Journal of Atmospheric Chemistry (2005) 52: 185–202
DOI: 10.1007/s10874-005-2007-7

Oxygen and Hydrogen Isotopic Signatures of Large Atmospheric Ice Conglomerations

J. MARTINEZ-FRÍAS[1], A. DELGADO[2], M. MILLÁN[3], E. REYES[2], F. RULL[1,4], D. TRAVIS[5], R. GARCIA[6], F. LÓPEZ-VERA[7], J. A. RODRÍGUEZ-LOSADA[8], J. A. MARTIN-RUBI[9], J. RAYA[2] and E. SANTOYO[10]

[1]*Planetary Geology Laboratory, Centro de Astrobiologia CSIC-INTA), Associated to the NASA Astrobiology Institute, Ctra de Ajalvir, km 4, 28850 Torrejón de Ardoz, Madrid, Spain, e-mail: martinezfrias@mncn.csic.es*
[2]*Estacion Experimental del Zaidin, CSIC, Prof. Albareda, 1 18008 Granada, Spain*
[3]*Fundación CEAM, Parque Tecnológico de Paterna, C/Charles Darwin, 14, 46980 Valencia, Spain*
[4]*Dpto. Física de la Materia Condensada, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Valladolid, P° Prado de la Magdalena s/n, 47005 Valladolid, Spain*
[5]*Department of Geography and Geology, University of Wisconsin-Whitewater, Whitewater WI, 53190, USA*
[6]*Museo Nacional de Ciencias Naturales (CSIC), José Gutiérrez Abascal, 2, 28006 Madrid, Spain*
[7]*Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain*
[8]*Dep. Edafología y Geología, Fac. Biología, U. La Laguna, 38206 La Laguna (Tenerife), I. Canarias, Spain*
[9]*Laboratorios IGME, La Calera, 1. 28760 Tres Cantos, Madrid, Spain*
[10]*Centro de Investigación en Energía, Universidad Nacional Autónoma de México, Priv. Xochicalco s/n Apdo. Postal 34, Temixco, Mor. 62580, Mexico*

(Received: 23 March 2004; accepted: 8 August 2005)

Abstract. Specific studies about the stable isotope composition ($^{18}O/^{16}O$ and D/H) of atmospheric icy conglomerations are still scarce. The present work offers, for the first time, a very detailed analysis of oxygen and hydrogen isotopic signatures of unusually large ice conglomerations, or "megacryometeors", that fell to the ground in Spain during January 2000. The hydrochemical analysis is based on the bulk isotopic composition and systematic selective sampling (deuterium isotopic mapping) of eleven selected specimens. $\delta^{18}O$ and δD (V-SMOW) of all samples fall into the Meteoric Water Line matching well with typical tropospheric values. The distribution of the samples on Craig's line suggests either a variation in condensation temperature and/or different residual fractions of water vapour (Rayleigh processes). Three of the largest megacryometeors exhibited unequivocally distinctive negative values ($\delta^{18}O = -17.2‰$ and $\delta D = -127$ ‰ V-SMOW), ($\delta^{18}O = -15.6‰$ and $\delta D = -112‰$ V-SMOW) and ($\delta^{18}O = -14.4‰$ and $\delta D = -100‰$ V-SMOW), suggesting an atmospheric origin typical of the upper troposphere. Theoretical calculations indicate that the vertical trajectory of growth was lower than 3.2 km. During the period in which the fall of megacryometeors occurred, anomalous atmospheric conditions were observed to exist: a substantial lowering of the tropopause with a deep layer of saturated air below, ozone depression and strong wind shear. Moreover, these large ice conglomerations occurred during non-thunderstorm conditions, suggesting an alternative process of ice growth was responsible for their formation.

Key words: hydrogen and oxygen isotopes, ice conglomeration, megacryometeors, tropopause

1. Introduction

Documented references regarding the fall of unusually large ice conglomerations go back to the first half of the 19th century (e.g. 1829 in Córdoba, Spain: 2 kg; 1851 in New Hampshire: 1 kg) (Corliss, 1983; Martinez-Frias and López-Vera, 2000, 2002). The best-documented fall of an ice chunk was April 2, 1973, in Manchester, England. The block weighed 2 kilograms and consisted of 51 layers of ice. Its origin was not determined (Griffiths, 1975). For many years the largest hailstone officially reported in the United States was one that fell at Potter, Nebraska, on 6 July 1928. It had a circumference of 43 cm and weighed 680 g. This record was surpassed on 3 September 1970 at Coffeyville, Kansas (USA). The giant hailstone measured 18 cm (7 inches) across, about 44 cm (17.5 inches) in circumference, and weighed more than 750 g (26 ounces) (Munoz, 2000). GWC (2004) describes the fall, in 13 August 1849, in Scotland of a huge ice block formed by hundreds of chunks of ice. On 22 June 2003 a record-size hailstone (7 inches in diameter and 18.75 inches in circumference) crashed into Aurora, Nebraska (USA). It is difficult to get an accurate weight for this stone because a chunk of it hit the gutter of a house and 40% of it was lost.

From 8th to 27th January 2000 numerous big ice conglomerations (weighing from around 300 g to more that 3 kg) fell in different parts of Iberian Peninsula under clear sky atmospheric conditions (Martinez-Frias *et al.*, 2000, 2001; BAMS, 2002; Brink *et al.*, 2003; Martinez-Frias and Rodriguez-Losada, 2004) producing damage to cars and an industrial storage facility. Following the occurrence of these unusually large of ice conglomerations, additional occurrences have been identified in Spain (Figure 1) as well as many others parts of the world (e.g. Argentina, Australia, Austria, Canada, Colombia, Italy, Mexico, New Zealand, Portugal, Sweden, The Netherlands, United Kingdom, USA). Due to the fact that many of these previous cases were not appropriately researched – hence the almost lack of scientific publications –, along with the apparent high frequency of the falls, a research program was initiated to accomplish the following: (1) confirm the atmospheric nature of the ice blocks, with some of them of up to 18 kg in weight; (2) determine their genetic conditions and the possible association with atmospheric conditions; (3) create an updated systematic database incorporating similar events around the world; (4) have the samples well preserved in freezer rooms for their study; (5) promote the creation of an international working group that can communicate through an electronic network, and (6) inform the public about the importance of reporting the occurrence of new falls.

