

# **Project of Strategic Interest NEXTDATA**

 $Scientific \ Report \\ for the \ reference \ period \ 01 - 01 - 2014 \ / \ 31 - 12 - 2014$ 

# WP 1.6 Paleoclimatic data from continental regions

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#### 1. Scheduled activities, expected results and Milestones

#### 2. Deliverables expected for the reference period

- D1.6.1: Palynological reconstruction of the last 2000 yr inferred from the Coltrondo peat bog.
- D1.6.2: Geochemical reconstruction of the last 2000 yr inferred from the Coltrondo peat bog.
- D1.6.3: Dating of the Coltrondo and Danta di Cadore peat bog sequences, with special emphasis on the last 2000 yr.
- D1.6.4: Coring the Danta di Cadore peat bog from lake sediments level down to the bedrock.
- D1.6.5: Coring of two Alpine lakes from Dolomitic region (Fosses and Federa lakes) for a total of 4 cores (about 1m long).

#### 3. Activities which have been actually conducted during the reference period

#### 3.1 Research activities

## Ortles firn/ice core

The Ortles firn/ice core has been processed. 114 sections, each one 0.70 m long, has been cut into subsamples for stable isotopes, pollen, therpens discrete analysis, as well as for the continuous flow analysis. Samples were cut with a modified commercial band saw, with a stainless steel blade and a polyethylene tabletop and guides. The table, guides and the blade were carefully cleaned with acetone and methanol to remove contamination before every use. All exposed ice surfaces were rapidly scraped with a stainless steel knife cleaned with 0.1% ultra-pure HNO<sub>3</sub> (Romil, Cambridge, UK), rinsed several times and carefully dried after each use. A specific cutting scheme has been developed in order to achieve subsamples characterized by a suitable geometry for the subsequent chemical analysis and, in the same time, to minimize the handling and cuts (Fig. 1).

For stable isotopes, therpens and pollens, the cutting resolution has been modified with the depth in order to achieve a sub-annual resolution along the entire core. In total, more than 2300 and 1980 samples have been prepared for stable isotopes and therpens, respectively (Tab. 1). For the continuous flow analysis (CFA) the core sections were cut to obtain ice with a cross-section of 32x32 mm and a length of 30-70 cm, depending on the core conditions.

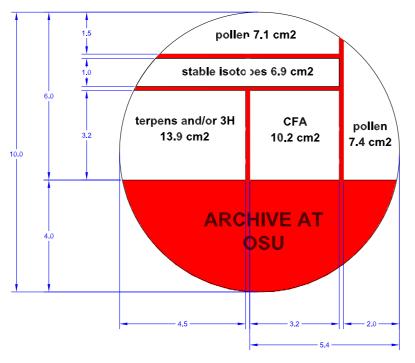


Fig. 1. Ortles ice core cutting scheme

Depth (m)		Stable isotopes		Pollens and therpens	
from	to	Resolution (cm)	# samples	Resolution (cm)	# samples
0.0	5.6	9	62	9	62
5.6	9.8	8	53	8	53
9.8	14.1	7	61	7	61
14.1	18.4	6	72	6	72
18.4	22.0	5	72	5	72
22.0	38.4	4	410	4	410
38.4	56.0	3	587	3	587
56.0	76.1	2	1000	3	667
		SUM	2316	SUM	1983

Tab. 1. Summary of Ortles discrete samples

About 1200 samples have just been analyzed for stable isotopes ( $\delta D$ ,  $\delta^{18}O$ ) and about 15 for  $^{3}H$ .

The extraction of glacio-chemical information from ice cores is a challenge exacerbated by the very low concentrations of some impurities, thereby demanding rigorous control of external contamination sources and very sensitive analytical techniques. High resolution chemical sampling profiles are normally required, especially for glaciers with low annual snow accumulation of fresh snow. The development of continuous ice-core melting systems over the last few years has considerably increased the temporal resolution with respect to the extremely labor-intensive and time-consuming traditional chiseling procedure.

During this first part of the project a new melting system has been planned, developed and then realized in the University Ca' Foscari workshop.

The melting system is hosted in a -20°C vertical freezer and consists of a melting head made of high purity (>99.9%) anodized Aluminum. The temperature of the melting head is regulated by a digital thermostat, normally fixed at 30°C, using an electrical heater coupled with a thermocouple.

