Seasonal impact of natural and anthropogenic emissions on the highest glacier of the Eastern European Alps

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Seasonal impact of natural and anthropogenic emissions on glacier

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Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

In June 2009, we conducted the first extensive glaciological survey of Alto dell’Ortles, the uppermost glacier of Mt. Ortles which at 3905 meters above sea level (m a.s.l.) is the highest summit of the Eastern European Alps. We analyzed snow samples collected from a 4.5 m snow-pit at 3830 m a.s.l. Here, we present a comprehensive data set including a large suite of trace elements and ionic compounds that comprise the atmospheric depositions over the past few years.

Trace element concentrations measured in snow samples are extremely low with mean concentrations at pg g\(^{-1}\) level. Only Al and Fe present median values of 1.8 and 3.3 ng g\(^{-1}\), with maximum concentrations of 21 and 25 ng g\(^{-1}\). The median EF\(_c\) values for Be, Rb, Sr, Ba, U, Li, Al, Ca, Cr, Mn, Fe, Co, Ga and V are lower than 10 suggesting that these elements originated mainly from soil and mineral aerosol. EF\(_c\) higher than 100 are reported for Zn (118), Ag (135), Bi (185), Sb (401) and Cd (514), demonstrating the predominance of non-crustal depositions and suggesting an anthropogenic origin.

Our data show that the physical stratigraphy and the chemical signals of several species were well preserved in the uppermost snow of the Alto dell’Ortles glacier. A clear seasonality emerges from the data as the summer snow is more affected by anthropogenic and marine contributions while the winter aerosol flux is dominated by crustal sources. For trace elements, the largest mean EF\(_c\) seasonal variations are displayed by V (with a factor of 3.8), Sb (3.3), Cu (3.3), Pb (2.9), Bi (2.8), Cd (2.1), Zn (1.9), Ni (1.8), Ag (1.8), As (1.7) and Co (1.6).

The chemical data are also discussed in light of the atmospheric stability and back-trajectories analyses in order to explain the observed seasonal variability and how human activities impact the high altitude environment in the Eastern Alps. The origin and behavior of air masses as inferred from the evaluation of 48-h back-trajectories show significant seasonal differences. However, the large changes in trace elements concentrations seem to be more related to the vertical structure of the troposphere at a regional scale rather than the synoptic weather patterns.
1 Introduction

Impurities trapped in snow and ice provide insight into past atmospheric composition and environmental variations. In particular, the study of trace elements and ionic compounds contribute to the understanding of changes in past atmospheric circulation and to estimating the relative contribution of different sources. Trace element measurements in ice cores from around the globe are suited for the determination of natural background concentrations and anthropogenic pollution (Barbante et al., 2009; Hong et al., 2009; Kaspari et al., 2009; Shotyk et al., 2005). During the past few decades, several reconstructions of trace elements and heavy metals in polar ice-cores, especially from Antarctica (Planchon et al., 2003) and Greenland (McConnell et al., 2002), demonstrate consistent anthropogenic pollution in recent snow samples. The European Alpine glaciers are located near densely populated and industrialized areas and have considerable potential to provide excellent archives for past air pollution. These glaciers may accurately document the environmental impact of anthropogenic emissions over the previous centuries as well as the efficacy of recent air pollution controls (Schwikowski, 2004).

The first heavy metal concentrations in Alpine firn and ice samples were obtained from the analysis of a 140 m snow/ice core drilled on the Col du Gouter, in the Mont Blanc Massif (4304 m a.s.l.). Van de Velde et al. (1999) determined the seasonal variations of several trace elements (Pb, Zn, Cu, Cd, Bi, Mn and Al) from 1960–1968. In addition, two other studies (Van de Velde et al., 1999, 2000) determined the concentrations of Co, Cr, Mo, Sb, Au, Ag, Pt, Pd and Rh, in the same ice core covering the last two centuries. Barbante et al. (2001) report the changes in post-World II uranium concentrations. Concentrations of many heavy metals (Cr, Cd, Zn, Co, Ni, Mo, Rh, Pd, Ag, Cd, Sb, Bi, Pt, Au, U) were also determined in a 109 m ice core drilled in 1982 on Colle Gnifetti, Monte Rosa massif, since 1650 AD (Barbante et al., 2004). Schwikowski et al. (2004) analyzed the same samples for Pb concentration and isotopes. Surprisingly, little attention has been paid to the investigation of heavy metals in fresh snow and
seasonal snow-pack from high altitude European Alpine areas and only few reliable
data concerning winter snow have been published (Gabrielli et al., 2008; Veysseyre et
al., 2001).

In contrast, ionic compounds have been extensively studied in Alpine snow and ice.
The historical records of major ion deposition on high-altitude glaciers from the West-
ern Alps were inferred from the following firn and ice cores: Col du Dome near Mont
Blanc (Preunkert et al., 1999), Colle Gnifetti (Sigl, 2009; Bolius, 2006) and Grenz-
gletscher (Eichler et al., 2004) in the Monte Rosa Group; and Fiescherhornngletscher
in the Bernese Alps (Eichler et al., 2004). Major ions were also determined in recent
snow from the Eastern Alps: Careser glacier (Novo and Rossi, 1998), Stubai glacier
(Kuhn et al., 1998), Sonnblick glacier (Puxbaum and Tscherwenka, 1998) and in the
snowpack of mid-altitude sites (1500–2650 m a.s.l.) in the Dolomites (Gabrieli et al.,

A general prerequisite for the preservation of climatic and environmental information
in glaciers is the presence of sufficiently cold firn temperatures and the absence of
significant meltwater percolation. Until now, these conditions were expected to occur
above 4000 m a.s.l. and 4300 m a.s.l. in the northern and southern sectors of the
European Alps, respectively (Schwikowski, 2004). Given this possible limitation, only
the Mont Blanc region, the Monte Rosa Massif and a few locations in the Bernese
Oberland were previously considered as possible drilling sites.