The stable isotopes of oxygen and hydrogen in water (vapour, liquid and ice) have become a significant tool used not only in hydrology and hydrogeology through routine application in studies investigating the origin and dynamics of surface and groundwater, but also in studies related to atmospheric circulation and climatic *and* palaeoclimatic investigations. The stable isotope composition ($^{18}O/^{16}O$ and D/H) is related to the "history" of the atmospheric vapour and the physical conditions

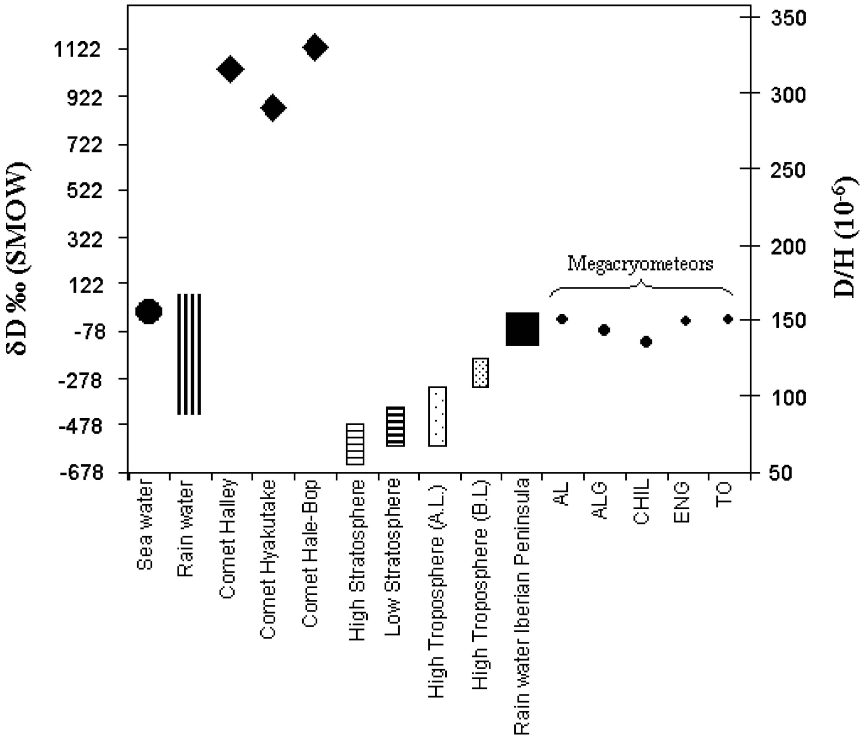

Figure 1. Hydrogen isotopic composition of the megacryometeors. Values of terrestrial and extraterrestrial water sources (Craig, 1961; Rozanski *et al.*, 1993; Zahn *et al.*, 1998; Deloule *et al.*, 1998) have been plotted for comparison.

occurring at the moment of condensation or crystallization (Craig, 1961; Dansgaard, 1964). Consequently, isotopic values of present and past precipitation gives very useful information regarding the atmospheric circulation, and, therefore, is a significant tracer in climatic and palaeoclimatic studies (Dansgaard *et al.*, 1993; Rozanski *et al.*, 1993; Thompson *et al.*, 1995, 2000; EPICA, 2004; among others). Various papers summarize the isotopic and chemical studies of atmospheric icy particles (hail) and the different conditions under which they can formed (Jouzel *et al.*, 1975, 1985; Gedzelman and Arnold 1994; Diamond and Harris, 1997; Souchez *et al.*, 2000), and have been extremely important towards better understanding the mechanisms that are responsible for ice nucleation and subsequent growth conditions. However, specific studies about the isotopic composition of atmospheric icy conglomerations (hailstones) are still scarce (Facy *et al.*, 1963; Federer *et al.*, 1982a,b; Jouzel *et al.*, 1985; Illinworth, 1989).

An icy conglomeration is called a hailstone when it reaches a diameter of around 5 mm or more (AMS, 2000). Broadly, they are the result of the updrafts and downdrafts that take place inside the cumulonimbus clouds of a thunderstorm, where supercooled water droplets exist. The turbulent updrafts and downdrafts within the cloud send the hailstones up and down several times, where they gather layer upon layer of ice. The number of layers in a hailstone reveals the number of up-down journeys it has made before falling to the earth. This “history” will mark its isotopic signature (Jouzel *et al.*, 1985). Thus, most hailstones acquire “onion skin” layers from travelling up and down in a storm. However, recent research (NWSFO, 2002) has shown that there is not one simple process of hail formation. Hailstones may actually form in several ways. Some can grow while balanced in an updraft and have little layering while others may form around raindrops that are carried high into the storm and freeze. Finally, some hailstones form around ice crystals before undergoing the aforementioned transport and growth processes.

The term megacryometeor was recently coined (Martinez-Frías and Travis, 2002) to name large atmospheric ice conglomerations which, despite sharing many textural, hydrochemical and isotopic features detected in large hailstones, are formed under unusual atmospheric conditions which clearly differ from those of the cumulonimbus clouds scenario (i.e. clear-sky conditions) (Martinez-Frias *et al.*, 2000; Brink *et al.*, 2003). In order to explain the causes that contribute to both the formation of initial ice nuclei and their later growth, several hypotheses have been proposed alluding to both terrestrial (Martínez-Frías *et al.*, 2000, 2001; Bosch, 2002; Brink *et al.*, 2003; Martinez-Frias and Rodriguez-Losada, 2004) and cosmic (Foot and Mitra, 2002) causes. Former hydrochemical analyses of these unusually large ice meteors are mainly focused on their distribution patterns of major, minor and trace elements (Martínez-Frías *et al.*, 2000, 2001; Santoyo *et al.*, 2002). The present work offers, for the first time, a detailed analysis of oxygen and hydrogen isotopic signatures of megacryometeors, based on both their bulk isotopic composition and systematic selective sampling (deuterium isotopic mapping) within each specimen. Additional information about the atmospheric scenario in which the Spanish ice fall events occurred is also given.

2. Samples and Methodology

The first Spanish fall of a megacryometeor struck a car in the locality of Tocina (Sevilla) witnessed by numerous people and producing damage to the vehicle. Some pieces were collected and preserved under the supervision of the Meteorological Service of La Cartuja. After this event, other similar cases occurred in the East of Spain and, fortunately, the specimens also were well preserved following the instructions of the head of the Meteorological Service of Valencia. Specific instructions were transmitted to all local Spanish authorities, to the Environmental Unit of the Spanish “Guardia Civil” (*SEPRONA*) and other environmental police officials, to safeguard the original features of the ice blocks. The ice blocks were kept in aseptic bags and immediately stored under refrigeration at approximately $-20\,^{\circ}\mathrm{C}$, to avoid textural changes, as well as to prevent possible contamination on the megacryometeor surface by water-steam condensation, or by the absorption of carbon dioxide from the environment. Thanks to this simple working routine, all samples of megacryometeors are currently maintained in freezer storages in the "Instituto del Frío" of the Spanish Council for Scientific Research. One of the authors of this article (JMF) personally coordinated the *modus operandi*, collected all the ice specimens and supervised their transportation and preservation procedures. Further information about their preservation can be found in Martinez-Frías and López-Vera (2000), in Santoyo *et al.* (2002) and on the website http://tierra.rediris.es/megacryometeors of the Spanish Thematic Network of Earth Sciences where, besides pictures and information about the falls, brief instructions for the proper maintenance and transportation of the ice blocks are given, including a copy of one of the *SEPRONA* reports.

