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# Environmental records from temperate glacier ice on Nevado Coropuna saddle, southern Peru

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**Abstract.** We investigated past climate variability and the zonal short and long-range transport of air masses in tropical South America using chemical, isotopic and palynological signals from a 42 m-long ice core recovered in 2003 from the saddle of the Nevado Coropuna, southern Peru (72°39' W; 15°32' S; 6080 m a.s.l.). We found that precipitation at this site depends mainly on the easterly circulation of air masses originated from the tropical Atlantic Ocean. Nevertheless, sporadic Pacific air masses arrivals, and strong cold waves coming from southern South America reach this altitude site. In spite of post-depositional effects, we were able to identify two strong ENSO (El Niño-Southern Oscillation) event signatures (1982–1983 and 1992) and the eruptive activity of the nearby Sabancaya volcano (1994).

#### 1 Introduction

Ice records provide significant information on past climatic and atmospheric conditions. Ice cores drilled in South America offer a continuous record from the equator to Patagonia (Vimeux et al., 2008). A new ice core was drilled in southern Peru in 2003 to study the short and long-range transport of air masses over a tropical site close to the Pacific coast. Furthermore, since some effects of El Niño-Southern Oscillation (ENSO) were recorded in ice cores from Peru (Henderson et al., 1999; Thompson, 2000), we expected to obtain a record



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of past ENSO from this site located in the western part of the Andes.

High-resolution studies may provide interannual to seasonal variability of the climate over the last centuries provided that the link between environmental conditions and the glaciological record is well defined. However even at high altitude, tropical glaciers may experience surface melting during the summer and sublimation during the dry season (Ginot et al., 2006). The influence of percolation and sublimation on chemical and isotopic records was discussed in many works (Davies et al., 1982; Eichler et al., 2001; Ginot et al., 2001; Hou and Qin, 2002; Schotterer et al., 2003; Li et al., 2006). These post-depositional processes have to be considered while interpreting the records. Pollen dispersal on ice caps has recently been proved to be an accurate tool to reconstruct air mass trajectories, prevailing winds and paleoenvironmental changes with an extremely fine resolution (Reese et al., 2003; Reese and Liu, 2005), with the advantage of not being affected by water percolation on temperate glaciers (Uetake et al., 2006).

Here we investigate the chemical, isotopic and palynological signals from an ice core extracted from the Nevado Coropuna mountain  $(72^{\circ}39' \text{ W}, 15^{\circ}32' \text{ S}, 6425 \text{ m a.s.l.})$ . In the next section we present the drilling site and the different analyses performed. Then, we present the results and discuss the interpretation of the records over the last few decades as well as the preserved environmental information and their implication on the zonal air masses circulation. Finally the fourth section contains the conclusions and perspectives of this work.

#### 2 Study area and methods

# 2.1 Drilling site and measurements performed during the field campaign

In June 2003, an ice core was drilled at the saddle glacier on Nevado Coropuna (6080 m a.s.l.), 100 km east from the Pacific Ocean on the western Andes in the Cordillera Occidental (Fig. 1), by the IRD (Institut de Recherche pour le Développement, France). Radar measurements showed that the ice thickness at the drilling site was approximately 110 m, but the drilling was stopped at 41.6 m in water saturated firn. In fact, several layers of wet firn and water were detected during the drilling. The firn meltwater may be originated in an area of penitents – melting and sublimation structures – observed on the northern slope of the glacier upstream from the drilling site. Penitent formation can produce a slanted meltwater flow that may run through the firn, potentially reaching the drilling site, and then joining a runoff observed downstream.

In addition eight snow pits from 30 to 350 cm in depth were dug during the drilling campaign (17 June–28 August 2003). Lysimeter measurements gave sublimation rates of 0.50 mm weq d<sup>-1</sup> in June and 0.23 mm weq d<sup>-1</sup> in August. The temperature was measured in the snow pits. A temperature increase was observed from  $-1^{\circ}$ C at the surface to  $-1.7^{\circ}$ C at 3.3 m depth (P. Wagnon, personal communication, 2003) indicating that at this site the ice is temperate. The surface temperature, recorded with an Automatic Weather Station (AWS) during the operation, never reached above  $-5^{\circ}$ C.