The highest peak of the Eastern Alps is Mt. Ortles (3905 m a.s.l.) located in the
Southern Rhaetian Alps, Italy. This area lies at the boundary between the central
and southern European climate regions (Davis et al., 2003) and therefore is subject to
a continental precipitation regime with the lowest precipitation amounts of precipitation
in the Alps which are lower by a factor of two to three from the Alpine average (Schwarb,
2000). The region near Mt Ortles is often referred to as the inner dry Alpine zone (Frei
and Schär, 1998). This low precipitation suggests that although Alto dell’Ortles has
a relatively low altitude for obtaining a conserved paleo-glaciological record, the glacier
could still contain ice up as old as several millennia. Supporting evidence for old ice
includes the discovery of the prehistoric Otztaler man (5200 BP) from the ablating ice at Similaun (3280 m a.s.l.), just 30 km west of the Alto dell’Ortles glacier (Baroni and Orombelli, 1996).

To evaluate the potential of Alto dell’Ortles glacier as a glacial archive for paleo-environmental studies, we conducted the first extensive glaciological survey in June 2009 (Gabrielli et al., 2010). This survey included various glaciological measurements, a ground penetrating radar (GPR) survey, drilling a 10 m shallow core and sampling a 4.5 m snow-pit. Here, we present a new comprehensive dataset of a large suite of trace elements and ionic compounds in snow sampled from the 4.5 m snow-pit at 3830 m a.s.l., near the summit of Mt. Ortles. The data are discussed in light of the available meteorological and atmospheric circulation data including the boundary layer depth, atmospheric stability and calculated back-trajectories. This compilation provides the first data for the seasonal variability of trace species deposition in the Eastern Alps and the impact of human activities on this high altitude environment.

2 Methods

2.1 Study area

Mt. Ortles (46°30’32’’ N, 10°32’41’’ E) is located in the northern Ortles-Cevedale massif in the Southern Rhaetic Alps (Provincia Autonoma di Bolzano, Alto Adige South Tyrol, Italy), and is the highest peak in the Eastern European Alps (3905 m a.s.l.) (Fig. 1). This section of the Ortles-Cevedale massif is composed by sedimentary rocks such as stratified dolomites with interblended laminated and slab-shaped black limestone (Desio, 1967). The northwestern flank of Mt. Ortles is covered by the Alto dell’Ortles glacier. The upper part of the glacier has a slope of 8–9 degrees which then flows to steeper bedrock to form two major tongues. The glacier surface area is 1.04 km² and ranges in elevation from 3905 to 3018 m a.s.l (Gabrielli et al., 2010).
2.2 Sampling procedure

Trace species concentrations in high altitude snow and ice samples are extremely low (ranging from ng g\(^{-1}\) to sub-pg g\(^{-1}\)). Therefore we collected the samples using the same stringent anti-contamination procedures used for collecting snow and firn in polar regions (Planchon et al., 2003). All sampling tools and low density polyethylene (LDPE) bottles were pre-cleaned with diluted ultra-pure HNO\(_3\) (Ultrapure grade, Romil, Cambridge, UK) and then rinsed several times with ultra-pure water (Purelab Ultra Analytic, Elga Lab Water, High Wycombe, UK).

The scientists wore clean-room clothing and polyethylene gloves during the sampling. First, the wall of the snow-pit was scratched with a polyethylene bar, scraping away any exposed area that may have been potentially contaminated during digging. We sampled by plunging LDPE vials perpendicularly into the snow-pit wall with a spatial resolution of \(\sim 5\) cm down to a depth of 4.2 m. The collected mass was between 50–90 g, depending on the density of the sampled snow layer. The bottles were capped, packed in double LDPE bags and transported to our laboratories where samples remained frozen until analysis. The snowpack stratigraphy was identified and physical parameters such as temperature, snow density, grain shape and size, hardness indexes (hand test and Swiss Rammesonde method) were measured (Cagnati, 2003). The form of the snow grains and their dimensions were established according to the International Association of Cryospheric Science classification (Fierz et al., 2009).

2.3 Sample preparation and chemical analysis

The samples were melted at room temperature in the LDPE sampling vials in a class 100 laminar flow clean bench. For the trace element analysis, 10 mL aliquots were transferred to 12 mL ultra-clean LDPE vials and acidified with ultra-pure HNO\(_3\) to obtain 2% solutions (v/v). Other 40 mL aliquots were transferred in previously washed polycarbonate 50 mL vials for electrical conductivity, major ions, TOC (Total Organic Carbon) and stable isotope analysis.
Concentrations of Li, Be, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ag, Cd, Sb, Ba, Ti, Pb, Bi and U were determined by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS; Element2, ThermoFischer, Bremen, Germany) equipped with a desolvation system (APEX IR, Elemental Scientific, Omaha, US). Working conditions and validation tests are described in detail in Gabrieli et al. (2010b). Anions (Cl\(^{-}\), NO\(_2\)\(^{-}\), NO\(_3\)\(^{-}\), SO\(_2\)\(^{-}\), PO\(_3\)\(^{-}\)) and cations (Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), K\(^{+}\), NH\(_4\)\(^{+}\)) were determined by two ion-chromatographic stations (ICS-1500, Dionex Corporation, Sunnyvale, US). The eluent used was 0.3 mM NaHCO\(_3\) and 2.7 mM Na\(_2\)CO\(_3\), eluent flow was conducted at 1.0 mL min\(^{-1}\) on a AG12A 200 × 40 mm column (Dionex). For cation analysis, the eluent used was methylsolfonic acid 20 mM at 1.5 mL min\(^{-1}\) rate on a CG12A 200 × 40 mm column (Dionex). The injection loop volume was set at 125 µL. TOC was measured by a catalytic oxidation system coupled with an infrared detector (Perkin Elmer5000, Waltham, MA, USA). Stable isotopes ratios (δD, δ\(^{18}\)O) were determined by mass spectrometry (Finnigan Mat Delta+, ThermoScientific, Bremen, Germany).