Textures of megacryometeors include zones of "massive ice", large isolated cavities, mm-sized oriented air bubbles, and ice layering. The thickness of the layers range from less than 1 mm to more than 1 cm. Also, tiny solid particles can be found randomly disseminated in the interior of the ice. Two types of sampling were performed: (1) for multi-elemental and stable isotopes (oxygen and hydrogen) analyses, and (2) a drilling process for the identification of deuterium distribution patterns. The procedure was done from the interior to the outer parts of the ice blocks and also considered the different ice layers and other fabric features, which were visible in the samples, to detect whether said textural differences were also reflected as isotopic variations. The ice cores were placed in aseptic bottles, where the cored samples were finally melted for ulterior isotopic analysis.

The isotopic study was carried out at the Stable Isotope Laboratory of the *Estación Experimental del Zaidín* (Granada, Spain) on eleven selected megacryometeors, weighing from around 300 g to more than 3 kg, and ranging in size from 5 cm to 26 cm diameter. Oxygen in water was analysed by the CO_2-H_2O equilibration method (Cohn and Urey, 1938; Epstein and Mayeda, 1953). To determine hydrogen isotopic ratios we used reduction with Zn at 450 °C as in the method described by Friedman (1953) and Coleman *et al.* (1982). Isotopic ratios were measured by a Finnigan MAT 251 mass spectrometer. The experimental error was $\pm 0.1‰$ and $\pm 1‰$ for oxygen and hydrogen, respectively, using EEZ-3 and EEZ-4 as internal standards that were previously calibrated vs. V-SMOW, SLAP and GIPS water.

3. Results and Discussion

3.1. OXYGEN AND HYDROGEN ISOTOPIC SIGNATURES

The possibility that the source of the megacryometeor water could be non-terrestrial was also considered and ruled out because its isotopic signature ($-25‰ > \delta D_{SMOW} > -127‰$) is very different from that reported for comets ($+1028‰ > \delta D_{SMOW} > +862‰$) (Deloule *et al.*, 1998) (Figure 1). In addition, $\delta^{18}O$ and δD (V-SMOW) of the samples fall onto the Meteoric Water Line (Craig, 1961) and consequently indicate an atmospheric origin. The distribution of the samples on Craig's line

Table I. Isotopic composition of megacryometeors (Spain)

Sample	δ^{18}O ‰ (V-SMOW)	δD ‰ (V-SMOW)
AL	− 4.99	−25.7
ALG	−11.36	−75.3
CHIL	−17.25	−127.1
ENG	− 6.29	−35.5
TO	− 4.52	−27.3
SEK	− 6.31	−35.4
OLLO	−15.57	−112.5
FEL	− 8.49	−52.0
FEL-B	− 7.96	−48.6
BUE	−14.44	−99.7
LAU	− 7.95	−43.5

Note. AL: Alcudia, ALG: Algemesí, CHIL: Chilches, ENG: Enguera, TO: Tocina, SEK: Sequeros, OLLO: Olloniego, FEL: San Feliz de Lena, BUE: Burgo de Ebro. LAU: Small hail.

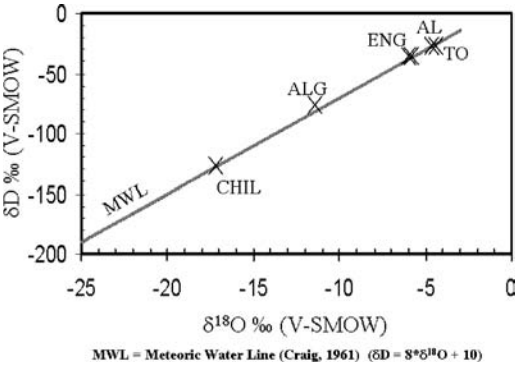

Figure 2. δ^{18}O (V-SMOW) vs. δD (V-SMOW) values of selected megacryometeors that fell in different areas of Spain. Note how the samples match with the Meteoric Water Line (Craig's Line). CHIL: Chilches, ALG: Algemesí, ENG: Enguera, AL: Alcudia, TO: Tocina.

(Table I, Figure 2) suggests either a variation in condensation temperature and/or different residual fractions of water vapour (Rayleigh processes) (Rozanski *et al.*, 1993). The most positive values are typical of rainwater in the Iberian Peninsula. Relatively negative isotopic values for the middle latitudes (Rozanski *et al.*, 1993; Longinelli and Selmo, 2004) were detected in the megacryometeors of Chilches (Castellon province) ($\delta^{18}O = -17.2‰$ and $\delta D = -127‰$ V-SMOW), Olloniego (Oviedo province) ($\delta^{18}O = -15.6‰$ and $\delta D = -112‰$ V-SMOW) and Burgo de Ebro (Zaragoza province) ($\delta^{18}O = -14.4‰$ and $\delta D = -100‰$ V-SMOW). The relationship between δ^{18}O and δD, displaying an excess of deuterium of 10‰

(typical of the Global Meteoric Water line), clearly indicates that the source of water has a minor contribution from evaporated surface continental waters (Moreira *et al.*, 1997; Jacob and Sonntag, 1991; Raya, 2003; McGuffie and Henderson-Sellers, 2004). Consequently, the water source of the megacryometeors comes from residual atmospheric moisture (rain water), showing the fingerprint of the typical Atlantic fronts which affect the Iberian Peninsula. Only the Algemesi megacryometeor (ALG in Figure 2) is plotted slightly to the left of the MWL, again indicating a very small contribution of evaporation of surface continental waters (Moreira *et al.*, 1997; Raya, 2003).

As previously described, continued deposits of supercooled water cause ice crystals to grow into hailstones that generally have passed through several stages of accretion, from the first stage (graupel), to small hail, to hailstones. Thus, the isotopic variability is a signature of the history of formation of the megacryometeors. Isotopic analyses of megacryometeors reveal that, like hailstones, they also exhibit a complex formation process in the atmosphere, which can be interpreted through the study of the variability of their oxygen and hydrogen isotopic ratios (Jouzel *et al.* 1985). Isotopic mapping of δD values of the growth layers in the studied samples (Table II) from different megacryometeors (see Tables I and II) displays: (1) significant general variations from $-24.4‰$ to $-126.4‰$ and (2) specific internal δD variations up to 15 parts per mille (i.e. Chilches, Figure 3; Table II). This internal variability is related to the temperature and consequently the vertical trajectory (Federer *et al.*, 1982). The tropospheric models of deuterium profiles under clear-sky conditions (Ehhat, 1974; Taylor, 1984; He and Smith, 1999) can be used to approximate the vertical theoretical trajectory of the megacryometeors during their growth (Table III). Figure 4 shows the graphical models for two megacryometeors, which were specifically selected because they show the most positive (Alcudia) and negative (Chilches) values of deuterium, respectively. Although the theoretical inference must be considered with caution, the range of δD values indicate that the growth of each megacryometeor took place under a narrow range of heights and temperatures. This graphical approximation has been made on the basis of the following considerations and/or limitations:

- Isotopic profiles of atmospheric water vapor in the troposphere are very scarce. However, the values obtained by Ehhat (1974) – an average decrease of 3.9 ppb/m, with the exception of the zone of the Atmospheric Boundary Layer (ABL) where the value is 2.2 ppb/m^{-1} have been confirmed by more recent studies (Taylor, 1984; He and Smith, 1999; Zahn *et al.*, 1998).
- Typical gradients of wet mode ($dt/dz = 5\,^{\circ}$C/km) have been considered to relate temperature and altitude.
- There is isotopic equilibrium between the ice and the water vapour (Merlivat and Nief, 1968). In any case, nucleation out of the equilibrium involves vertical trajectories shorter.