#### 2.2 Climatic conditions

Within a perimeter of 60 km around the Nevado Coropuna, 15 meteorological stations (operated by the peruvian SENAMHI, Servicio Nacional de Meteorologia e Hidrologia) provide important local climatic information. Monthly mean precipitation and air temperature are available from 1964 to 2003. Data series from the four highest stations (Andagua: 3590 m; Arma: 4270 m; Orcopampa: 3780 m; Salamanca: 3200 m), spanning 22 to 35 years, have been selected for a statistical study according to the consistency of the records. Seasonal temperature amplitudes are small. Contrastingly, seasonal precipitation amplitudes are very strong with most of the precipitation events taking place during the austral summer: 70 to 90% of the annual precipitation occurs from December to March (Fig. 2). A drastic decrease of precipitation was observed in 1982-1983 and 1992 during strong El Niño events (Fig. 2). It is worth noting that other notable El Niño episodes (such as in 1997) are not obvious in the precipitation records.

# 2.3 Chemical, isotopic and palynological analysis of the ice-core

The saddle core was prepared in clean cold room facilities  $(-15^{\circ}C)$  at the LGGE (Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France). Samples were prepared for soluble ions, water stable isotopes, and pollen analyses using adequate decontamination procedures giving resolutions of 4.5 cm, 7.0 cm and 70 cm, respectively. Tritium (<sup>3</sup>H) activity was measured for some selected core segments to localize the maximum activity peak at Paul Scherrer Institut (Villigen, Switzerland). Chemical measurements were performed by conductivity-suppressed Ion Chromatography using a Dionex ICS 3000 at the LGGE's clean room facilities. Profiles of organic and inorganic anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, methanesulphonate, mono and dycarboxylic acids) and cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>,  $Ca^{2+}$ ) were obtained for the first 22 m of the ice-core with an experimental precision ranging from 1-10% for concentrations above  $3 \text{ ng g}^{-1}$  and 10-40% for concentrations below  $3 \text{ ng g}^{-1}$ . The  $\delta^{18}$ O and  $\delta$ D of the ice were measured at the LAMA (Laboratoire Mutualisé d'Analyse des isotopes stables de l'eau, Montpellier, France) with an Isoprime Mass Spectrometer. The experimental precision of the isotopic analysis was 0.5‰ for  $\delta$ D and 0.08‰ for  $\delta$ <sup>18</sup>O. Highresolution  $\delta D$  measurements were performed down to 42 m, but only the first 22 m are discussed here in relation to the chemical signals. A continuous  $\delta^{18}$ O profile was measured along the top 11 m of the core. Pollen and micro charcoals were counted using a light microscope at magnifications of 400 and 1000. Pollen identifications were performed using the IRD South American reference collection based at Montpellier.

#### 3 Results and discussion

#### 3.1 Upward water vapor flow

The AWS data set was used in an energy balance model described by Wagnon et al. (2003) and coupled with a heat flow model in order to compare measured and simulated snow temperatures. At 30 cm depth, the model is able to reconstruct the daily amplitude and shape of measured snow temperatures variations, but with a  $-4^{\circ}C$  bias and too high value of snow thermal conductivity. This indicates that a deep source of energy increases the thermal conductivity of the snow. The best hypothesis for this  $-4^{\circ}$ C bias is related to an internal energy production, probably due to convection of water vapor saturated air through the snowpack from the temperate zone (0°C at 4 m depth) towards the cold surface (A. Gilbert, personal communication, 2008). The vapor would likely originate from the phreatic flow produced by the melting of the upslope penitents, which seems to run through the firn.



**Fig. 1.** Map of the Andes showing the location of the Nevado Coropuna and a schematic distribution of the weather stations located around (Salamanca, Arma, Orcopampa and Andagua). The Coropuna glacier is located in the western part of the Andes (Cordillera Occidental) in Peru. A zoom in UTM coordinates of the drilling site is included.

#### 3.2 Dating and accumulation rates

Tritium activity was used to identify a stable reference horizon in the ice core. The maximum <sup>3</sup>H fallout deposit related to tropospheric nuclear weapon tests took place in 1964/67 in South America (Groeneveld, 1977; Schotterer, 1998). We attribute the maximum deposition located at about 22 m depth in the saddle core to the years 1964–1965. In addition, dust markers were used to date the core by counting seasonal layers (Fig. 4). At this site,  $Ca^{2+}$  and  $Mg^{2+}$  originate from erodible soils and are deposited during the dry season (their

marine fraction is negligible: 2.5% and 5.2%, respectively). The mean accumulation rate calculated for the past 38 years is  $0.58 \text{ m yr}^{-1}$  (0.39 m we yr<sup>-1</sup>).

