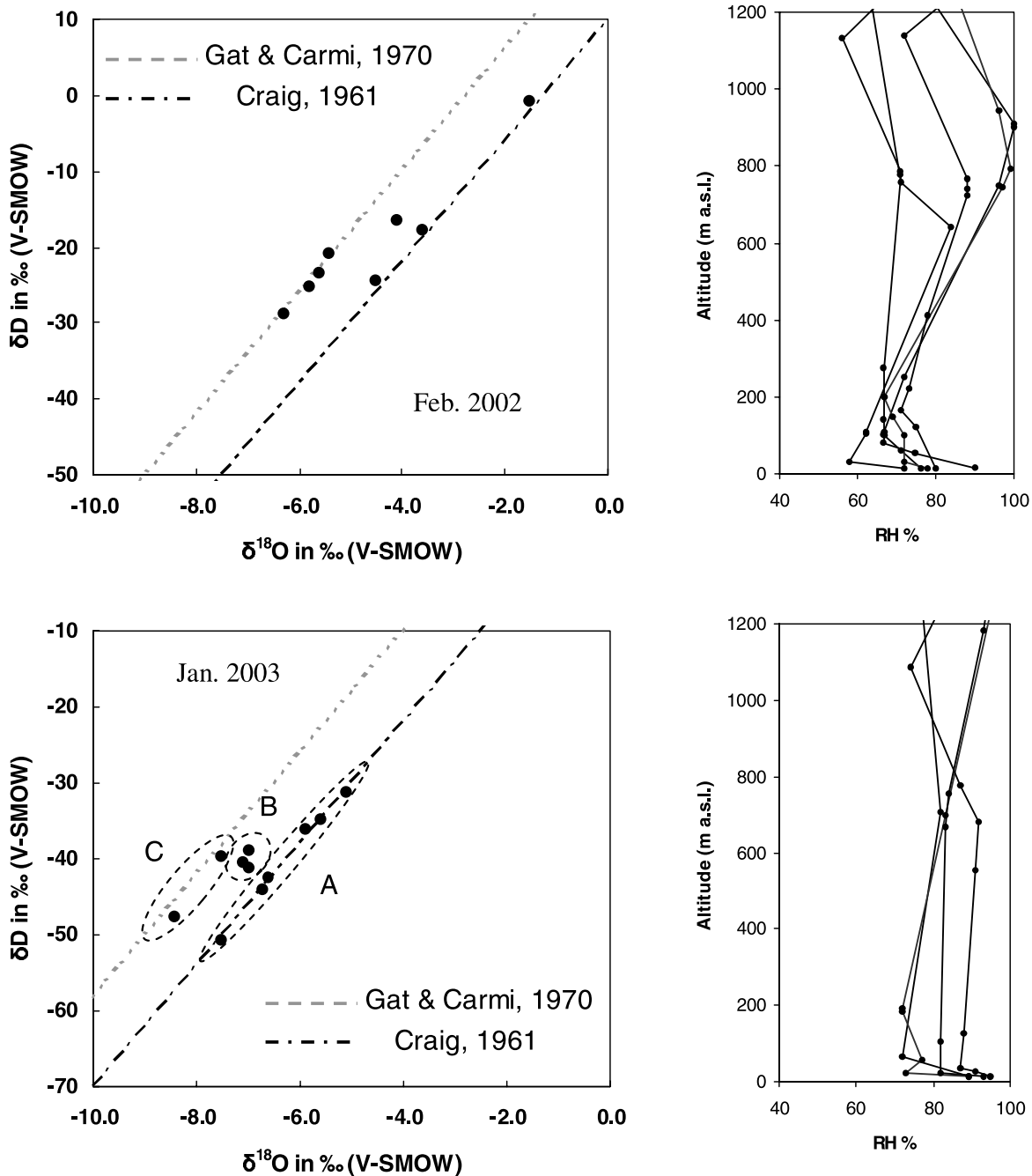
Figure 7. (top left) δD‰ versus δ^{18}O‰ diagram for monthly isotopic composition referred to February 2002. A few rainy days were registered in February 2002 and, on the basis of EUMETSAT images, air masses coming from the Atlantic Ocean probably generated orographic clouds also in M. Grande and S. Ninfa that showed values close to that of M. Inici and M. Sparagio. (top right) Vertical profiles of relative humidity (16429 LICT Trapani observations at 00Z 07, 06Z 07, 12Z 07, 18Z 07 and 00Z 08). (bottom left) δD‰ versus δ^{18}O‰ diagram for monthly isotopic composition referred to January 2003. (bottom right) Vertical profiles of relative humidity (16429 LICT Trapani observations at 06Z 24, 12Z 24, 18Z 24 and 00Z 25).