Table II. δD variations in selected megacryometeors (different layers)

Sample	δD ‰ SMOW	Sample	δD ‰ SMOW	Sample small hail	δD ‰ SMOW
Alcudia		**Chilches**			
AL-1	−24.4	CHI-1	−111.5	**La Unión**	
AL-2	−27.2	CHI-2	−113.8	LAU-1	−46.0
AL-3	−33.6	CHI-3	−121.6	LAU-2	−44.7
AL-4	−24.3	CHI-4	−118.6	LAU-3	−46.3
AL-5	−26.8	CHI-5	−124.3	LAU-4	−46.9
AL-6	−26.3	CHI-6	−126.2	LAU-5	−44.3
AL-7	−30.3	CHI-7	−117.1	LAU-6	−46.9
AL-8	−28.2	CHI-8	−115.6	LAU-7	−46.7
AL-9	−40.2	CHI-9	−112.6	LAU-8	−46.8
AL-10	−41.3	**Tocina**		LAU-9	−49.4
AL-11	−39.3	TO-1	−32.1	LAU-10	−49.9
AL-12	−36.3	TO-2	−34.7	LAU-11	−48.7
Algemesí		TO-3	−30.2	LAU-12	−42.3
ALG-1	−76.4	TO-4	−31.2	LAU-13	−42.5
ALG-2	−78.3	TO-5	−28.1	LAU-14	−46.9
ALG-3	−74.3	TO-6	−27.1	LAU-15	−48.5
ALG-4	−74.2	TO-7	−33.1	LAU-16	−45.2
ALG-5	−74.6	TO-8	−30.5	LAU-17	−40.8
Enguera		TO-9	−30.0	LAU-18	−43.8
ENG-1	−37.2	TO-10	−32.7	LAU-19	−44.7
ENG-2	−44.0	TO-11	−26.0	LAU-20	−44.0
ENG-3	−42.1	TO-12	−25.0		

Note. the significant isotopic heterogeneity. LAU: small hail.

The only existing data of water vapour δDv for this period are from South of Spain (Granada, 680 m above m.s.l.). These values range between −95‰ to −115‰ (9 samples) for January 2000 (Raya, 2003) which is incompatible with non-equilibrium precipitation at least near the ground level (with the exception of the CHIL, OLLO and BUE specimens). On the other hand, ice precipitation in isotopic equilibrium conditions, implicates a source of water vapour more negative and consequently, from a theroretical point of view (δDv values of different localities can be very different), a higher altitude of formation.

3.2. ATMOSPHERIC SCENARIO FOR IBERIAN PENINSULA

The mean height of the tropopause depends on the location, particularly the latitude and also depends on the season (Sturman and Tapper, 1996). Thus, at latitudes

Table III. Vertical trajectory calculated from the δD values(δD_{ic})

Megacryometeors	Maximum δD_{ic}	[1]Cal. δD_V	Minimum δD_{ic}	[2]VT-ABL (km)	[3]VT (km)
Alcudia	−24.3	−149.5	−41.3	3.2	1.0
Algemesí	−74.2	−119.4	−78.3	0.9	0.3
Chilches	−111.5	−236.6	−126.2	2.7	0.9
Tocina	−25.0	−149.9	−34.7	1.8	0.6
Enguera	−35.6	−160.9	−44.0	1.4	0.5

Note. The vertical trajectory have been calculated from the four following data/equations: (1) equation of Merlivat and Nief (1968), (2) the minimum δD_{ic}, (3) the calculated $\delta D_v^{(1)}$; (4) the gradients ($dt/dz = 5$ °C/km) and (5) ($d\delta/dz$), which relate temperature and δD_v with altitude.

[1] Calculated δD_v values of atmospheric water vapour at ground level (from maximum δD values of the hailstones).

[2] The longest vertical trajectory is obtained considering an average decrease $d\delta/dz = 2.2$ ppb m^{-1} (typical values for the ABL) (Ehhat, 1974).

[3] The shortest vertical trajectory is obtained considering an average decrease $d\delta/dz = 3.9$ ppb m^{-1}.

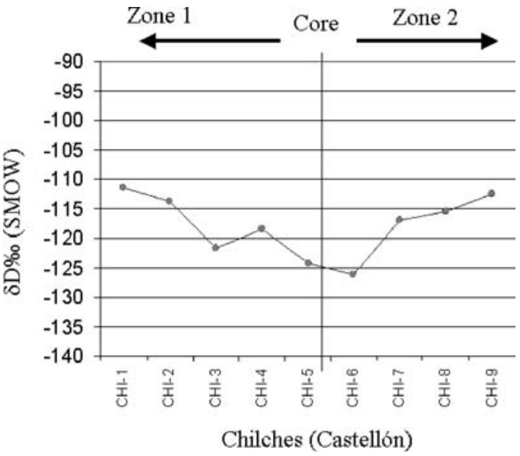

Figure 3. δD variations in various parts of the megacryometeor specimen that fell in Chilches (Castellón). Note the significant isotopic heterogeneity.

above 60°, the tropopause is less than 9–10 km above sea level; the lowest is less than 8 km high, above Antarctica and above Siberia and northern Canada in winter. The highest average tropopause is over the oceanic warm pool of the western equatorial Pacific, about 17.5 km high, and over Southeast Asia, during the summer monsoon, the tropopause occasionally peaks above 18 km. Cold conditions lead to a lower tropopause because of less convection. In certain meteorological situations,

