

# Monitoring the fall of large atmospheric ice conglomerations: a multianalytical approach to the study of the Mejorada del Campo megacryometeor

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Certain local atmospheric anomalies, such as the formation of unusually large ice conglomerations (megacryometeors), have been proposed to be a potential natural hazard for people and aviation, as well as geoindicators for fingerprinting larger-scale atmospheric environmental changes. On March 13th 2007, at approximately 10:15 am, an ice chunk weighing about 10 kg fell from the clear-sky and crashed through the roof (around 15 m) of an industrial storage house in Mejorada del Campo, a town located 20 km east from Madrid. The megacryometeor monitoring follow-up and the original investigation presented here includes, for the first time, both logistic and scientific collaboration between the Laboratory of the Environment, Criminalistic Service (SECRIM, the Spanish “Guardia Civil”) and academic and scientific institutions (universities and the Spanish National Research Council). We propose that the management procedure of the incident, along with the detailed scientific research and combination of analytical methodologies in different laboratories, can serve as a protocol model for other similar events.

## Introduction

Environmental monitoring is the foundation for selecting management approaches and safety procedures, for developing predictive modelling and process research, and for integrating the scientific information necessary to make key decisions.<sup>1</sup> In accordance with current scientific priorities for the International Global Atmospheric Chemistry (IGAC),<sup>2</sup> the new directions in environmental strategies encourage the study of the atmosphere 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 (megacryometeors), have been proposed to be a potential natural hazard<sup>3</sup> for people and aviation, as well as geoindicators<sup>4</sup> for fingerprinting larger-scale atmospheric chemical and physical changes.<sup>5–12</sup> By the study of atmospheric soundings from NOAA, and NCEP/NCAR reanalysis data of the upper troposphere, the formation of megacryometeors has been linked to undulations of the tropopause (mean upper tropospheric temperature gradient for 19 ice fall events occurred

for the past five years combined was significantly greater than climate normals), ozone anomalies and strong wind turbulence.<sup>6,9,11,12</sup> This is of relevance from the environmental point of view, given that observations suggest that: (1) the mixing ratio of water vapour in the stratosphere has increased by 20–50% from the 1960s to the mid-1990s<sup>13</sup> and (2) interchanges of water vapour, favoured by tropopause disturbances, can play a central role in atmospheric chemistry, influencing heterogeneous chemical reactions, with subsequent implications in climate change, as part of a global long-term trend. Cooler stratospheric temperatures appear when there is more water vapor present, and water vapor also leads to the breakdown of ozone molecules.<sup>14,15</sup> The megacryometeor monitoring follow-up and the original investigation presented here on the most recent ice fall event, which occurred in Spain in 2007, includes for the first time both logistic and scientific collaboration between the Laboratory of the Environment, Criminalistic Service (SECRIM, Spanish “Guardia Civil”) and academic and scientific institutions (universities and the Spanish National Research Council). We propose that the management procedure of the incident, along with the scientific research and combination and comparison of analytical methodologies in different laboratories, can serve as a protocol model for other similar events.

## Monitoring and research of megacryometeor incidents

Our monitoring and research study of the clear-sky ice fall events was initiated in January 2000, in the context of a multidisciplinary scientific commission that was coordinated by the Spanish National Research Council (CSIC). A specific website was established, electronically hosted by the Thematic Network