equations for isotopic fractionation during evaporation of falling drops apply equally well to fractionation during condensation because the rate-limiting step in both processes is the diffusion of the vapor in the atmosphere. Although condensation of droplets is a nonequilibrium process, it usually seems to occur in isotopic equilibrium between cloud droplets and atmospheric vapor because super saturation in clouds is normally modest [*Stewart*, 1975]. Nevertheless, the
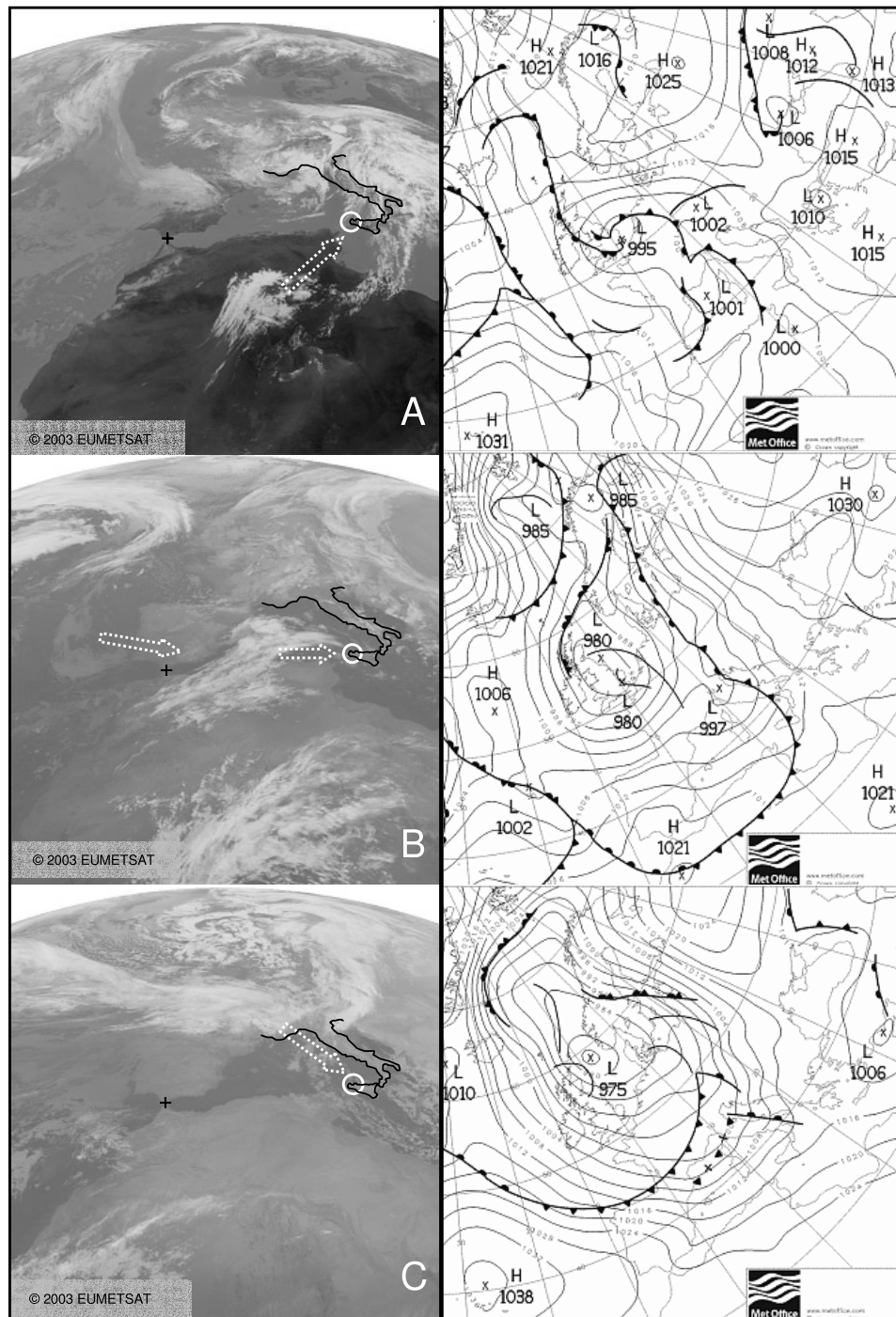
Figure 8. Selected infrared images and synoptic charts of Europe. (a) In June 2002 it rained mainly on the 6 and 7 June. The air masses came from the southwest. (b) In January 2003 it rained mainly on the 24 January. The air masses came from the Atlantic Ocean. (c) In February 2003 it rained mainly on the 4 February. The air masses came from the north (see text for details). Images on the left were provided by EUMETSAT dissemination service, and images on the right are © British Crown copyright 2006, published by the Met Office UK.