3 Results and discussion

3.1 Character of the data

3.1.1 Trace elements concentrations and fluxes

The trace elements and ionic compounds show a pronounced variability in concentrations (Table 1). Trace element concentrations measured in snow samples are extremely low with mean concentrations at pg g\(^{-1}\) level. Only Al and Fe present median values of 1.8 and 3.3 ng g\(^{-1}\), with maximum concentrations of 21 and 25 ng g\(^{-1}\), respectively. Ti, Mn, Zn, Sr and Ba include maximum values higher than 1.0 ng g\(^{-1}\) while median concentrations are between 0.21 and 0.69 ng g\(^{-1}\). In Table 2, trace element concentrations in the Alto dell’Ortles glacier snow are compared to those from the Colle Gnifetti firn/ice.
core in the Monte Rosa Group (Gabrieli, 2008; Barbante et al., 2004; Schwikowski et al., 2004). Although the magnitude is comparable, the trace elements concentrations from the Alto dell’Ortles snow pit are generally lower than those determined in the recent Colle Gnifetti firn (1980–1993). For instance, Pb concentrations are 15 times lower in Alto dell’Ortles while Ba, V, Mn, Zn, Fe and Al are about 3–5 times lower. This variation in concentrations can be explained by differences in regional precipitation where the estimated snow accumulation on the Alto dell’Ortles glacier over the last 3 years ranged from 550 to 1050 mm w.e. (Gabrielli et al., 2010) while at Colle Gnifetti accumulation ranged from 210 to 450 mm w.e. (Jenk et al., 2009; Doescher et al., 1995). As the concentrations may be dependent upon accumulation rates it is therefore more representative to calculate deposition fluxes of trace elements (Table 2). The fluxes of Ba, Mn, Fe and Al, which are major constituents of rock and soil, are 50–75% lower at the Alto dell’Ortles with respect to those at Colle Gnifetti during the last 50 years, suggesting a lower crustal dust deposition on Mt. Ortles. The recent deposition of trace elements, such as Cu, Pb, Zn and Cd, on the Alto dell’Ortles is about one order of magnitude higher than at Colle Gnifetti during pre-industrial time (before 1700), but lower than from 1950 to 1993 (the most recent available data). For instance, the Pb flux on the Alto dell’Ortles glacier is about 85 µg m$^{-2}$ yr$^{-1}$, which is double that of Colle Gnifetti before the 18th Century (43 µg m$^{-2}$ yr$^{-1}$) but about 25 times lower than in the time window from 1950 to 1983. Despite the distance between these two areas (about 200 km), this might be consistent with a continuous decrease of heavy metals in European emissions from anthropogenic sources during the last few decades (Pacyna and Pacyna, 2001). The emission inventories of heavy metals in Italy (available at the website: http://webdab1.umweltbundesamt.at/scaled_country_year.html?cgiproxy_skip=1) demonstrate a general reduction from 1990 to 2006 for Pb (−94%), Cr (−38%), Cd (−17%), Ni (−5%) and Cu (−4%). During this time period, As and Zn increase by 11% and 8%, respectively.

In order to evaluate the relative trace element contributions from rock and soil dust versus other sources such as anthropogenic emissions and sea-salt, we calculated the
crustal enrichment factors (EFc). EFc is defined as the concentration ratio of a given metal to that of a conservative element (in this work we use Ti) which derives mainly from rock and soil dust, normalized to the same concentration ratio characteristic of the upper continental crust (Wedepohl, 1995). For instance, the EFc for Pb is:

$$\text{EFc}_{\text{Pb}} = \frac{[\text{Pb}]/[\text{Ti}]}{[\text{Pb}]/[\text{Ti}]}_{\text{snow}} / [\text{Pb}]/[\text{Ti}]}_{\text{upper crust}}.$$

The crustal dust is transported to the Alto dell’Ortles glacier from several areas (see Sect. 3.5), and therefore may be characterized by elemental compositions that are significantly different from the upper crustal mean. This mixing leads to a higher uncertainty in the determination of the EFc. For this reason we assume that only calculated EFc values that are larger than 10 suggest a pronounced contribution from non-crustal sources. The median EFc values for Be, Rb, Sr, Ba, U, Li, Al, Ca, Cr, Mn, Fe, Co, Ga and V are lower than 10 suggesting that these elements originated mainly from rock and soil dust. For Ti, Pb, Ni, and Cu, median EFc values are between 10 to 100, where a few samples contain an EFc lower than 10. This difference suggests that for these elements the anthropogenic contribution is generally important even if it is not always predominant with respect to natural sources. EFc higher than 100 are reported for As (107), Zn (118), Ag (135), Bi (185), Sb (401) and Cd (514), demonstrating the predominance of non-crustal depositions and suggesting an anthropogenic origin.

### 3.1.2 Possible anthropogenic sources of the trace elements

Stationary fossil fuel combustions contribute more than 85% to the total European anthropogenic inputs of As, V, Mn, Ni and Tl while non-ferrous metal production is the major source of Zn (Pacyna and Pacyna, 2001). Potential anthropogenic sources of Sb emission to the atmosphere are numerous and include coal combustion, Pb and Cu smelting, refuse incineration, retardants for plastics and textiles, catalysts in PET production and are a constituent of automobile brake pads (Smichowski, 2008). The combustion of leaded gasoline is the major source of atmospheric Pb emission on the global scale even if its use rapidly decreased starting in the 80s (Schwikowski et al., 2008).
2004). According to the calculated inventories of atmospheric emissions in Italy, in 2006 the automobile source represents less than 2% of total Pb fallout while in 1990 it accounts for 78%. Secondary sources of Pb are non-ferrous production, chemical industry, steel, bullets and batteries making, coal burning, and refuse incineration (Shotyk et al., 2005). At the present time, the major atmospheric Pb sources are industrial combustion processes (80%). Industrial combustion and smelting activities contribute 23% and 72% to the Zn emissions and 38% and 19% to the Cd emissions. The main As sources are industrial combustion (83%) and electricity production (9%). For Ni, 60% of the total emissions are related to combustion processes while maritime activities contribute up to 36%. Bi is emitted by fossil fuel combustion, refuse incineration. Bi compounds are used for manufacturing alloys, solder, metallurgical additives, cosmetics, medicines, and recent new Pb-replacement alloy.