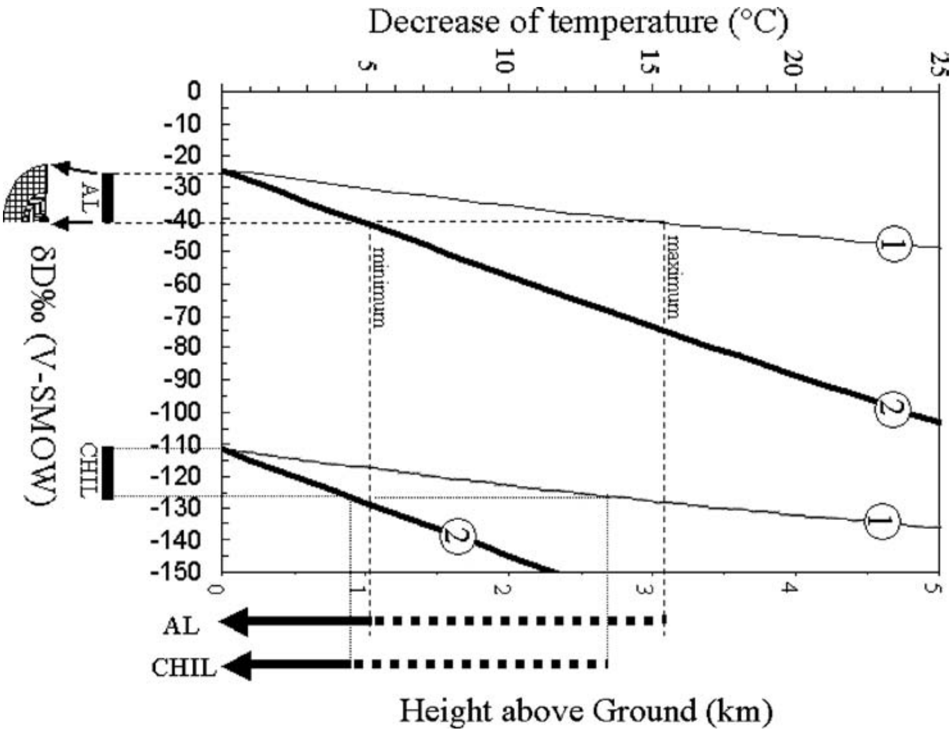

Figure 4. δD values of two selected megacryometeors versus virtual profiles (height, temperature). The specimens that have been represented correspond to the megacryometeors displaying the most positive (AL = Alcudia) and negative (CHI = Chilches) values, respectively. In clear sky days the isotopic composition of the water vapour decreases with the altitude, however turbulent or laminar conditions have been related with the gradients. As previously discussed, isotopic profiles of atmospheric water vapour in the troposphere are scarce (Taylor, 1972, 1984; Ehhat, 1974; He and Smith, 1999; Zahn *et al.*, 1998) Specifically for this area and period, the average decrease $d\delta/dz = 3.9$ ppb (2.2 ppb m^{-1}, for the ABL; 0 m to 2200 m) (Ehhat, 1974) has been considered. Typical gradients of wet mode ($dt/dz = 5\,^{\circ}$C/km) have been considered to relate temperature with altitude. For the vertical trajectory calculus, we have considered the most external layer (usually the least negative δD values) as the end of ice formation. Curves 1 and 2 start at this "end point". Curve 1 is particularly applicable for the Atmospheric Boundary Layer (ABL) and curve 2 for the nuclei that originated at higher altitudes (see Table III). The curves have been calculated with the equation which relates the isotopic fractionation of hydrogen to temperature in the ice-vapor system (Merlivat and Nief, 1968). The maximum and minimum δD values allow us to calculate the minimum (continuous arrow) and maximum (discontinuous arrow) altitudes of nucleation (right side of the graphic). It is important to note that during the impact there is a fragmentation of the megacryometeor. Consequently, this figure represents minimal trajectories and/or altitudes. The isotopic values are given in δ per mil vs SMOW (Standard Mean Oceanic Water) (δD = (Rsample-RSMOW/RSMOW) × 1000; 1 pmm = 6.42‰ for deuterium).

the height of the tropopause can abruptly decrease over short time and space scales producing tropopause “folds”. Recently, there has been evidence suggesting that higher frequencies of tropopause folding events (Beekmann *et al.*, 1997) are occurring at northern mid-latitudes where a large percentage of aircraft movements take place (Ebel *et al.*, 2000). Tropopause folds, undulations and disturbances are related to storm systems, cyclonic vorticity and wind shear (Hirschber and Fritsch, 1991; Bertin *et al.*, 2001) and influence the exchange and mixing in the boundary between the upper troposphere and the lower stratosphere of ozone, water vapour and aerosols (Park and Lee, 2001; Roelofs *et al.*, 2003; Ovarlez *et al.*, 1999; Wimmers and Moody, 2003). In addition, Santer *et al.* (2003) have suggested that changes in tropopause height may be a useful “fingerprint” of some climate anomalies, stressing that the simulated increase in tropopause height over 1979–1997 is a robust, zero-order response of the climate system to forcing by well-mixed greenhouse gases and stratospheric ozone depletion. Finally, it is important to note that interchanges of water vapour, favoured by tropopause disturbances, could play a central role in atmospheric chemistry, influencing the heterogeneous chemical reactions (Oltmans and Hofmann, 1995).

Atmospheric soundings from NOAA were collected for the days prior to and during the occurrence of the megacryometeors in Spain (mainly 10–17 January) (Santoyo *et al.*, 2002). Soundings from La Coruña, Santander, Zaragoza, Madrid, Palma (Balearic Islands), Murcia and Gibraltar were the closest available (Figure 5). The soundings were plotted and analysed to assess the evolution of the temperature, humidity and wind profiles (Table IV).

3.2.1. *La Coruña*

10 Jan. 2000. The sounding at 11 UTC shows a strong subsidence inversion at $\approx$2000 m and the tropopause at $\approx$200 hPa corresponding to a height of $\approx$11,400 m. The winds at that height are from the north-northeast at 40 knots. A similar situation is maintained for the sounding at 23:00 UTC with an increase in wind speed at 200 hPa (to 45 knots) and change of wind direction to north-northwesterly.

11 Jan. 2000. The sounding at 11 UTC shows a lower subsidence inversion extending from $\approx$750 m to 2500 m, while the tropopause has sunk to $\approx$250 hPa corresponding to a height of $\approx$10,500 m. The winds at that height are from the north at 20 knots. In the sounding at 23:00 UTC the subsidence inversion has risen and become stronger and the wind speed at 250 hPa is northerly and has increased to 25 knots.

12 Jan 2000. The sounding at 11 UTC is very similar to the one at 23:00 the previous day. It shows a very dry stratum between $\approx$1850 m to 5500 m, while the tropopause has risen to $\approx$200 hPa ($\approx$11,400 m), and the winds at that height are from the northwest at 20 knots. In the sounding at 23:00 UTC the tropopause has sunk again to $\approx$250 hPa and the winds are westerly at 30 knots.

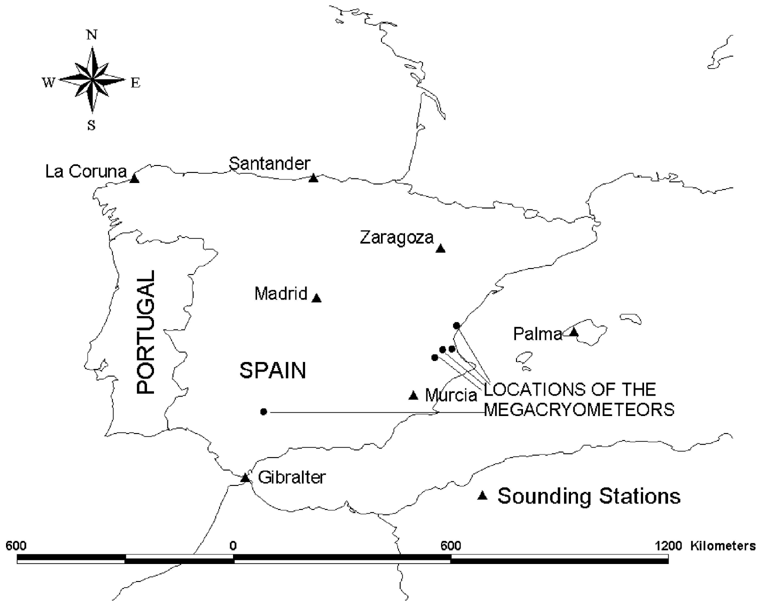

Figure 5. Simplified map of Spain showing the location of falls of megacryometeors (circles) and sounding stations (triangles).