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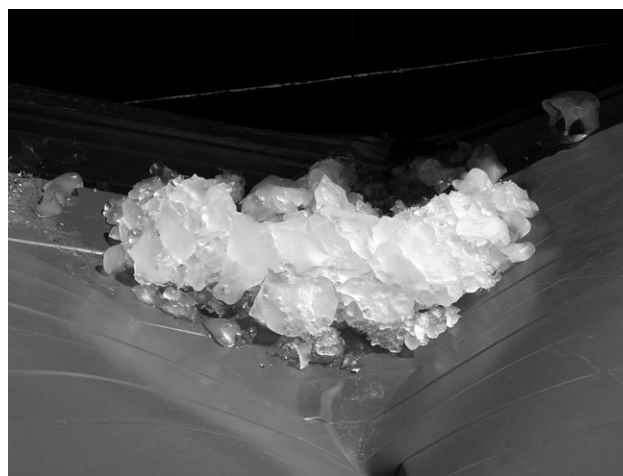
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of Earth Sciences in Spain ‘*Tierra*’, in which pictures, incident information and scientific results were included.<sup>16</sup> After almost eight years of monitoring and research, it has become evident that megacryometeors are not classical big hailstones, ice from aircrafts (waste water or tank leakage), nor the simple result of icing processes at high altitudes. They display textures, hydrochemical features and oxygen and hydrogen isotopic values which unequivocally confirm they are the result of complex formation processes within the atmosphere. More specifically, the megacryometeors’ water is consistent with the Craig’s Global Meteoric Water Line<sup>17</sup> and their isotopic ranges ( $-25\text{‰} > \delta\text{D}_{\text{SMOW}} > -127\text{‰}$ ;  $-4.52\text{‰} > \delta^{18}\text{O}_{\text{SMOW}} > -17.25\text{‰}$ ) are clearly tropospheric.<sup>11</sup> At present, no model is able to satisfactorily explain what factors cause the ice nucleation and growth,<sup>18,19</sup> or how megacryometeors can actually be formed and maintained in the atmosphere. Nevertheless, any model should involve the existence of an ice-supersaturated region (ISSR), that is, a supersaturated but cloud free airmass,<sup>20,21</sup> connected with extreme atmospheric turbulence, associated with the observed tropopause undulation.<sup>6,11</sup> In this sense, theoretical calculations, based on experimentally-obtained  $\delta\text{D}_{\text{SMOW}}$  variations, indicate that the vertical trajectory in effective growth of the megacryometeors was lower than 3.2 km.<sup>11</sup> It is important to note that a detailed historical review of such ice fall events verifies that there are many documented references of similar falls of large blocks of ice which go back to the first half of the 19th century (prior to the invention of aircrafts).<sup>22–24</sup> It is still too early to ascertain whether there is a real multiplication effect of the number of megacryometeor incident exclusively due to natural causes (now there is a statistical artifact in the analysis as the information circulates very fast and we can know rapidly what is happening in different parts of the world). Nevertheless, and mainly after 1950, the number of megacryometeor hits has apparently increased. More than 100 events have been witnessed and recorded, affecting practically the entire planet (Argentina, Australia, Austria, Canada, Colombia, India, Italy, Japan, Mexico, New Zealand, Portugal, South Africa, Spain, Sweden, The Netherlands, United Kingdom and the USA).<sup>3,11,12</sup> From 2001 to 2006, a total of 52 ice-fall events have been witnessed and recorded. Verifiable effects include the megacryometeors’ crashing (some of them weighing more than 100 kg) through roofs or producing small impact craters (*i.e.*, La Milana, Soria, Spain; Surrey, UK; Oakland, California, USA).<sup>25</sup> As of this writing, 12 new documented ice falls have been recorded in 2007, eight in the USA, two in The Netherlands, one in the UK and one in Spain: the Mejorada del Campo megacryometeor.

### Incident description

On March 13th 2007, at around 10:15 am, an ice chunk weighing roughly 10 kg fell from clear-sky and crashed through the roof (around 15 m) of an industrial storage house in Mejorada del Campo, a town located 20 km east from Madrid.<sup>26</sup> The workers were in the interior of the premises, and were witnesses of the “dry and very strong noise” caused by the impact. Due to the arrangement and elongated shape of the metallic material plates of the roof, a pronounced dent and an irregular hole of around 2 m x 1 m, were produced. A significant part of the ice chunk stayed deposited on the concavity of the dented part of the



**Fig. 1** Megacryometeor which fell on 13th March 2007, crashing through the roof (around 15 m) of an industrial storage house in Mejorada del Campo, Madrid. The picture shows the fragments of the ice chunk, which stayed deposited in the concavity of the dented part of the roof (see text for approximate weight and size).

roof (Fig. 1), whereas other ice fragments fell into the interior of the industrial storage room. The plates of plaster underlying the metallic material of the roof were also broken by the impact. The ice was white and semi-transparent, displaying a nearly equidimensional arrangement of the fragments (Fig. 1). Fortunately, the incident caused only material damage and nobody was hurt. Experts from the SECRIM, investigated the incident, ruling out other hypotheses (*e.g.* vandalism). Some ice pieces were collected and transported using portable freezers (the same day of the event), to perform the first set of hydrochemical analyses in the SECRIM’s Laboratory of Environment of the “Guardia Civil”, and the rest of the ice was preserved under frozen conditions for later studies. Subsequently, a second sampling of the ice was carried out on April 13th 2007. Various megacryometeor fragments were moved, also under controlled conditions, by two SECRIM members (one of them is the first author of the present article), to the Planetary Geology Laboratory of the Centro de Astrobiología (CAB).