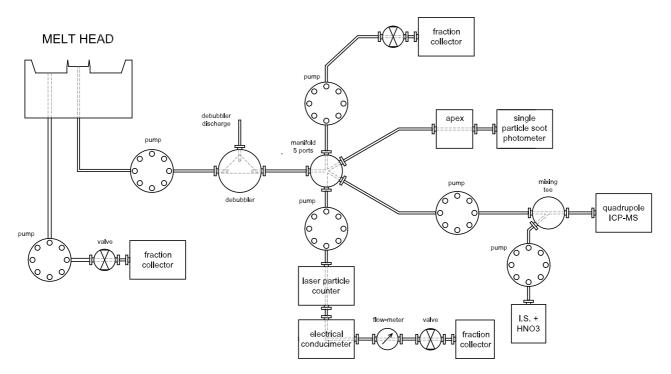


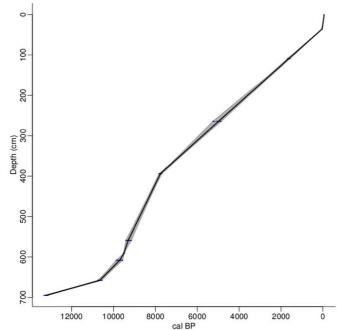
Fig. 2. Continuous flow analysis (CFA) scheme

### Danta di Cadore and Coltrondo peat cores

Both the Coltrondo e Danta di Cadore peat cores have been fully processed, providing subsamples for physical, biological and chemical measurements.

The entire cores were first frozen at -18°C, immediately after collection and then cut in cold conditions into 2 sub-cores. One sub-core was preserved for continuous X-Ray Fluorescence (XRF) core scanner analysis, while the other was used for chemical and physical measurements. This second sub-core was cut into 1-cm slices and each slice was then divided into 6 squares to obtain several subsamples. The outside edges were discarded to ensure that only the uncontaminated part of each sample was used for analysis. The subsamples were taken from the same position in each slice. The table, guides and saw were carefully cleaned with acetone and methanol in order to remove any potential contamination that could interfere with the subsequent measurements. The cutting resolution was fixed at 10 mm and about 700 and 250 subsamples have been prepared for the Danta di Cadore and Coltrondo bogs, respectively.

For both peat bog cores the age-depth relationship is based on Accelerator Mass Spectrometry (AMS) <sup>14</sup>C, and <sup>210</sup>Pb and <sup>137</sup>Cs measurements. At now information about age-dating is available only for Danta di Cadore peat bog core. For radiocarbon determinations samples were collected from the core at different depths, cleaned with Milli-Q water and dried at 105°C and then submitted for radiocarbon analysis to the Chrono Centre, Queens University of Belfast. Radiocarbon ages were calibrated as calendar years before present (cal BP) with the CALIB 6.0 software. The results are presented with 95% confidence intervals and 2σ-ranges. In addition to the <sup>14</sup>C age dating, the upper 40 cm layers of the bog core were dated using <sup>210</sup>Pb and <sup>137</sup>Cs measurements. For <sup>210</sup>Pb and <sup>137</sup>Cs determination, dried peat samples were analyzed by direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory using Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detectors.



Depth (cm)	<sup>14</sup> C yrs BP	Estimated 2σ range (age cal BP)	Median value (age cal BP)	Analysed fraction
109	1713 ± 23	1555 - 1695	1619	Bulk peat
264	4388 ± 45	4850 - 5060	4957	Wood
394	6939 ± 31	7687 - 7839	7763	Wood
559	8287 ± 33	9198 - 9421	9303	Wood
591	8497 ± 37	9466 - 9539	9506	Wood
608	8728 ± 39	9554 - 9824	9686	Wood
658	9427 ± 43	10554 - 10764	10658	Wood
695	11338 ± 53	13110 - 13330	13221	Pisidium shells

Fig. 3. Dating of the Danta di Cadore Peat cores

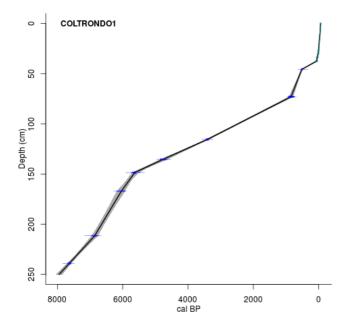


Fig. 4 Dating of the Coltrondo peat cores

Peat components were measured quantitatively by loss-on-ignition (LOI). After recording the peat wet weight, samples were dried at  $105^{\circ}$ C overnight and the dry mass was weighed using a KERN balance Alt 220-4-NM (1 mg resolution). The ash content was measured after placing dried samples for 5 hours in a muffle furnace at  $550^{\circ}$ C. To be sure that all organic material was oxidized, we tested selected samples at  $900^{\circ}$ C. The difference between the two ashing temperatures was less than 0.2% in the final weight.