3.1.3 Ionic compounds concentrations and fluxes

The mean concentrations of ionic compounds in snow of Alto dell’Ortles are approximately three orders of magnitude higher than those of the trace elements, with a range in means from 19 ng g$^{-1}$ for K$^+$ to over 377 ng g$^{-1}$ for NO$_3^-$ (Table 1). The mean concentrations of SO$_4^{2-}$ and NO$_3^-$, and NH$_4^+$ are 297 ng g$^{-1}$, 377 ng g$^{-1}$ and 205 ng g$^{-1}$, respectively. These compounds are produced by the atmospheric oxidation of their precursor gaseous species, SO$_2$, NO$_x$ and NH$_3$, primarily emitted by anthropogenic sources and in particular the combustion of fossil fuels, high-temperature combustions and agriculture. In Table 3, the ionic compounds concentrations are compared with those determined in other Alpine sites. The measured mean concentrations for SO$_4^{2-}$, (163–677 ng g$^{-1}$), NO$_3^-$ (151–1297 ng g$^{-1}$) and NH$_4^+$ (41–259 ng g$^{-1}$) are within the reported ranges determined in other recent snow and ice samples in the European Alps (Gabrieli et al., 2008, 2010a; Novo and Rossi, 1998; Kuhn et al., 1998; Puxbaum and Tscherewenka, 1998). These recent concentrations are higher by several factors (3–10) than those observed in the Colle Gnifetti core in pre-industrial times (before
The highest concentrations of ionic compounds are generally observed in snow samples from low-medium altitudes (1000–2500 m a.s.l.) in the Eastern Alps (Dolomites, Sonnblick, and Careser). This can be explained considering that the Dolomites and Careser represent the first geomorphologic barrier that may block the pollutants originating from the heavily populated and industrialized Pô Valley (Weiss et al., 1999). In addition, these relatively low mountain areas are also affected by the convective transport of local pollutants from the bottom of the valleys.

The high correlation between Cl$^-$ and Na$^+$ ($R^2 = 0.90$, 95% confidence) and their mean mass ratio (1.43±0.21) is close to the marine ratio of 1.8, demonstrating a prevalent marine origin of these two ions. The slight Na$^+$ excess could be attributed to a minor contribution from crustal sources such as gypsum which is present in regional closed-basin lakes. This correlation is in accordance with results from other glaciological records in the Western Alps (Eichler et al., 2000; Schwikowski et al., 1999; Maupetit and Delmas, 1994) but not consistent with data from winter snow collected in the Eastern Alps at low-medium elevation (Gabrielli et al., 2008). In the Eastern Alps a slight Cl$^-$ excess is attributed to a minor anthropogenic HCl contribution. As this excess and range (5 to 291 ng g$^{-1}$) is greater than ratios related to sea-salt deposition (Gabrielli et al., 2008). Using Cl$^-$ as the marine reference, we calculated the non sea sulfate (NSS) contribution to the total SO$_4^{2-}$ budget as:

$$[\text{SO}_4^{2-}]_{\text{NSS}} = [\text{SO}_4^{2-}]_{\text{snow}} - [\text{Cl}^-]_{\text{snow}} \cdot ([\text{SO}_4^{2-}]_{\text{marine}}/[[\text{Cl}^-]_{\text{marine}}])$$

The marine contribution of SO$_4^{2-}$ is almost negligible, and accounts on average for 6% of total.

The ionic fluxes on Ortles are similar to those observed at Colle Gnifetti, Careser and Stubai (330–1250 m w.e. yr$^{-1}$) but much lower than at Col du Dome, Fiescherhornletscher and Grenzgletscher, where the accumulation is higher ($\sim$1400 to $\sim$2700 mm w.e. yr$^{-1}$). For example, SO$_4^{2-}$ fluxes range from 220 to 360 mg m$^{-2}$ yr$^{-1}$ in sites with accumulation lower than 1250 mm w.e. yr$^{-1}$ and from 510 to 1040 mg m$^{-2}$ yr$^{-1}$ in others where the accumulation is higher than 1400 mm w.e. yr$^{-1}$. 

1700) (Sigl, 2009).
(Table 3). This positive relationship between accumulation and ionic fluxes indicates that wet-deposition likely represents the most efficient scavenging process of SO$_4^{2-}$ in high-altitude mountainous areas. The comparison between deposition on Mt. Ortles and Careser is of particular interest because these two glaciers are only ∼15 km apart from each other and, for this reason, are likely to be comparable. The fluxes of NO$_3^-$ (300 to 430 mg m$^{-2}$ yr$^{-1}$) and SO$_4^{2-}$ (240 to 360 mg m$^{-2}$ yr$^{-1}$) are up to ∼50% greater at Careser, and for Cl$^-$ are up to 6 times greater ranging between 48 to 270 mg m$^{-2}$ yr$^{-1}$. This evidence is consistent with the southern position and lower altitude of Careser and the consequent major impact of pollutants and sea-salt transport from the south.