### Experimental

The ice samples (several pieces weighing a total of 842 g) were kept in aseptic bags and immediately stored under refrigeration at approximately  $-20\text{ }^{\circ}\text{C}$ , 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. A previous stage of the characterization analysis was to remove the external part of the ice using an aseptic cutter. The set of analyses performed (all of them from liquid aliquots of the ice samples) comprises the combination of pH and conductivity, differential scanning calorimetry (DSC), ion chromatography (IC), inductively coupled plasma mass spectroscopy (ICP-MS), electrothermal atomic absorption spectroscopy (ETAAS) with a graphite furnace, stable isotope mass spectrometry (SIMS), solid phase micro-extraction-gas chromatography-mass spectrometry (SPME-GC-MS), and microbiological analysis.

The pH and conductivity determination was carried out using a CRISON pH-meter (mod. Basic 20) and a MeterLab™ PHM220 pH-meter, and a CDM210 conductivity-meter (Radiometer, Copenhagen, Denmark), respectively (NIST standard calibration). Independent measurement analyses were performed in SECRIM and CAB laboratories. Thermal analysis of selected ice samples was performed in a DSC 2920 of TA Instruments. Temperature and heat flow were calibrated in the common manner, using the onset temperatures of the melting of indium (429.75 K) and an empty pan was used as reference. The sample (20–25 mg) was put into a hermetically sealed aluminium pinhole pan. The sample was cooled from ambient down to  $-50\text{ }^{\circ}\text{C}$ , and reheated at  $3\text{ }^{\circ}\text{C min}^{-1}$  up to  $150\text{ }^{\circ}\text{C}$ . For a comparison, this same procedure was also applied to MilliQ® water and tap water from the locality of Mejorada del Campo. The anion content was determined using a Dionex LC20 chromatograph equipped with a ED 40 electrochemical detector, a GP50 gradient pump and a AS 40 autosampler, a CD25 suppressed conductivity detector and an anion self-regenerating suppressor ASRS ULTRA II, 4 mm (Autosuppression Recycle mode).

Quantitative multielemental analysis was performed by means of an inductively coupled plasma source mass spectrometer (ELAN9000 Q-ICP-MS) equipped with a Rytan™ cross-flow nebulizer, a Scott spray chamber and a Cetac ASX-510 autosampler. The sampler transport to the nebulizer was established by a peristaltic pump. In order to obtain maximum precision, the instrument was optimized daily, using a solution containing 10 ppb of Mg, Cu, Rh, Cd, In, Ba, Ce, Pb and U to obtain maximum  $^{103}\text{Rh}$  intensity, as well as an oxide and double charge ion levels (lower than 3%). Regarding the reagents and standard samples, multielement external standard working solutions were prepared by accurate dilution of two commercial ICP-MS standards, covering the whole mass range: Certipur® ICP multielement standard solution VI (Merk) and multielement calibration solution 2 (PerkinElmer).

The acids employed in the sample treatment are suprapur grade (Merk), and high purity water ( $18.2\text{ m}\Omega$ ) from a MilliQ® water system (Millipore) was used. Several aliquots were sampled from the interior of the megacryometeor. Likewise, additional tap water samples from Mejorada del Campo and Madrid, and Madrid rainwater were analyzed for comparison following the same analytical routine. The quality control of the analysis process was studied monitoring the recovery of the internal standard during the analysis and of all the elements in the quality control standard. Determination of arsenic content was specifically performed by a Perkin Elmer AAnalyst 600 atomic absorption spectrometer, equipped with a longitudinal Zeeman-effect background corrector and an AS-800 autosampler. The standard PerkinElmer THGA transversely heated graphite furnace atomizer with integrated platform was used. An electrode-less discharge lamp (EDL) was used for the determination of As ( $\lambda = 193.7\text{ nm}$ ). The isotopic study was carried out at the Stable Isotope Laboratory of the Estación Experimental del Zaidín (Granada, Spain). Oxygen in water was analysed by the  $\text{CO}_2\text{-H}_2\text{O}$  equilibration method.<sup>27,28</sup> To determine hydrogen isotopic ratios we used reduction with Zn at  $450\text{ }^{\circ}\text{C}$ .<sup>29,30</sup> Isotopic ratios were measured by a Finnigan MAT 251 mass spectrometer. The experimental error was