13 Jan. 2000. The sounding at 11 UTC shows that the tropopause has sunk to ≈350 hPa (≈8000 m) with winds from the west at 60 knots at that level. Below that level the atmosphere is near saturation all the way to the surface (apparently no clouds were observed). Strong surface winds are present with marked directional shear at the 850 hPa level. The sounding at 23:00 UTC shows a further sinking of the tropopause to ≈400 hPa (≈7000 m) and marked wind directional shear. The layer below remains near saturation all the way to the surface

14 Jan. 2000. In the sounding at 11 UTC the tropopause remains at ≈350 hPa (≈8000 m) with winds at 30 knots at that level. The atmosphere remains close to saturation below that level all the way to the surface. The sounding at 23:00 UTC shows again sinking of the tropopause to ≈400 hPa (≈7000 m) and winds from the East at 40 knots.

After this date the tropopause rises and reaches the 200 hPa level by 23:00 UTC, on Jan 17.

3.2.2. *Santander*

The evolution of the soundings from Jan 10 to Jan 17 is very similar to that observed in La Coruña. The lowest observed tropopause height occurs on 14 Jan. at ≈400 hPa (≈7000 m). The lower atmosphere is also near saturation all the way down from this level to the surface.

Table IV. Depth of the moist surface layer as deduced from soundings at the times shown

Hour	Day	Coruña	Santander	Gibraltar	Madrid	Zaragoza	Murcia	Palma
11:00 Z	7	2.5 S	2.5 S	1. S	1.5 S	1.5 S	–	0.5 S
23:00 Z		2. S	2.8 S	1. S	1.5 S	2.8 S	1.4 S	1. S
11:00 Z	8	2.5 S	3. S	1. S		3.3 S		4.3 S
23:00 Z		2.8 S	4.5 S?	0.6 S	4. S	3.5 S		4.5 S
11:00 Z	9	2.2 S	5. T	3.5 T	5.5 T	–	4.2 S	3.3 S
23:00 Z		1.5 S	2.5 S?	4.5 T	7.5 T	6.5 T		5.5 S?
11:00 Z	10	2. S	1. S	7.0 T	4.5 S	–	4.3 ?	3. S
23:00 Z		1.5 S	1.5 S	3. S	3. S	6. T	7. T	4.5 S?
11:00 Z	11	1. S		3. S	3.3 S	2.4 S	3(+) ?	4.3 S
23:00 Z		2. S		2.4 S	1.6 S		5.5 T?	4.3 S
11:00 Z	12	2. S		2.2 S				3. S
23:00 Z		2. S	2.3 S	1. S			1.8 S	3. S
11:00Z	**13**	**8.3 T**	**3.3 S**	**1.5 S**	**2.5 S**	**2.2 S**		**2.5 S**
11:00 Z		**7.3 T**	**7. T**	**5.5 T**		**3.8 S**	**1.8 S**	
11:00 Z	**14**	**7.5 T**	**7. T**	**5.5 T**	**6. T**	**–**	**6. T**	**1.8 S**
23:00 Z		**7. T**	**6. T**	**5.6 T**		**5(+)T**	**7. T**	**7. T?**
11:00 Z	**15**	**7. T?**	**6. T**	**6.5 T**	**5.6 S**	**7. T**	**2.5 S**	
23:00 Z		**7. T**	**1.5 S**	**7. T**	**2. S**	**6(+)T**	**3(+) S**	**7.5 T**
11:00 Z	16	1. S	1.5 S	7.2 T	2. S	–	4–7 T	2. S
23:00 Z		1. S	1.2 S	9. T	2. S	–	2. S	2. S
11:00 Z	17	0.5 S	1.2 S	7.5 T	1.5 S	–		1.8 S
23:00 Z		0.5 S	0.8 S	1.5 S	1. S	–	1. S	

Note. S: Indicates that the layer is capped by a clearly defined inversion aloft; T: Indicates a moist layer capped by a low(er) tropopause; -: Indicates no sounding available; Indicates a dry(er) airmass.

3.2.3. *Zaragoza*

The evolution of the soundings from Jan 10 to Jan 17 starts with a tropopause at ≈300 hPa (≈9000 m) on Jan 10. The lowest tropopause height observed occurs at 24:00 Jan 14, at ≈400 hPa (≈7000 m). The atmosphere is also near saturation all the way down from this level on Jan 14 and 15.

3.2.4. *Madrid*

The evolution of the soundings starts with a tropopause at ≈400 hPa (≈7000 m) on Jan 09. It rises and remains at ≈250 hPa (≈10,500 m) the following days, and sinks again to ≈400 hPa (≈7000 m) at 11:00 on Jan 14. It remains at this height during the rest of the 14th, the 15th and 16th. In these soundings the humidity in the lower layer, however, remains low.

3.2.5. *Murcia*

The data series is inconsistent, no evolution can be established.

3.2.6. *Palma*

The series is incomplete. On Jan 10 the tropopause is at ≈250 hPa (≈10,500 m). On the 13th it appears at ≈300 hPa (≈9000 m) and it sinks to ≈400 hPa (≈7000 m) at 12:00 on Jan 16, with very high humidity all the way below this level to the surface.

3.2.7. *Gibraltar*

The tropopause starts at ≈400 hPa (≈7000 m) at 11:00 on Jan 10; it rises to ≈250 hPa (≈10,500 m) by 11:00 UTC Jan 13th and sinks down to ≈400 hPa (≈7000 m) by 23:00 on Jan 14, where it remains for most of the 15th and 16th, again, with very high humidity all the way below this level to the surface.

3.2.8. *Composite Summary of All Soundings Combined*

The analysis of the soundings indicates that the tropopause sank from a level of 250 hPa (≈10,500 m), on the days prior to the event, to a lower level of ≈400 hPa (≈7000 m) on the days of the events. This process was not observed simultaneously at all stations and seems to have propagated from northwest to east and then to south. Along with the amount of sinking, the other significant factor is the accompanying increase in humidity (near saturation) observed in all cases (except over Madrid). Ozone anomalies and wind shear were also found to exist occurring simultaneously with the tropopause undulations, and data from the World Area Forecast Centre (London) (Martinez-Frias *et al.*, 2002) also confirmed the low tropopause height values.