However, Ca$^{2+}$ flux is one order of magnitude lower at Careser than Ortles. This decrease indicates a significantly lower deposition of carbonate dust on Careser as Ca$^{2+}$ is the prevailing crustal ion in the snowpack from the mountain areas dominated by carbonate-rich bedrock. The detected fluxes are consistent with the geological characteristics of these two sites. The area near Careser is characterized by metamorphic rocks (mica-schist, gneiss, granites), while the Ortles group is comprised of sedimentary rocks including dolomite and black-banded limestone. This flux difference is consistent with the literature, where measured Ca$^{2+}$ concentrations in Eastern Alpine winter snow differ between limestone (300–600 ng g$^{-1}$) and metamorphic (80–220 ng g$^{-1}$) bedrock (Gabrielli et al., 2008).

Very few Total Organic Carbon (TOC) data in snow and ice from high altitude Alpine sites are presented in the literature. In an ice core from Colle Gnifetti, the TOC concentrations increased from 66 to over 614 ng g$^{-1}$ in the time period between 1890 and 1975 (Lavanchy et al., 1999). TOC concentrations in the Ortles samples range from 180 to 1620 ng g$^{-1}$, with a median value of 310 ng g$^{-1}$ and a median TOC flux of 245 mg m$^{-2}$ yr$^{-1}$.
3.2 Stratigraphic and glaciological observations

Two main density transitions were detected at 240 ± 30 cm and 360 ± 30 cm of depth from twelve snow depth soundings carried out on the upper part of the Glacier Alto dell’Ortles. A comparison of the physical and chemical profiles sampled in the snow pit is reported in Fig. 2. The vertical variations in grain shape and size, snow density and hardness index are compared to the vertical profiles of $\delta^{18}$O and NH$_4^+$. The upper 60 cm of the snowpack are characterized by medium-size rounded particles, with the presence of partially decomposed precipitation particles. The snow density ranged from 270 to 310 kg m$^{-3}$, and the hardness index is approximately 250 N. These features are consistent with recently deposited dry snow subjected to destructive metamorphic processes. A visible weak dust horizon above a melt-freeze crust was recorded at 60 cm. This layer represents the first clear stratigraphic discontinuity that differentiates the recent 2009 spring snow from the 2008/2009 winter snow. From 60 to 270 cm, the density increased from 300 kg m$^{-3}$ to 400–440 kg m$^{-3}$, and the hardness to from 250 N to 1000–1500 N. In the layers between 60 to 90 cm, medium size rounded particles (0.8 mm), faceted rounded particles and solid faceted particles were recovered, indicating kinetic growth processes triggered by temperature gradients. From 90 to 140 cm, a succession of small/medium size (0.2–1.0 mm) rounded particles layers and thin ice lenses formations(< 10 mm) were visible. Considering that no evidence of winter melting was found, the origin of these mm-scale ice lenses is probably due to wind activity, which is particularly intense on the Alto dell’Ortles glacier during winter. The dust layer at 130 cm is probably due to a weak Saharan deposition occurring on the 1 and 2 April 2009. This deposition can be inferred by considering the back-trajectories from Alto dell’Ortles glacier (see Sect. 3.5) and the Saharan event recorded at the Jungfraujoch (Collaud Coen et al., 2004) high alpine research station (2580 m a.s.l.; 46°33’ N, 07°59’ E; Collaud Coen, personal communication). From 140 to 270, the snow layers were characterized by large rounding-faceted crystals (1.5–3.0 mm), which are indicative of growth regime transition forms typical of the cold and dry snowpack.
The second strong stratigraphic discontinuity is constituted by the thick ice lens (about 5 cm) at 280 cm. Below this discontinuity, all of the crystals that are characteristic of a dry-snowpack disappear and melt forms were observed. The density and the hardness index progressively increased up to 450–500 kg m\(^{-3}\) and 2000–2500 N, respectively. The grain shape was dominated by melt forms and, in particular, by large rounded polycrystals (3.0–3.5 mm) which are generally produced by sequential melt-freeze cycles in low water content conditions such as a pendular regime. Since the particle size of the polycrystals increases as a function of the number of melt-freeze cycles, these layers can be formed only during the summer ablation period at the high elevation of the Alto dell’Ortles glacier. The discontinuity at 275 cm likely represents the transition between the 2009 and the 2008 snow. Solid faceted particles were found above a thick melt-freeze crust at 60–65 cm and above the thick ice lens at 280 cm. This kinetic-growth form appears when the rounded particles are subjected to a large increasing vertical temperature gradient in the snow. This suggests that ice and melt-freeze layers act as an effective physical barrier, able to influence the small-scale thermal regime and, perhaps, the meltwater percolation and wet/dry migration processes of both particulate and soluble trace species trapped in the snow. At 395 cm we observed a dust layer in correspondence with a thick ice lens (2.0 cm) while the layers from 395 to 450 cm (the base of the snow-pit) were characterized by large rounded polycrystals. This thick ice lens and associated dust layer could indicate the transition between the 2007/2008 snow but, since no other information could be inferred from the stratigraphy, is instead corroborated by additional chemical evidence (e.g. high Cu and Cd concentrations, see below).

The \(\delta^{18}O\) profile which can be used as proxy of air temperature during precipitation confirms the seasonal reconstruction inferred from the snow-pit stratigraphy, showing higher values during warm periods (between 0–60 and 260–345 cm) and lower during cold periods (between 60–260 and 345–400 cm). We also verify a correspondence between the highest \(\delta^{18}O\) values and peaks in \(\text{NH}_4^+\), which is an anthropogenic component that is mostly deposited in the summer (Gabrielli et al., 2010). The chemical
signature of the 2008/2007 snow transition appears less evident, and may be due to the smoothing effect of meltwater percolation during the 2007 and 2008 summers. A visible dust layer and a corresponding slight increase in NH$_4^+$ were observed at 395 cm concentrations was recorded, perhaps suggesting the presence of the 2007 summer layer below 390–400 cm. The seasonal $\delta^{18}$O pattern is complicated and variations may be due to water percolation between the layers more than the advection history of the wet air masses that deliver precipitation. In summary, the results of the snow-soundings and the physical and chemical stratigraphic observations indicate that the transitions between the 2009/2008 and the 2008/2007 snow were at about 280 and 385 cm, respectively.