Each 1-cm slice was sealed in a polyethylene bag and then squeezed with constant pressure to extract the pore water following the protocol defined by Givelet et al. (2004). Subsamples of this pore water were immediately analyzed for pH and electrical conductivity (EC) using a CRISON multiprobe MM 40+. Pore water samples were centrifuged for 10 minutes at 3000 rpm using a Rotina 38, HETTICH. Once centrifuged, pore water samples were analyzed at the University of Venice using an AGILENT 7500cx collision/reaction cell inductively coupled plasma mass spectrometer (CRC-ICP-MS) equipped with a CETAC ASX-520 auto-sampler to determine the concentrations of 36 major and trace element.

#### Federa and Fosses lake sediments coring

The two lakes selected are Lake Fedèra and Fosses. Fedèra is a typical lake Dolomite high altitude that lies within the municipal area of Cortina d'Ampezzo, in the province of Belluno. Although it is free of inlets and outfalls, the lake level remains fairly constant throughout the year thanks to underground springs that feed the water. Situated at the base of the majestic eastern wall of the Croda da Lago. Fosses lakes are located within the Regional Park of the Ampezzo Dolomites, in a karst depression there two lakes.



Fig. 5. Coring of the Federa and Fosses lakes

The coring fieldwork was done on 2nd and 3rd October 2014 respectively on Lake Fosses Grande and Fedèra. In each lake using a gravity corer from a small boat 3 (Fedèra) and 4 (Fosses Grande) parallel cores where recovered. All the cores were ca. 60cm in length (Fig. 5). The cores were sealed, kept at 4°C and transported to CNR-ISE for the subsequent analysis and subsampling. Once in the laboratory, on each core a whole core magnetic susceptibility analysis have been performed with a Bartington loop sensor (MS2C). This analysis measured the magnetic susceptibility that is the degree of magnetization of a material in response to an applied magnetic field. If magnetic susceptibility is positive, then the material can be paramagnetic, ferromagnetic, ferrimagnetic, or antiferromagnetic. In this case the magnetic field is strengthened by the presence of the material. Alternatively, if magnetic susceptibility is negative the material is diamagnetic. As a result, the magnetic field is weakened in the presence of the material. Changes in magnetic susceptibility correlate with changes in sedimentary provenance and/or diagenetic environment. Magnetic susceptibility records are therefore useful for inter-core correlation.

#### 3.2 Applications; technological and computational aspects

The novel melting system for the continuous decontamination and analysis of Alpine firn and ice cores has been designed, built and tested at the CNR-IDPA laboratories in Venice. Very good results have been obtained in terms of decontamination efficiency, precision, accuracy and robustness.

In consideration of the very high-quality level of the melting system, two foreign Universities (The Ohio State University – Byrd Polar Research Center, Ohio, Columbus, USA; Inha University, Seoul, Korea) asked for our availability to provide them similar system. During

2014 a very basic version of our melting system has been provided to the Byrd Polar Research Center. In October 2014 the system has been installed by our researchers.

#### 3.3 Formation

SEGNANA M., (2014): Handling and numerical analysis of palaeoecological data, Göttingen, 15-20 June, 2014.

#### 3.4 Dissemination

GABRIELI J., (2014): European history of atmospheric pollution from an ice core extracted at Colle Gnifetti. Byrd Polar Research Center, The Ohio State University, Columbus, OH, USA, 23 October, 2014.

Gabrieli J., Barbante C., Poto L., Segnana M., (2014): Dimostrazione di un sistema di fusion di carote di ghiaccio. La Notte dei Ricercatori, Rettorato Ca' Foscari, Venezia, 26 September, 2014.

## 3.5 Participation in conferences, workshops, meetings

GABRIELI J., (2014): Climatic reconstruction in the Eastern Alps: high-resolution multi-proxy study from ice-cores and peat bogs. *Climate variability in Italy during the last two millennia – Italy 2k*, Accademia Nazionale dei Lincei, Roma, 02 December, 2014.

SEGNANA M., (2014): Mid- to Late Holocene in the Dolomites (Eastern Italian Alps): climate and environmental dynamics inferred from pollen and geochemical analyses. *SGI-SIMP*, Milano, 11 September 2014.

Poto L., (2014): Two thousand years of atmospheric metal depositions recorded by the ombrotrophic peat bog of Danta di Cadore (North-Eastern Italy). *SGI-SIMP*, Milano, 11 September 2014.

SEGNANA M., (2014): Holocene environmental and climatic dynamics in the Dolomites (Eastern Italian Alps) reconstructed from pollen and geochemical analysis. *DEUQUA*, Innsbruck, 25 September 2014.