$\pm 0.1\text{‰}$  and  $\pm 1\text{‰}$  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. An organic compounds analysis was performed by solid phase microextraction (SPME) coupled with GC-MS: *c.a.* 4 mL of the megacryometeor sample was heated in a vial closed with a septum at  $70\text{ }^{\circ}\text{C}$  for 45 min. A  $100\text{ }\mu\text{m}$  CAR-polydimethylsiloxane (CAR-PDMS) fibre was then exposed to the headspace, keeping the sample at the same temperature for a further 45 min. Analytes on the fibre were then thermally desorbed in the injection port of a Perkin Elmer Autosystem XL-Turbomass GC-MS instrument at  $290\text{ }^{\circ}\text{C}$  for 4 min (split less mode). The analysis was performed using a capillary column (5% diphenyl-95% dimethylpolysiloxane,  $30\text{ m} \times 0.25\text{ mm ID}$ ,  $0.25\text{ }\mu\text{m}$  film) and using He as carrier gas. The temperature was raised from  $40\text{ }^{\circ}\text{C}$  (4 min) to  $150\text{ }^{\circ}\text{C}$  at a rate of  $15\text{ }^{\circ}\text{C min}^{-1}$ , held for 2 min,  $150\text{ }^{\circ}\text{C}$  to  $255\text{ }^{\circ}\text{C}$  at  $5\text{ }^{\circ}\text{C min}^{-1}$ , held for 15 min, and  $255\text{ }^{\circ}\text{C}$  to  $300\text{ }^{\circ}\text{C}$  at  $10\text{ }^{\circ}\text{C min}^{-1}$ , and held for 1 min. The mass spectrometer was operated under EI mode, at an ionization energy of 70 eV,  $m/z$  range 30–600, transfer line at  $300\text{ }^{\circ}\text{C}$ . In addition to all these techniques, a microbiological analysis of the external part of the ice samples was also carried out.

## Results and discussion

The megacryometeor water has a pH in the range of from 7.05 to 7.86 ( $\pm 0.10$ ), and conductivity values from 56.4 to 69.2 ( $\pm 7$ )  $\mu\text{S cm}^{-1}$ . Thermal analysis of the ice indicates melting values ranging from  $-0.09\text{ }^{\circ}\text{C}$  to  $3.12\text{ }^{\circ}\text{C}$  ( $316.4\text{ J g}^{-1}$ ) and boiling values from  $99.34\text{ }^{\circ}\text{C}$ – $104.32\text{ }^{\circ}\text{C}$  ( $1959\text{ J g}^{-1}$ ) (Fig. 2). Likewise, main ranges ( $\text{mg l}^{-1}$ ) of F,  $\text{BrO}_3$ , Cl,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  are the following: F: 0.52–0.68;  $\text{BrO}_3$ : <LQ–0.13; Cl: 6.41–8.37;  $\text{NO}_2$ : <LQ;  $\text{PO}_4$ : 0.70–0.83 and  $\text{SO}_4$ : 3.38–3.73. Table 1 displays a summary of the main hydrochemical results of the ice obtained by ICP-MS. Arsenic content was below detection limit (1.08 ppb) in all cases. Isotopically, the distribution of the samples (35 points of isotopic analyses covering different parts of the ice fragments;  $-9.76\text{‰} > \delta^{18}\text{O}_{\text{SMOW}} > -10.70\text{‰}$  and  $-49\text{‰} > \delta\text{D}_{\text{SMOW}} > -56\text{‰}$ ) in the Craig's line verify that they match the Meteoric Water Line,<sup>17</sup> providing evidence of a direct condensation of the ice from atmospheric (unequivocally tropospheric) water

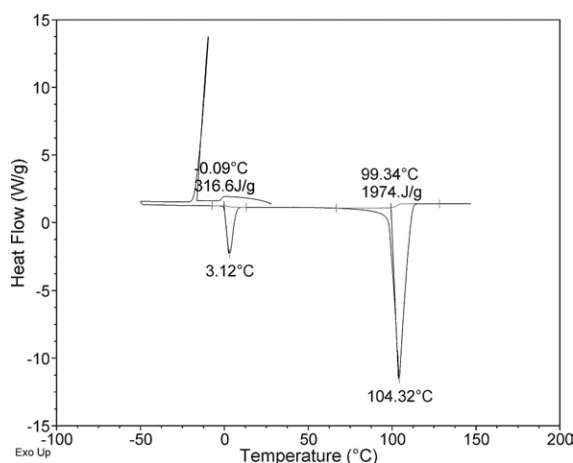


Fig. 2 DSC of the ice, showing the ranges of melting and boiling values.