3.3 Principal Component Analysis (PCA)

A PCA has been applied to the entire dataset, of 82 snow samples where each sample was analyzed for 22 trace elements, 8 major ions, $\delta^{18}$O and TOC to evaluate the aggregation between variables in light of different trace species provenance and sources. PCA is an statistical method in which linear combinations of the original variables are created that characterize maximum possible variance in the data (Scott et al., 2000). The PCA is a multivariate statistical technique often used for explore large and awkward datasets, and here this method has been applied to confirm the stratigraphic observations.

Figure 3 shows the biplot graph which represents both the variables (vectors) and the cases (points) distribution. The first four principal components account for more than 80% of the total variance in the dataset. The first component (PC1) which accounts for 57% of the total variance has comparable negative loadings for all the trace elements and major ions. The second PCA component (PC2) accounts for 12% of the total variance and has positive loadings for Mg$^{2+}$, Ca$^{2+}$, Li, Rb, Sr, Ba, Al, Ti, Fe, Ga, Mn, Co, U and negative loadings for $\delta^{18}$O, TOC, NO$_3^-$, SO$_4^{2-}$, Cl$^-$, Na$^+$, NH$_4^+$, As, Cd, Sb, Pb, Bi, V, Ni, Cu, Zn, and therefore separates crustal materials from anthropic and marine variables.. Cr, Ti and K$^+$ are not discriminated by PC2 indicating that...
the sources of these elements are various. In particular, the $K^+$ depositions may not only be linked to marine sources but also with terrestrial emissions, such as biomass burning (Simoneit, 2002).

The association between $\delta^{18}O$ and anthropogenic species indicates the predominant seasonal pattern of the anthropogenic pollutant deposition. In contrast, the crustal element inputs do not appear to be seasonally dependent. All of the samples characterized by negative scores in the PC2 correspond to summer layers, as inferred from the stratigraphic analysis. Interestingly, this seasonal separation is extremely well defined except for a few samples (summer samples at 55, 60, 260 and 305 cm and a winter sample at 120 cm).

Despite having different sources, the concentrations of Cl$^-$ and Na$^+$ the two major proxies of sea-salt, and anthropogenic species are well correlated indicating a similar origin area or transport pathway. This correlation is in contrast with results from an ice-core from the Grenzgletscher glacier (Eichler et al., 2004), where sea-salt related species correlated with crustal dust elements. We suggest that the origin of the sea-salt aerosol deposited on the Eastern Alps is either the Adriatic Sea or it is injected into the air masses during the transport over the Pò Valley, whereas in Western Alps the sea-salt aerosol mainly arrives from the southwest.

3.4 Seasonality of the chemical variables

Profiles of selected ionic compounds and trace elements are reported in Fig. 4a and b. The $\delta^{18}O$ record shows a well defined seasonal pattern, with maximum values of up to $-5.8\%$ (summer) and minimum values of $-24.1\%$ (winter), which are typical values for Alpine precipitation at high altitude sites (Schotterer et al., 1997). All of the anthropogenic ions (NO$_3^-$, NH$_4^+$, SO$_4^{2-}$) show a pronounced seasonal pattern with low winter concentrations which increase in spring and peak in summer. NO$_3^-$ and NH$_4^+$ show the most pronounced seasonality with summer to winter mean concentrations ratios of 4.2 and 5.3, respectively. For SO$_4^{2-}$, the summer to winter ratio is 3.6 while the
sea salt contribution to $\text{SO}_4^{2-}$ does not show any evident seasonal variation but always accounts for 10–20% of the total.

The seasonal variations of $\text{K}^+$, $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ are less pronounced, demonstrating a quite constant deposition of crustal elements. Concentrations of the marine species $\text{Cl}^-$ and $\text{Na}^+$ follow a seasonal pattern comparable to those of $\text{NH}_4^+$ and other anthropogenic species, except for a few large isolated peaks in winter. The $\text{Cl}^-$/$\text{Na}^+$ ratio fluctuates around the mean value of 1.4, close to the average sea salt value of 1.8, except in the snow pit section from 320 to 340 cm of depth, where this is ranging between 2.4 and 3.0. According to the stratigraphy (Sect. 3.2), this layer is characterized by large rounded polycrystals (3.5 mm) produced as a consequence of subsequent melt-freeze cycles. The ionic compounds are leached from snow during melt post-depositional process with different efficiencies on the base of the atomic characteristics of the ions and their interaction with the ice crystal lattice. For instance, the elution sequence derived both from laboratory and field experiments demonstrate that $\text{Cl}^-$ is well preserved while $\text{SO}_4^{2-}$ and $\text{Na}^+$ are strongly affected by meltwater (Eichler et al., 2001). The TOC profile records the highest concentrations from the surface to a depth 65 cm, corresponding to the beginning of the 2009 warm season, while displaying few seasonal variations in the deeper sections of the snow pit. This behavior suggests a more efficient leaching by meltwater percolation than that of $\text{NH}_4^+$ and other anthropogenic compounds.

The EFc profiles of Cd, Sb, Zn, Cu and Pb correlate with each other where their respective concentrations peak in tandem (Fig. 4b). The largest mean EFc seasonal variations for trace elements are displayed by V (by a factor of 3.8), Sb (3.3), Cu (3.3), Pb (2.9), Bi (2.8), Cd (2.1), Zn (1.9), Ni (1.8), Ag (1.8), As (1.7) and Co (1.6). For elements which are most likely anthropogenic, EFc values increase during summer periods by factors of 1.3 (Tl) to 3.8 (Cu) but, even during the winter season, their values remain largely higher than 10, indicating a predominant anthropogenic origin. As reported for the terrigenous ions $\text{K}^+$, $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ the crustal trace elements also demonstrate limited EFc seasonal variations, ranging from factors of 1.0 (Ti, Be, Li, Al, Sr) to 1.4 (Ba, Rb, U). This diminished seasonality confirms that although the
magnitude of the crustal inputs is influenced by different sources, seasonal transport and deposition processes, the main anthropogenic and natural sources are common during all the seasons.