first step in droplet formation implies the diffusion of water molecules around the condensation nuclei; therefore kinetic effects should be expected to occur. When clouds form, it takes a long time before rain starts to fall, therefore the droplets have enough time to reach isotopic equilibrium with the surrounding vapor. In orographic clouds the life time of droplets is always very short since they form where a lifting is induced by orography and dissolve quickly when surround-
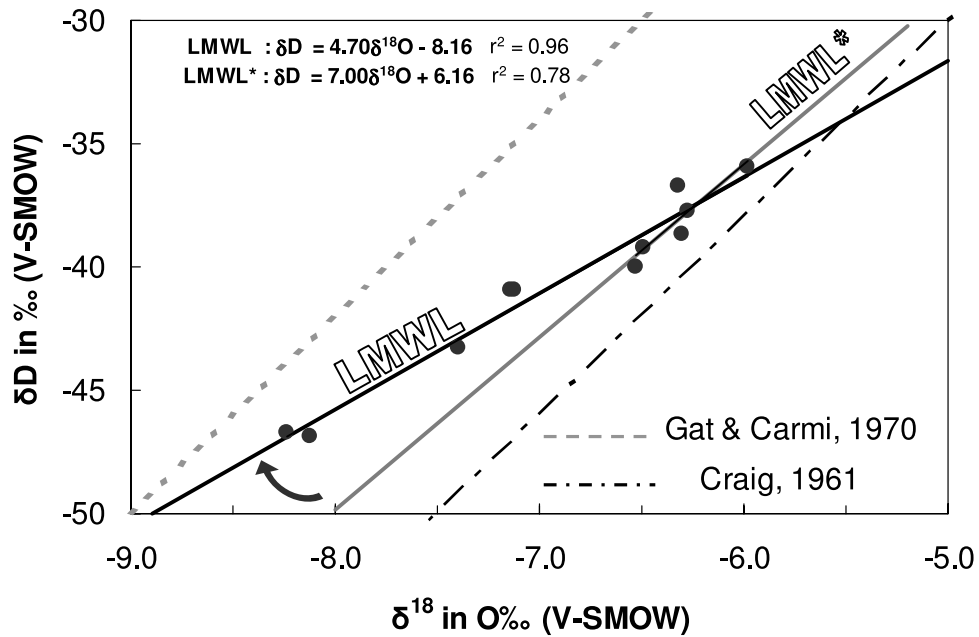
Figure 9. Local Meteoric Water Lines (LMWL and LMWL*) plotted and compared to the Global Meteoric Water Line (GMWL) defined by *Craig* [1961] and to the Mediterranean Meteoric Water Line (MMWL) defined by *Gat and Carmi* [1970]. Mean volume weighted values have been used (see text for details).

ing conditions are reestablished. Under these conditions in-cloud droplets cannot be in isotopic equilibrium with the surrounding vapor. Therefore the liquid phase may be at last enriched in deuterium.

7. Hypothetical Isotopic Composition of Orographic Cloud Droplets

[25] Orographic clouds can be considered as being a particular kind of fog, so that some information about their isotopic composition may by deduced from studies of that phenomena. However, we must take into account the fact that none of the fog collectors can avoid isotopic exchange and, hence, reequilibration between the liquid phase and vapor. Generally fog is isotopically enriched compared to local rain [*Gonfiantini and Longinelli*, 1962; *Aravena et al.*, 1989; *Ingraham and Matthews*, 1995; *Scholl et al.*, 2002]. A famous example of upslope fog that occurs during the formation of orographic clouds may be observed in Hawaii. *Scholl et al.* [2002] analyzed the isotopic composition of fog collected at East Maui; the collected samples showed an isotopic signature that was more enriched than that of the local rainfall. *Harris et al.* [1999] found high values of deuterium excess in the groundwater of Table Mountain (Cape Peninsula, South Africa). The area, characterized by a typically Mediterranean climate, is famous for the cap cloud that forms over the top of the mountain that enhances the amount of local precipitation. Springs on the slopes of Table Mountain show d values about 5‰ higher than the groundwater collected a few kilometers to the south, in the Cape Flats Aquifer. The mechanism proposed in this paper would justify the observation of *Harris et al.* [1999].