**Table 1** ICP-MS hydrochemical results showing the ice composition of the Mejorada del Campo megacryometeor (MJC-m). MJC-tw: Mejorada del Campo tap water. M-rw: Madrid rainwater. M-tw: Madrid tap water. BDL: below detection limit. ND: non detected, LOD: limit of detection. The operating parameter setting is the following: RF power (W): 1000. Nebulizer gas flow: 0.89 l min<sup>-1</sup>. Lens voltage: 7.25 volts. Analog Stage voltage: -1900 volts. Pulse stage voltage: 1100 volts. Sweep/reading: 6. Reading/replicate: 1. Replicate: 1

ppb	MJC-m	MJC-tw	M-rw	M-tw	LOD
Ca	5333.6	9430.1	7437.8	7655.5	3.79
Na	7900.3	5931.1	1342	4494.9	1.25
Mg	655.1	1705	376.8	1308.3	0.81
Al	130.3	76.5	80.1	388.7	0.51
Si	253.3	2089.3	280.1	1766.7	1.29
P	239.7	ND	110.5	5.1	2.86
K	1853.6	792.9	603.1	610.5	6.49
Sc	BDL	1	BDL	0.9	0.17
V	BDL	BDL	1.9	BDL	1.02
Cr	2	1.7	ND	1.2	0.32
Mn	10	1.7	12.3	9.6	0.23
Fe	74.8	30.3	39.1	268.4	2.73
Co	BDL	BDL	0.7	BDL	0.4
Ni	2.239	BDL	1.6	1.6	0.9
Cu	36.5	3.6	11.7	491.1	1.29
Zn	180.2	4.6	88.2	136.7	0.84
Ge	ND	ND	ND	ND	0.75
As	BDL	BDL	BDL	BDL	1.08
Rb	BDL	BDL	BDL	BDL	3.22
Sr	26	44.7	23.3	31.1	2.37
Y	0.1	BDL	0.1	0.1	0.1
Zr	ND	ND	BDL	ND	0.25
Cd	2.1	BDL	BDL	ND	0.85
Ba	12.2	6.9	11.1	6.8	2.42
La	BDL	BDL	BDL	BDL	1.74
Ce	BDL	BDL	BDL	BDL	1.38
Pr	BDL	BDL	BDL	BDL	1.63
Nd	BDL	BDL	BDL	BDL	0.25
Sm	BDL	BDL	BDL	BDL	0.37
Pb	4	BDL	5.5	0.5	0.25

vapour. Regarding the analysis by GC-MS, it is important to note that no organic compounds were detected in the ice samples, which were specifically extracted from the interior of the megacryometeor fragments. Finally, in order to determine the biological contamination of the ice, three aliquots of ice-melt water were sampled from the surface of the megacryometeor and plated onto solid media with nutrient agar (Panreac Cultimed) for selective growth culture. Subsamples were removed for PCR amplification of 16S rDNA. The subsequent cloning and sequencing of the samples, using a 3130 Genetic Analyzer and the Microseq software (Applied Biosystem), revealed the following species: *Brevundimonas intermedia*, *Kocuria rosea*, *Achromobacter sp.*, *Sphingomonas sp.*, *Pantoea sp.* and *Acinetobacter sp.*

Basically, the circumstances surrounding the Mejorada del Campo incident and the hydrochemical and isotopic features determined in the ice samples are in a good agreement with previous results<sup>6,10,11</sup> concerning other megacryometeors. It is well known that precautionary principles require that environmental managers should be prudent when making decisions, where there is still an incipient understanding about the underlying scientific issues. As previously defined, although several hypotheses have been advanced, no geophysical model is able to adequately give explanation of what factors cause the ice

nucleation and growth, or how megacryometeors can be actually formed and maintained in the atmosphere.<sup>6,9-11</sup> However, it is a fact that tropospheric ice chunks, weighing tens of kilograms, do fall provoking verifiable hazards without a clear knowledge about the environmental implication of the whole process that rules their formation in the atmosphere (more or less anthropogenically related). This article offers new data about the Mejorada del Campo megacryometeor and documents the value of having both civil and scientific institutions involved in conducting follow-up investigation of such atmospheric ice falls. Institutions should be ready and alert to the need for proper environmental and logistic responses to these incidents.