4. Conclusion

In accordance with current scientific priorities for Global Atmospheric Chemistry Research in Europe, the new directions in environmental strategies encourage that the atmosphere be studied in its entirety, taking into account the interactions and modifications occurring at different scales. Certain local atmospheric anomalies, such as the formation of unusually large ice conglomerations, could be indicative of larger-scale atmospheric chemical and physical changes.

This paper offers the first isotopic characterization of megacryometeors, and examines the atmospheric scenario in which the ice fall events occurred. The detailed hydrochemical analysis of hydrogen and oxygen in megacryometeors verify that they formed from atmospheric vapour, having typical tropospheric values and generally coinciding with the ranges found in precipitation occurring in the Iberian

Peninsula. This supports the original results obtained by Martinez-Frías *et al.* (2000, 2001) and Santoyo *et al.* (2002). The most negative isotopic signatures (detected in three specimens) also indicate a high-altitude atmospheric origin involving environmental conditions that are typical of the upper troposphere or residual water which is relatively impoverished in heavy isotopes (Rayleigh effects). Theoretical calculations indicate that the vertical trajectory in effective growth of the megacryometeors was lower than 3.2 km. The appearance of the megacryometeors took place under unusual meteorological conditions that included: (1) a sudden drop in the tropopause over Spain, (2) a moisture increase within the entire depth of the tropopause, near saturation but with no condensation, and (3) a total lack of convective precipitation anywhere over Spain at the time, (4) ozone depression and (5) wind shear. This is just a statement of observed facts. Additional mechanisms (i.e. extra ionization, external perturbation of the system, injection of ion concentration from aircraft condensation trails, (Martinez-Frias and Travis, 2002)) are also being considered as possible contributors to the formation of the initial ice nucleation.

Acknowledgments

This work was supported by the Spanish Council for Scientific Research. Special thanks to the National and Local Police and Guardia Civil, in particular, to SEPRONA. Also thanks to two anonymous referees for their valuable comments and suggestions.

References

AMS, 2000: *Glossary of Meteorology*, 2nd Edition, ISBN 1-878220-34-9, 850 pp.

BAMS, 2002: *The sky is falling*. News section V. 83, 12.

Beekmann, M., Ancelet, G., Blonsky, S., De Muer, D., Ebel, A., Elbern, H., Hendricks, J., Kowol-Santen, J., Mancier, C., Sladkovic, R., Smit, H. G. J., Speth, P., Tickl, T., and Van Haver, P., 1997: Regional and global tropopause fold occurrence and related ozone flux across the tropopause, *J. Atmos. Chem.* (28), 29–44.

Bertin, F., Campistron, B., Caccia, J. L., and Wilson, R., 2001: Mixing processes in a tropopause folding observed by a network of ST radar and lidar, *Annales Geophysicae* **19**, 953–963.

Brink, K., Travis, D., and Martinez-Frías, J., 2003: Upper tropospheric conditions associated with recent clear-sky ice falls. *57th Annual Meeting, The Wisconsin Geographical Society*, September 19–20, UW-Eau Claire.

Cohn, M. and Urey, H. C., 1938: Oxygen exchange reactions of organic compounds and water, *J. Amer. Chem. Soc.* **60**, 679–687.

Coleman, M. L., Shepherd, T. J., Rouse, J. E., and Moore, G. R., 1982: Reduction of water with zinc for hydrogen isotope analysis, *Anal. Chem.* **54**, 993–995.

Corliss, W. R., 1983: Ice falls or hydrometeors, in: W. R. Corliss (ed.), Tornados, Dark Days, *Anomalous Precipitation and Related Weather Phenomena. A Catalogue of Geophysical Anomalies*. The Sourcebook Project. P.O. Box 107, Glen Arm, MD 21057, pp. 40–44.

Craig, H., 1961: Isotopic variations in meteoric waters, *Science* **133**, 1702–1703.

Dansgaard, W., 1964: Stable isotopes in precipitation, *Tellus* **16–5**, 461–469.

Dansgaard, W., Johnsen, S. J., Clauson, H. B., Dahl-Jensen, D., Gundestrup, N. S., Hammer, C. U., Hvidberg, C. S., Steffensen, J. P., Sveinbjornsdottir, A. E., Jouzel, J., and Bond G., 1993: Evidence for general instability in past climate from a 250 kyr ice-core record, *Nature* **364**, 218–220.

Diamond, R. E. and Harris, C., 1997: Oxygen and hydrogen isotope composition of Western Cape meteoric water, *S. Afr. J. Sci.* **93**, 371–374.

Ebel, A. Feldmann, H., Offermann, D., and Schäler, B., 2000: Meso-scale studies of composition and transport in the tropopause region, *AFO2000 Newsletter* **2**, 7–10.

Ehhalt, D., 1974: Vertical profiles of HTO, HDO, and H_2O in the troposphere, NCAR, Natl. Cent. for Atmos. Res.., Boulder, Colo. Tech. *Note NCAR/-TN/STR-100*, 131 pp.

Epstein, S. and Mayeda, T. K. 1953: Variation of the 18O/16O ratio in natural waters, *Geochim. Cosmochim. Acta* **4**, 213–224.

Facy, L., Merlivat, L., Nief, G. and Roth, E. 1963: The study of the formation of a hail-stone by means of isotopic analysis, *J. Geophys. Res.* **68**, 3841–3848.

Federer, B., Brichet, N., and Jouzel, J., 1982a: Stable isotopes in hailstones 1. The isotopic cloud model, *J. Atmos. Sci.* **39–6**, 1323–1335.

Federer, B., Thalmann, B., and Jouzel, J., 1982b: Stable isotopes in hailstones 2. Embryo and hailstone growth in different storms, *J. Atmos. Sci.* **39–6**, 1336–1355.

Foot, R. and Mitra, S., 2002: Ordinary atom-mirror atom bound states: A new window on the mirror world, *Phys. Rev. D* **66**, 061301.

Friedman, I., 1953: Deuterium content of natural water and other substances, *Geochim. Cosmochim. Acta* **4**, 89–103.

Gedzelman, S. D. and Arnold, R., 1994: Modeling the isotopic composition of precipitation, *J. Geophys. Res.* **99**, 10455–10571.

Griffiths, R. F., 1975: Observation and analysis of an ice hydrometeor of extraordinary size, *Met. Mag.* **104**, 253–260.

GWC, 2004: Gungahlin Weather Centre http://members.optusnet.com.au/~darrengiles/articles/factsandfigures.htm.

He, H. and Smith, R. B., 1999: Stable isotope composition of water vapor in the atmospheric boundary layer above the forests of New England, *J. Geophys. Res-Atmospheres* **104**, 11657–11673.

Hirschberg, P. A. and Fritsch, J. M., 1991: Tropopause undulations and the development of extratropical cyclones: Part II: Diagnostic analysis and conceptual model, *Mon. Weat. Rev.* **119**, 518–550.

Illingworth, A., 1989: Growth of large hailstones, *Nature* **337** (6209), 691–691.

Jacob, H. and Sonntag, C., 1991: An 8-year record of the seasonal variation of ^{2}H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany. *Tellus* **43B**, 291–300.