#### 3.3 Multi-site snow pits investigations

The eight snow pits dug during the drilling campaign showed spatial homogeneity of the chemical signal. Sublimation effects on chemical and isotopic records were noticeable after 2 months of exposure to the dry climate between 1 July (pit N°7) and 28 August (pit N°8): a visual comparison of



**Fig. 2.** Annual and monthly mean precipitation at selected SENAMHI-Peru stations: Salamanca  $(15^{\circ}30' \text{ S}, 72^{\circ}50' \text{ W})$ , Andagua  $(15^{\circ}29' \text{ S}, 72^{\circ}20')$ , Orcopampa  $(15^{\circ}15', 72^{\circ}20')$ , Arma  $(15^{\circ}24', 72^{\circ}46')$ .

the chemical and isotopic profiles suggests an offset of about 6 cm downward between pit profiles N°7 and N°8 (Fig. 3). According to calculation based on the data recorded by the automatic weather station, 17 mm weq total sublimation occurred between 1 July and 28 August, corresponding to approximately 6 cm of snow (the surface snow density was measured at  $0.2 \,\mathrm{g}\,\mathrm{cm}^{-3}$ ), in agreement with the depth shift. During this period Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup> showed an enrichment factor of 2.00-2.25 which reveals that in addition to sublimation, dry deposition took place during the sampling period. Other species, NH<sub>4</sub><sup>+</sup>, F<sup>-</sup>, HCOO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  $SO_4^{2-}$ , showed enrichment values of 0.68–1.21, pointing to a conservative enrichment or dry deposition or atmospheric reemission depending on their molecular form (as salt or acid). The water isotopes showed also enrichment at the surface between pit N°7 ( $\delta D$ =-28.8‰) and pit N°8 ( $\delta D$ =-9.84‰) possibly due to the effect of sublimation.

#### 3.4 Water stable isotopes

To examine the influence of kinetic processes on the isotopic signal we analyzed a running  $\delta D/\delta^{18}O$  slope calculated over 11 contiguous measurements (80 to 90 cm) between the surface and 11.5 m (Fig. 4). In the upper 3 m the slope  $\delta D/\delta^{18}O$ , close to 8 (the value of the Global Meteoric Water Line) (Dansgaard, 1964), indicates that no sublimation or refreezing of meltwater occurred. The low ice temperature and the strong variations in  $\delta D$  and  $\delta^{18}O$  indicate a good preservation of the isotopic signal in this part of the core. If we consider that the variations observed are seasonal, we can count up to 4 annual cycles (Fig. 4): this dating is in slight disagreement with calcium counting (1996/97 at 3 m). Between 3.0 and 10.5 m the  $\delta D/\delta^{18}O$  slope varies between 0.5 and 9.1



**Fig. 3.** Composition of chemical  $(ng g^{-1})$  and isotopic profiles (‰) from pit N°7 dug the 1st july 2003 (gray line) and pit N°8 dug the 28 August 2003 (black line).

and the isotopic signal seems to be affected by kinetic fractionation processes. A strong homogenization identified as melt-freeze and percolation processes occurred and drastically smoothed the signal below 3 m. Some studies of temperate ice cores showed in the same way the preservation of the isotopic signal in the upper meters (corresponding to 1 to 5 year records) and a gradual homogenization below (He et al., 2002; Nakazawa and Fujita, 2006). In addition to vertical percolation, the signal may be affected by the upward water flow of vapor induced by the slanted meltwater flow coming from the penitents. Therefore, water isotopes cannot be quantitatively used to study the past climatic conditions on Coropuna.