3.5 Meteorological and atmospheric conditions

In order to explain the observed differences in the seasonal deposition of trace species to the Alto dell’Ortles glacier we have investigated the atmospheric pathways from the source regions to the study area. We computed the daily back-trajectories from Alto dell’Ortles glacier (at 3850 m a.s.l.) from 2007 to 2009, using the Hybird Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT 4.8), provided by the National Oceanic and Atmospheric Administration (NOAA), which is a tool to simulate air particles transport and deposition (Draxler and Rolph, 2010; Draxler, 2003). We used the global dataset archive (GDA) containing 29 meteorological single level variables (at the surface) and 6 upper levels variables (for a total of 23 vertical levels from 1000 to 20 hPa) to calculate 48-h back-trajectories. For each day, we preformed two model runs at 00:00 and 12:00 UTM. The model results are summarized in Fig. 5. Air masses from western quadrants (from SW to NW) represent more than 84% of the total during summer (JJA), and 63–73% in the other seasons. Northern trajectories (NW to NE) are larger in autumn (SON), and fewer in winter (DJF), representing 28% and 14% of the wind sources, respectively. Southern air masses (SE to SW) characterize the 32% of spring winds (MAM), 27% in autumn and about 21% in winter and summer. The longest 48 h trajectories originate from the west and cover a mean distance of 2450 km, while the trajectories from the northern, southern and eastern quadrants are shorter (1710, 1310 and 1220 km, respectively). These trajectories are generally longer in DJF and SON than in MAM and JJA. In DJF the mean trajectories lengths from W and SE are 1270 and 3050 km, respectively, while in JJA they are 705 and 1955 km (about 40% shorter). The back-trajectories containing a predominant ascending behavior, which are often associated to cyclonic fields, are more frequent in JJA where they comprise 65% of the total and comprise 55% of the trajectories for all the other periods of the
year. Ascending air masses originate generally from the south and southeast (64–85% of the total) but in JJA ascending air mass trajectories from the east represent more than 80% of total eastern fluxes.

Despite the significant seasonal differences in the origin and behavior of air masses, as inferred from the evaluation of 48-h back-trajectories, these origins hardly explain the large changes in concentrations that are observed in the snow pit chemical profiles. In fact, a fundamental parameter that has to be taken into account to explain the seasonal variation in concentrations is the vertical structure of the troposphere at a regional scale. In winter, the Alto dell’Ortles glacier lies within the free troposphere because the vertical motions are inhibited by low-altitude thermal inversions with very stable atmospheric stratifications (Kappenberger and Kerkmann, 1997). In Fig. 6, we summarize the averaged monthly variations in the maximum boundary layer depth (BLD), at the meteorological station of Milano-Linate Airport (~100 km SW of Mt. Ortles), obtained by analyzing the daily balloon data over 2007–2009. The BLD was deduced by analyzing the thermal profiles inferred from balloon launches (every day at 00:00 and 12:00 UTM and, in case of particularly unstable meteorological conditions, also at 06:00, 09:00, 15:00, 18:00 and 21:00 UTM), and by identifying the daily maximum altitude of the thermal inversion. The balloon data are available at the University of Wyoming website: http://weather.uwyo.edu/upperair/europe.html. We choose the Milano-Linate station because it is indicative of the tropospheric vertical structure of the Pò Valley, the main anthropogenic area which affects the air quality over Alps (Seibert et al., 1998). The maximum daily boundary layer depth is much higher during summer than winter due to stronger insolation that enables more effective convection. In December and January, during only 15–20% of the days the boundary layer depth is higher than 2000 m while during 52–57% of the days a very stable layer below 500 m caps the well-mixed boundary layer below 500 m. In these conditions, the pollutants emitted at the bottom of the valley cannot be lifted by thermal convection and are confined in a relatively small volume. During the spring, the BLD rises rapidly and, from April to September, the maximum daily BLD was higher than 2000 m a.s.l. and remains
at this elevation for ~70% of the days. With this rapid rise in the BLD, pollutants are lifted by a synoptically influenced flow, or directly injected to the free troposphere and then transported horizontally by the synoptic flow and then are able to move across Europe.

Figure 8 summarizes the averaged monthly stability situations during the period 2007/2009, according to the Pasquill classification (Pasquill, 1961) at the Milan Linate airport and over the Alto dell’Ortles glacier. This stability is estimated by using the meteorological data (GDA meteorological archive) from the open-source READY system (Real-Time Environmental Applications and Display sYstem), provided by the Air Resources Laboratory of NOAA. In Milan about 60–80% of the days from October to February are characterized by stable or neutral atmospheric conditions, with 17–38% of days characterized by slightly unstable conditions and only 2–4% by moderately and extremely unstable conditions. From March to September, unstable meteorological situations dominate, representing 70–80% of the total. At the Alto dell’Ortles glacier, stable meteorological conditions are rare when compared to Milan. In general we note a higher frequency of moderately and extremely unstable conditions during the entire year with a particular increase from October to February when unstable conditions predominate for about 20–25% of the total compared with only 2–4% of the time at Milan. From March to June even slightly stable situations are completely absent while neutral conditions account for only 12–16% of the total days. In July, moderately and extremely unstable conditions represent more than 74% while 26% of the days are slightly unstable.