Jouzel, J., Merlivat, L., and Roth, E., 1975: Isotopic study of hail, *J. Geophys. Res.* **80**, 5015–5030.

Jouzel, J., Merlivat, L., and Federer, B., 1985: Isotopic study of hail – the delta-D-delta-O-18 relationship and the growth history of large hailstones, *Q. J. Roy. Meteor. Soc.* **111**, 495–516.

Leigh, R., 1999: The April 1999 Sydney Hailstorm, *Natural Hazard Quaterly* **5**, 2.

Martínez-Frías, J. and López-Vera, F., 2000: Los bloques de hielo que caen del cielo. Antecedentes y fenomenología reciente, *Rev. Ens. Cien. Tierra.* **8–2**, 130–136.

Martínez-Frías, J., López-Vera, F., García, N., Delgado, A., García, R., and Montero, P., 2000: Hailstones fall from clear Spanish skies, *News Notes Geotimes* **45–6**, 11.

Martínez-Frías, J. and Travis, D., 2002: Megacryometeors: Fall of atmospheric ice blocks from ancient to modern times, in: S. Leroy and I. S. Stewart (eds.), *Environmental Catastrophes and Recovery in the Holocene*. Abstracts Volume. Brunel University, West London (UK), pp. 54–55.

Martínez-Frías, J., Millán, M., García, N., López-Vera, F., Delgado, A., García, R., Rodríguez-Losada, J. A., Reyes, E., Martín Rubí, J. A., and Gómez-Coedo, A., 2001: Compositional heterogeneity of hailstones: Atmospheric conditions and possible environmental implications, *Ambio.* **30–7**, 452–455.

Martinez-Frias, J. and Rodríguez-Losada, J. A., 2004: Atmospheric megacryometeor events versus small meteorite impacts: Scientific and human perspective of a potential natural hazard. *International Council for Science (ICSU) Workshop*: Comet/asteroid impacts and human society, November 27–December 2, 2004 Santa Cruz de Tenerife, Tenerife, Canary Islands (Spain) (abstract).

McGuffie, K. and Henderson-Selle, A., 2004: Stable water isotope characterization of human and natural impacts on land-atmosphere exchanges in the Amazon Basin, *Journal of Geophysical Research* **109**, 1–25.

Merlivat, L. and Nief, G., 1967: Isotopic fractionation of the solid-vapor and liquid-vapor changes of state of water a temperatures below 0 °C, *Tellus* **19**, 122–127.

Moreira, M. Z., Sternberg, L. S. L., Martinelli, L. A., Victoria, R. L., Barbosa, E. M., Borates, C. M., and Nepstads, A. C., 1997: Contribution of transpiration to forest ambient vapour based on isotopic measurements, *Global Change Biology* **3**, 439–450.

Munoz, R., 2000: Hail. Fact Sheet. http://www.ucar.edu/communications/factsheets/Hail.html

National Weather Service Forecast Office, NWSFO, 2002: What about hail? NOAA http://tgsv5.nws.noaa.gov/er/box/hail.html.

Oltmans, S. J. and Hofmann, D. J. 1995: Increase in lower-stratosphere water vapour at a mid-latitude Northern Hemisphere site from 1981 to 1994, *Nature* **374**, 146–149.

Ovarlez, J., Velthoven, P., and Schlager, H., 1999: Water vapor measurements from the troposphere to the lowermost stratosphere: Some signatures of troposphere to stratosphere exchanges, *J. Geophys. Res.* **104**, 16973–16978.

Park, C. B. and Lee, C. H., 2001: Tropopause folding effect on Ozone Observation measured by Lidar and sonde over Suwon station, *NDSC 2001 Symposium*, September (Arcachon, France).

Raya, J., 2003: Composición isotópica del vapor de agua atmosférico en el Sureste de la Península Ibérica, *Doctoral Thesis Univ. Granada*. 418 pp.

Roelofs, G. J., Kentarchos, A. S., Trickl, T., Stohl, A., Collins, W. J., Crowther, R. A., Hauglustaine, D., Klonecki, A., Law, K. S., Lawrence, M. G., von Kuhlmann, R., and van Weele, M., 2003: Intercomparison of tropospheric ozone models: ozone transports in a complex tropopause folding event. *J. Geophys. Res.* (abstract) http://www.phys.uu.nl/∼roelofs/werk/abstracts_files/abstract10.html

Rozanski, K., Araguás, L., and Gonfiantini, R., 1993: Isotopic patterns in modern global precipitation, in: *Climatic Change in Continental Isotopic Records* (AGU) Geophysical Monograph 78 pp. 1–36.

Santoyo, E., García, R., Martínez-Frías, J., López-Vera, F., and Verma, S. P., 2002: Capillary Electrophoretic analysis of inorganic anions in atmospheric hailstone samples, *Journal Chromatography A* **956**, 279–286.

Santer, B. D., Wehner, M. F., Wigley, T. M.L., Sausen, R., Meehl, G. A., Taylor, K. E., Ammann, C., Arblaster, J., Washington, W. M., Boyle, J. S., and Brüggemann, W., 2003: Contributions of anthropogenic and natural forcing to recent tropopause height changes, *Science* **301**, 479–483.

Souchez, R. A., Jouzel, J., Lorrain, R., Sleewaegen, S., Stievenard, M., and Verbeke, V., 2000: A kinetic isotope effect during ice formation by water freezing, *Geoph. Res. Letters* **27–13**, 1923–1926.

Sturman, A. P. and Tapper, N., 1996: *The Weather and Climate of Australia and New Zealand* (Oxford, UK) 476 p.

Taylor, C. B., 1972: The vertical variations of isotopic composition of tropospheric water vapour over continental Europe and their relations to tropospheric structure, *Inst. Nucl. Sci. Report.* ISN-R-107, 45 pp. Lower Hutt, New Zealand.

Taylor, C. B., 1984: Vertical-distribution of deuterium in atmospheric water-vapor: Problems in application to assess atmospheric condensation models, *Tellus* (Series B) **36B**, 67–70.

Thompson, L. G., Mosley-Thompson, E., Davis, M. E., Lin, P. N., Henderson, K. A., Cole-Dai, J., Bolzan, J. F., and Liu, K. B. 1995: Late glacial stage and holocene tropical ice core records from Huascarán, Peru, *Science* **269**, 46–50.

Thompson, L. G. T., Yao, T., Thompson, E., Davis, M. E., Henderson, K. A., and Lin, P.-N., 2000, Sep 15: A High-Resolution Millennial Record of the Monsoon from Himalayan Ice Cores, *Science* pp. 1916–1919.

Wimmers, A. J. and Moody, J. L., 2003: Calibration of GOES water vapor spatial gradients with tropopause folding events, *American Meteorological Society Annual Meeting*. Abstract. P2.31.

Zahn, A., Barth, V., Pfeilsticker, K., and Platt, U., 1998: Deuterium, oxygen-18, and tritium as tracers for water vapour transport in the lower stratosphere and tropopause region, *J. Atmospheric Chem.* **30**, 25–47.