[26] The isotopic composition of orographic cloud droplets is expected to be enriched both in ^{18}O and in D, since it

represents the first step in the condensation of marine vapor and it also is expected to have high values of deuterium excess as previously discussed. In Figure 11, the hypothetical isotopic composition of orographic cloud droplets is plotted. (see caption for detail).

8. Temporal Variation of Deuterium Excess

[27] If we analyze the temporal variation of *d*, some useful information on the mesoscale circulation paths can
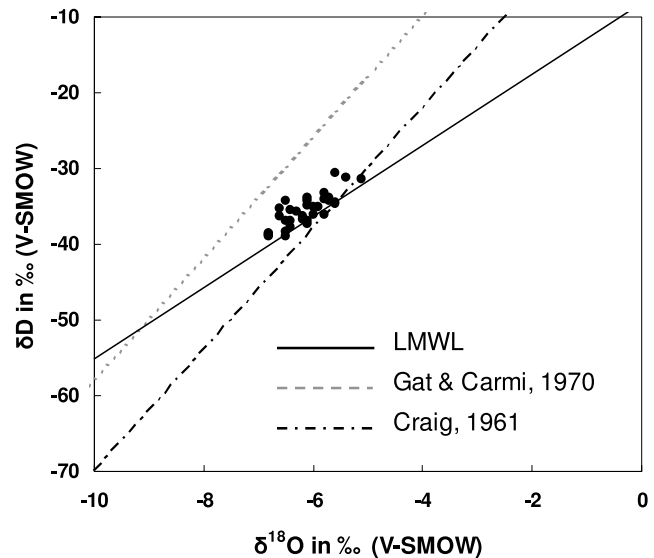

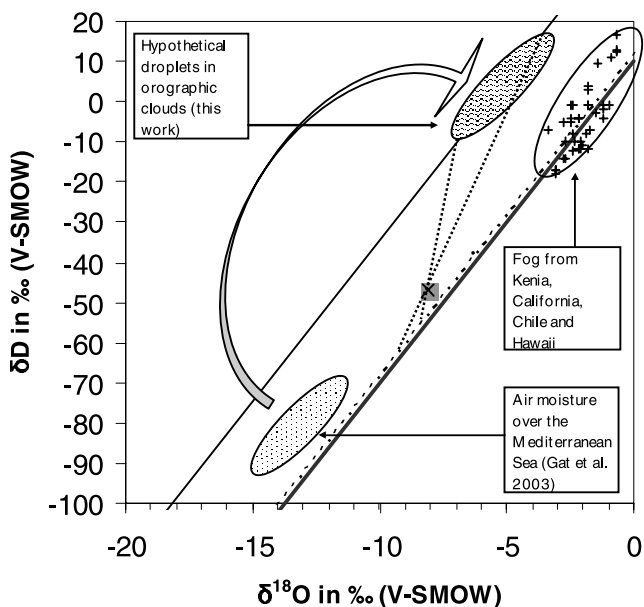**Figure 10.** δD‰ versus δ^{18}O‰ diagram. Local groundwater samples are plotted. The LMWL, GMWL and MMWL are also drawn.

Figure 11. δD‰ versus δ^{18}O‰ diagram. The solid bold line indicates the GMWL ($d = 10$). The dashed line has $d = 12.5$ (i.e., the average mean weighted values of the coastal sites). The solid line has $d = 45$ (i.e., the computed deuterium excess for orographic cloud droplets). The shaded dot indicates the mean weighted composition of the precipitation at Mount Inici. The dotted lines indicate the two possible mixing lines between orographic cloud water and higher-level cloud water.

be deduced. In Figure 12 mean weighted values of d have been compared with the mean values of Global Network for Isotopes in Precipitation (GNIP) database computed by *Araguás-Araguás et al.* [2000] for the Northern Hemisphere, and with the mean monthly temperatures of western Sicily. The high seasonal variation in d-excess between summer and winter reflects the climatic features and circulation patterns of the studied area. In fact, when cold air masses, characterized by low relative humidity, travel over seawater, kinetic fractionation produces high deuterium excess values in the vapor, whereas the movement of warm air masses, usually characterized by high relative humidity, leads to lower deuterium excess values. According to the above mentioned theoretical considerations., during June 2002 hot air masses came from Algeria (Figure 8a) and produced precipitations with a very low deuterium excess, whereas in February 2003 cold air masses coming from the North Sea produced precipitation with very high values of d (Figure 8c).