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# Research highlights

Natural atmospheric processes cause formation of megacryometeors

## Getting to the truth of falling ice chunks

A massive lump of ice falling from the sky and landing at your feet is not what you would expect on a lovely sunny day, but unusual events like these have been known to happen. People have often speculated whether they could be giant hailstones or maybe ice from aircraft, but a team of Spanish scientists has found that the answer actually lies within complex natural processes in the atmosphere.

Jesus Martinez-Frias at the Centre for Astrobiology, Madrid, and a multidisciplinary team of scientists have looked at the formation of large ice conglomerations, known as megacryometeors, in our atmosphere. There have been more than 100 recorded events of ice chunks falling from the sky, explains Martinez-Frias, but up to now their formation has not been fully understood.

The team focussed on a ten kilogram ice chunk which fell from a clear sky in a town close to Madrid in 2007 - the Mejorada del



Campo megacryometeor. Using a multianalytical approach the team found that the chunks have the texture, hydrochemical features and isotopic values that prove they come from atmospheric processes. The water in the megacryometeor is clearly tropospheric, explains

**The 2007 Mejorada del Campo megacryometeor crashed through the roof of an industrial storage unit**

Martinez-Frias.

Martinez-Frias uses the analogy of an atmospheric 'symptom' to say that the real cause of these ice chunks will only be 'diagnosed' with an interdisciplinary approach. 'Megacryometeors do fall. This is an indisputable fact and we encourage other scientists to study these events all around the world to ascertain whether they obtain similar results and reach similar conclusions about their formation.'

Bernd Michael Rode, professor of theoretical and inorganic chemistry at the University of Innsbruck, Austria, says, 'the team's work shows that our atmosphere still provides surprising and unresolved problems'. He echoes the words of Martinez-Frias, saying that this field of research 'requires interdisciplinary co-operation on a very wide scale'.

*Katherine Davies*

### Reference

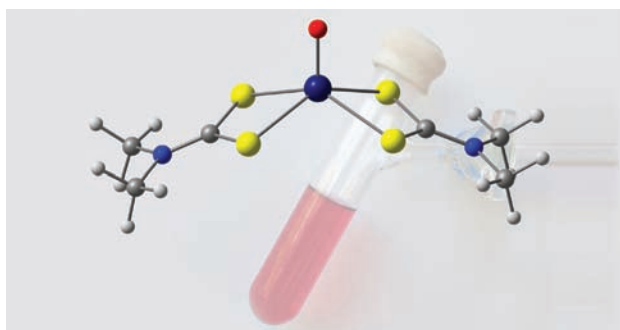
F Alamilla Orellana *et al.*, *J. Environ. Monit.*, 2008, DOI: 10.1039/b718785h

High-valent metal oxides for the hydrogenation of alkynes and sulfoxides

## From oxidation to reduction

Researchers in Portugal have developed high-valent metal oxides for hydrogenating alkynes and sulfoxides, using inexpensive hydrogen.

Beatriz Royo and co-workers at the University of Lisbon exploited catalysts normally used for oxidations, such as olefin epoxidation and oxygen transfer. An earlier unconventional hydrosilylation of carbonyl groups with a high-valent rhenium oxide catalyst prompted us to further investigate these catalysts, says Royo. The team has extended the role of this and a similar molybdenum catalyst to reductive processes using hydrogen, a cheaper and more convenient reducing agent than silane. The catalysts are even capable of catalysing the selective hydrogenation of alkynes



to alkanes - a challenging task in organic synthesis, says Royo.

The molybdenum catalyst,  $\text{MoO}_2\text{Cl}_2$ , also possesses high catalytic activity in the deoxygenation of sulfoxides using hydrogen, which may have important advantages in terms of green chemistry, explains Royo. The procedure replaces

**Oxidation catalysts have been utilised in reductive processes**

### Reference

P M Reis *et al.*, *Dalton Trans.*, 2008, 1727 (DOI: 10.1039/b719375k)

phosphines, expensive metals and environmentally hazardous reducing agents, and has the added advantage of producing only water as a by-product.

Werner Thiel, professor of inorganic chemistry at the University of Kaiserslautern in Germany, is impressed by the work. He says that the researchers have exceeded the expectations for these types of catalysts, and that they have 'opened the door for other researchers to find further applications of high-valent transition metal compounds in reductions'.

Royo says that the team is now studying the mechanism of these processes, and an important goal for the future is to develop systems for enantioselective reductions. *Roxane Owen*