#### 3.5 Dampening of major ions

Along the ice-core record, an abrupt dampening of the signal of  $SO_4^{2-}$ ,  $NO_3^{-}$ ,  $NH_4^+$  and to a lesser extent  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $F^-$  is observed (Fig. 4). Since the ratio  $Cl^-/Na^+$  is a good indicator of meltwater percolation (Eichler et al., 2001; Ginot et al., 2009) we used it to determine the limits of the perturbed and unperturbed chemical signals. As detected with the  $\delta D/\delta^{18}O$  slope, we observe that the upper first meters are unperturbed by meltwater. The Cl/Na mass ratio is  $1.5\pm0.2$  g g<sup>-1</sup>, which is in good agreement with the fresh snow from pit measurements. Conversely, between 2.1 m and 5.0 m the Cl/Na mass ratio increases up to  $6.1\pm1.0$  g g<sup>-1</sup>, and below 5.0 m, the Cl/Na reaches values as high as



**Fig. 4.** Isotopic, chemical, palynological and stratigraphical profiles of the first 22 m of the ice-core.  $\delta D$  is given in permil units (‰), ion concentrations in microequivalents per liter, Cl/Na mass ratio in [g/g], pollen concentrations in number of grains per liter. MS<sup>-</sup> stands for methanesulfonate. Vertical arrows indicate annual layers. Discrepancies between isotopic and calcium markers may be due to the arrival of dry season markers more than once for some years or too many calcium peaks counted.

Depth (m)

Asteraceae

Nothofagus

 $23.5\pm2.1$  g g<sup>-1</sup> (Fig. 4). This implies that below 2.1 m ions are leached with different efficiencies from the snowpack. Sampling resolution is high enough to count seasonal cycles in spite of snow compaction, so high standard deviations indicate a conserved register. For this reason, the elution sequence is determined using a statistical approach based on the diminution of the variance of the concentration of each ion along the record. The decrease of variance indicates loss of the specie along the profile. The elution sequence is then  $SO_4^{2-}>NO_3^->Mg^{2+}>NH_4^+>Ca^{2+}>Na^+>K^+>Cl^->Br^-.$ It is uncertain why  $SO_4^{2-}$  is particularly strongly removed and why Cl<sup>-</sup> and Br<sup>-</sup> are the less perturbed species. Other studies showed different mobility behaviors among chemical species (Davies et al., 1982; Eichler et al., 2001; Li et al., 2006). The elution may be driven by leaching after ion relocation induced by snow metamorphism (Davis et al., 1995; Cragin et al., 1996). Evidence is observed for  $SO_4^{2-}$  which was more concentrated in the ice layers below 2 m than in the bulk snow, implying a favored presence in the liquid phase. Sulfate may be excluded from the ice lattice during snow metamorphism (weak percolation or vapor pumping), and seasonal melting of the snow-pack would drain it more easily from the grain boundaries. The conservation of a fraction of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cl<sup>-</sup> can be explained by the fact that dry deposition and sublimation concentrate these species in layers, and that layered species are less affected by melt-water than homogenously distributed ions (Davis et al., 1995). Alternatively, one may explain ion losses by the flow of meltwater through the snowpack. Below  $\sim 12 \,\mathrm{m}\,\mathrm{Ca}^{2+}$  recovers some of its original variability, pointing to a less effective leaching below this depth. This tends to confirm that a slanted melt-water flow may have run through the snow pack, but only between 5 and 12 m (Fig. 4).

#### 3.6 Preserved climatic and environmental signals

#### 3.6.1 The chemical register

At depths 2.1 m (1998/99) and 5 m (1994) clear tropospheric volcanic signals are observed, characterized by the presence of naked eye visible dust, high concentrations of  $SO_4^{2-}$ ,  $Cl^-$ , and peaks of  $F^-$  and  $H^+$ . The Sabancaya volcano (90 km eastward from Coropuna) had an important degassing event during August/September 1998, and one of its largest eruptions in May 1994. HYSPLIT forward trajectories (Draxler and Rolph, 2003) for Sabancaya's eruptions confirm that the plume passed over the drilling site in May 1994 but we did not find such evidence for the 1998 event, the source of which remains unidentified.

The chemical signature at Nevado Coropuna is mostly continental (Fig. 4). Average chloride to sodium mass ratio (Cl/Na) in the first upper meters of the snow is  $1.5\pm0.2 \text{ g g}^{-1}$ , which is closer to halite (Cl/Na=1.4 g g<sup>-1</sup>) than to sea-salt ratio (1.8 g g<sup>-1</sup>, Keene et al., 1986) pointing to a terrige-

nous origin. Bromide (not shown) is associated to the halite signal and the most probable source of this element is the salt lakes/flats located southeastern from the Coropuna, as it was the case for other trace elements in the Illimani ice core (Correia et al., 2003). The snow pit study showed that the best conserved terrigenous signals (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>) are associated with dry deposition. They are likely to be transported in the free troposphere since during the winter dry and warm air uplifting is privileged. Another continental feature in the core and pits is the seasonal variation of  $NH_4^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ . Their signals are not in phase with the  $Ca^{2+}$  profile, which indicates a different deposition period.  $NH_4^+$ may be associated to the summer productivity of the forest and  $SO_4^{2-}$ ,  $NO_3^{-}$  and part of the  $NH_4^+$  to the biomass burning period (Andreae and Browell, 1988). It seems that these species, associated to wet deposition (summer and autumn), are more susceptible to be leached by the seasonal changes of the snow pack.