9. Conclusions and Implications

[28] The mean isotopic composition of the precipitation in the studied area is similar along the coast line, whereas it changes slightly in inland areas and more significantly over hills. The local contribution of orographic clouds to the total amount of rainfall in the studied area has been taken into consideration. The local vapor forms mainly on the Mediterranean Sea, which is a classic example of reservoir producing water vapor characterized by high deuterium excess. However, the high values of d found in the precip-
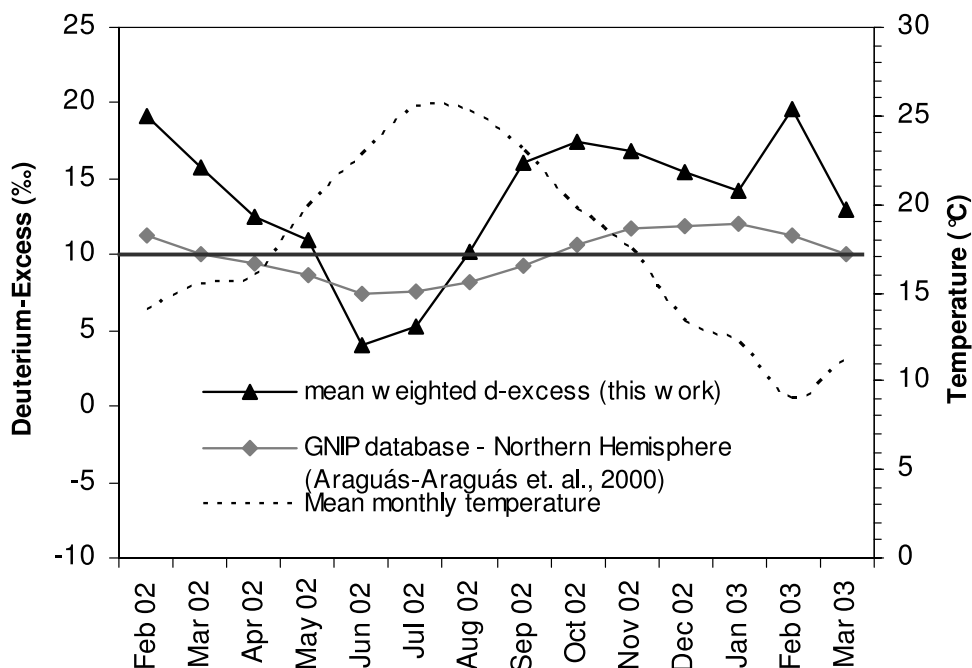

Figure 12. Deuterium-excess versus time. Mean weighted d-excess values of the period February 2002 to March 2003 are compared with the mean values of Global Network for Isotopes in Precipitation (GNIP) database computed by *Araguás-Araguás et al.* [2000] for the Northern Hemisphere and mean monthly temperature of western Sicily (Trapani Birgi Airport). The high shifts in d-excess between the summer and winter periods are due to the climatic features of the studied area.

itation of the main reliefs can only be explained by invoking another factor able to enhance deuterium excess.

[29] Similarly to evaporation, when droplets of orographic clouds form, the higher diffusivity of $^1H^2H^{16}O$, with respect to $^1H_2^{18}O$, produces an enrichment of deuterium in the liquid phase. Droplet formation may be considered a mainly diffusive process, so that a kinetic effect is expected, whereas after formation, isotopic exchange leads to isotopic equilibrium with the surrounding vapor.

[30] We have modeled the isotopic evolution of rain falling through orographic clouds (seeder-feeder mechanism) that partially contributes to the total amount of rainfall at the ground. On the basis of the relative contribution of seeder and feeder clouds, the mean hypothetical deuterium excess value of orographic clouds has been computed to be close to 45. In addition, the droplets of the orographic clouds should be enriched as they represent the first condensate fraction of the surrounding marine vapor. The high values of deuterium excess computed for orographic cloud droplets have been discussed taking into account the fact that kinetic fractionation during condensation can also occur.

[31] The results obtained also imply that where orographic precipitations occur, the local isotopic composition could shift significantly with respect to the surrounding areas.

[32] Even though the process has been described in the central Mediterranean area, which is characterized by peculiar features, the orographic d-excess contribution could well change the isotopic composition of precipitation significantly wherever orographic clouds form.

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