GABRIELI J., (2014): A novel firn/ice-core melter system for continuous ICP-QMS trace element analysis. *CGI – Glaciological Symposium*, Torino, 20 September 2014.

Рото L., (2014): Late Glacial to Holocene deglaciation of the Piave basin: new insights from an ombrotrophic peat bog. *CGI – Glaciological Symposium*, Torino, 20 September 2014.

SEGNANA M., (2014): Holocene climate dynamics in the Eastern Italian Alps: a multi-proxy study from ice and peat bogs. EGU, Wien, 27-30 April 2014.

SEGNANA M., (2014): Mid- to Late Holocene climate and environmental variation in the Dolomites (Eastern Italian Alps) inferred from pollen and geochemical analyses. *EPPC*, Padova, 26-31 August 2014.

DREOSSI G., (2014): Comparing weather station and isotopic data in the new Alpine ice core drilling site of Mt. Ortles (South Tyrol, Italy). *CGI – Glaciological Symposium*, Torino, 20 September 2014.

#### 4. Results obtained during the reference period

- 4.1 Specific results (Data libraries, Measurements, Numerical simulations, etc)
  - Geochemical data (ICP-MS data; trace elements, rare earth elements, Pb isotopes) of Danta di Cadore peat Bogs (excel file; resolution 1 cm from 0 to 120 cm of depth).

- Geochemical data (ICP-MS data; trace elements, rare earth elements, Pb isotopes) of Coltrondo peat Bogs (excel file; resolution 1 cm from 0 to 100 cm of depth).
- -Geochemical data (XRF-CS data; trace elements) of Danta di Cadore peat Bogs (excel file; resolution 2.5 mm from 0 to 700 cm of depth).
- -Geochemical data (XRF-CS data; trace elements) of Coltrondo peat Bogs (excel file; resolution 2.5 mm from 0 to 100 cm of depth).

#### 4.2 Publications

Poto L., Gabrieli J., Crowhurst S., Agostinelli C., Spolaor A., Segnana M., Cairns W.R.L., Cozzi G., Barbante C., (2014): Cross calibration between XRF and ICP-MS for high spatial resolution analysis of ombrotrophic peat cores for paleoclimatic studies. *Analytical and Bioanalytical Chemistry*, 407, 379-385.

Gabrieli J., Barbante C., (2014): The Alps in the age of the Anthropocene: the impact of human activities on the cryosphere recorded in the Colle Gnifetti glacier. *Rendiconti dei Lincei*, 25, 71-84.

4.3 Availability of data and model outputs (format, type of library, etc) No model outputs are available

#### 4.4 Completed Deliverables

- Dating of the Coltrondo peat-bog core.
- Dating of the Danta di Cadore peat-bog core.
- Installation of a melting system for continuous decontamination/analysis (dust, trace elements, conductibility, black cabon) of Alpine firn/ice cores.
- Collection of two sediment cores from Dolomitic high-altitude lakes.
- Extensions of the Danta di Cadore peat-bog core to the bedrock.

# 5. Comment on differences between expected activities/results/Deliverables and those which have been actually performed.

The planned roadmap has been followed without delays or substantial problems.

#### 6. Expected activities for the following reference period

#### Ortles firn / ice core

- Development and testing of the melting system; connection and calibration of all the instruments.
- Decontamination of the Ortles ice core through melting system.
- High-resolution black carbon profile.
- High-resolution trace elements profiles.
- High-resolution electrical conductivity profile.
- Collection of discrete samples for further discontinuous analyses.
- Validation of experimental datasets.
- Continuation of stable isotopes ( $\delta D$ ,  $\delta^{18}O$ ) analysis (>80% of total samples number).
- Development of a preliminary depth/age model.

#### Danta di Cadore and Coltrondo peat-bog

- Continuation of pollen measurements in Danta di Cadore peat bog samples.
- Publication of palinological data of the Coltrondo peat bog.
- Publication of geochemical data of the Colrondo and Danta di Cadore peat bog.
- Installation of a meteorological station on the Danta di Cadore bog and acquisition of meteorological data.
- Monthly sampling of surface waters and precipitations in the Danta di Cadore.

# Fosses and Federa sediment cores

- Processing of cores and samples preparation.
- Dating of the cores using <sup>210</sup>Pb and <sup>14</sup>C techniques.
- Surface Image analysis and XRF will be performed in collaboration with the Institute of Geology, University of Bern (Dr. Anselmetti & H. Vogel).
- Biological analysis will be performed at CNR-ISE.