Surprisingly, information concerning marine arrivals at this site is scarce: few important peaks of sea salt and methanesulfonic acid ( $MS^-$ , an indicator of marine biogenic activity) were found, showing evidence of sporadic secondary marine aerosol inputs from the Pacific Ocean (Fig. 4).

#### 3.6.2 The palynological archive

According to the origin and ecology of the species identified in the ice core, we divided the results into two groups. The local taxa are characterized by Asteraceae tubuliflorae, *Polylepis* and Poaceae. The alien taxa, which cannot grow on the slope of the Coropuna (Kuentz et al., 2007) are *Quercus, Podocarpus* and *Nothofagus. Quercus* is a tree of the Andean forest whose habitat limit does not go further south than southern Colombia, *Podocarpus* is a conifer of the Andean forest, common on the slopes of the eastern Cordillera, and *Nothofagus* is a tree from the Patagonian forest whose limit stops in the temperate latitudes of Chile.

The deposition of both Quercus and Podocarpus (Fig. 4) at Nevado Coropuna is related to the arrival of northeasterly air masses. The precipitation or the pollen depositions have been weaker (in time or in intensity) and the climate drier when the local taxa became dominant in the pollen content. We identified two peaks of local species concentrations at about 11-12 m (Polylepis) and 6.5 m (Asteraceae tubuliflorae and Poaceae) associated with the presence of dust layers at the same depth (Fig. 4). The depths 11-12 m and 6.5 m may correspond to the dry years 1982-1983 and 1992, respectively, corresponding to El Niño episodes when a strong decrease of precipitation is observed. The presence of Nothofagus (at depths 3.3, 5.9 and 12.1 m) can only be attributed to the existence of a strong southern circulation allowing southern air masses to reach the latitude of Nevado Coropuna. Cold waves are air masses coming from high latitudes and going northward as far as Brazil, Peru or Bolivia. They are four times more frequent in winter than in summer (Ronchail,

1989) and cold wave arrivals were reported in southern Peru in stations located between 3000 and 4000 m a.s.l. (Quispe and Avalos, 2006). Considering that we found only three layers of *Nothofagus* in the upper 22 m of the core (Fig. 4), we propose that only the strongest cold waves can reach the highest part of the Andes, and that this phenomenon is not uncommon.

#### 4 Conclusion and perspectives

Our results demonstrate that post-depositional processes affect the primary information in the records from the Coropuna saddle core. Sublimation affects the chemical and isotopic records. In addition we identified downward percolation of surface meltwater, a slanted water flow and a consequent upward water vapor flow that may have leached most of the chemical species and homogenized the isotopic record. Although the record is disturbed to some extent, climatic information and some particular events can be identified such as nearby volcanic activity. Most of the ice impurities have a continental origin and pollen types found on the ice cap evidence westward-southward transport of air masses over the continent. Thus, as for the eastern Cordillera (Vimeux et al., 2005), moisture originated from the tropical Atlantic Ocean and recycled over the Amazon Basin is likely to control precipitation over the western Cordillera. In addition our results indicate that strong cold waves from southern South America and sporadic marine aerosol inputs from the Pacific Ocean can reach the Coropuna glacier. We identified only two El Niño periods (1982-1983 and 1992) in our records, whereas other ENSO episodes were not recorded. The identified ENSO periods are characterized by an outstanding diminution of precipitation recorded by the high altitude meteorological stations. This leads to a longer exposure of the surface to radiation, which favored enrichment of chemical species and pollen by sublimation.

In August 2003 two 34.2 m long ice cores were extracted from Coropuna south summit glacier (6450 m a.s.l.), and another 146.3 m core from the crater (6310 m a.s.l.) by OSU/Byrd Polar Research Center. Future work will deal with the comparison of our results with those ice-cores as well as other environmental records from the Andes.

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