The pollutants emitted from the heavily industrialized and populated Pò Valley during the winter season are thus trapped by the very stable low-altitude boundary layer produced by the strong thermal inversion which therefore limits transfer to the free troposphere. Low velocity vertical winds are often not sufficient to penetrate the boundary layer and to lift polluted air from the lower to the upper tropospheric levels. For this reason during winter when the Alto dell’Ortles glacier almost permanently lies above the boundary layer altitude, is likely uninfluenced by local/regional anthropogenic emissions.
emissions produced in the Southwestern Pò Valley. The winter western atmospheric fluxes and depositions to the Alto dell’Ortles glacier likely represent continental air quality background conditions at similar elevations, except during the rare unstable winter meteorological conditions such as Foehn events. The Alpine Foehn, is a rain shadow wind which results from the subsequent adiabatic warming of air which has released most of its moisture on windward slope. The geographical position and altitude of Mt. Ortles suggests that it is directly affected by the northern upslope wind which can effectively transport pollutants from the bottom valley areas of Austria and Southern Germany.

During the rest of the year, the meteorology is characterized by vertical exchanges between the low level and free troposphere, allowing the mass transfer from local (Val Venosta in the north and Val di Sole in the south) and regional sources (Pò Valley) to high elevations. Pollutants from the Pò Valley are transferred vertically to the injection layer and then dragged by synoptically influenced flows to the Alpine barrier where they are effectively lifted by upslope winds triggered during the daytime by the solar radiation. These vertical motions often produce shallow cumulus clouds above the crests and linked small-scale convective precipitation allows wet deposition of transported pollutants and trace species.

4 Conclusions

This work provides an initial insight into the occurrence of numerous trace elements and major ions in fresh snow from Alto dell’Ortles, the highest glacier in the Eastern Alps. The fluxes of Ba, Mn, Fe and Al are 50–75% lower with respect those on Colle Gnifetti during the last 50 years providing evidence for relatively low recent crustal dust deposition on Mt. Ortles. The ionic fluxes to Mt. Ortles are similar to those to Colle Gnifetti, Careser and Stubai but much lower than to Col du Dome, Fiescherhorn-gletscher and Grenzgletscher. The PCA applied to the entire dataset provides a clear separation between trace species originated from crustal, (Mg, Ca, Li, Rb, Sr, Ba, Al,
Seasonal impact of natural and anthropogenic emissions on glacier

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Acknowledgements. This work is a contribution to the Ortles project, a program supported by the Fire protection and civil division of the Autonomous Province of Bolzano (Michela Munari) in collaboration with the Forest division of the Autonomous Province of Bolzano (Paul Profanter, Barbara Folie) and the National Park of Stelvio (Wolfgang Platter). This is the Ortles project publication 2. For the field operations we thank: Volkmar Mair, (Geologic Office of the Autonomous Province of Bolzano), Reinhard Pinggera (Forest Division of the Autonomous Province of Bolzano) Philipp Rastner (EURAC), Karl Krainer (University of Innsbruck) Paul Val-lelonga (Niels Bohr Institute, Copenhagen), Matteo Cattadori (Museo Tridentino di Scienze Naturali) and Toni Stocker (Alpine Guides of Solda). We also thank Anselmo Cagnati and Andrea Crepaz (Arabba Avalanche Centre, ARPAV), for the useful comments about the stratigraphic observations. We are also grateful to Ping-Nan Lin (Byrd Polar Research Center, The Ohio State University) for the stable isotopes analyses. Finally, the authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.arl.noaa.gov/ready.php) used in this publication.
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Table 1. Main statistics of the species determined in the snow pit on the glacier Alto dell’Ortles. The concentrations of the trace elements are expressed in pg g\(^{-1}\) while the ionic compounds in ng g\(^{-1}\).

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Table 2. Average concentration and fluxes of trace elements in snow samples collected in the Glacier Alto dell’Ortles snow pit and in the Colle Gnifetti ice core, Monte Rosa, in the time periods 1950–1980, 1980–1993 (Gabrieli, 2008) and pre-1700 (Barbante et al., 2004).

<table>
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Table 3. Mean concentration and fluxes of major ions in snow and ice samples in different Alpine sites: Glacier Alto dell’Ortles snow pit (mean accumulation \( \sim 800 \) mm w.e.), Colle Gnifetti firn/ice core (Monte Rosa; mean accumulation 330 mm w.e.), Col du Dome firn/ice core (Mont Blanc, mean accumulation 2450 mm w.e. yr\(^{-1}\)), Fiescherhornigletscher firn/ice core (Bernese Alps; mean accumulation 1400 mm w.e. yr\(^{-1}\)), Grenzgletscher firn/ice core (Monte Rosa; mean accumulation 2700 mm w.e. yr\(^{-1}\)), Careser (Ortles-Cevedale, Italian Eastern Alps; accumulation 1040 mm w.e. yr\(^{-1}\)), Stubai (Austrian Tyrolean Alps; accumulation 1250 mm w.e. yr\(^{-1}\)), Sonnblick (Austrian Tyrolean Alps), Dolomites (Eastern Italian Alps). The “w” associated with the period indicates that only winter snow was sampled.

<table>
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<tr>
<th>Site</th>
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<th>Period</th>
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<th>Mean fluxes (mg m(^{-2}) yr(^{-1}))</th>
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<td>2005–2009</td>
<td>NH(^+_4) 208 Ca(^{2+}) 281 SO(^{2-}) 297 NO(^{-3}) 377 CI(^-) 60</td>
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<td>1500–1700</td>
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<td>Col du Dome (^c)</td>
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<td>1988–1993</td>
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<td>Fiescherhornigletscher (^d)</td>
<td>3890</td>
<td>1945–1983</td>
<td>NH(^+_4) 79 Ca(^{2+}) 100 SO(^{2-}) 366 NO(^{-3}) 167 CI(^-) 52</td>
<td>NH(^+_4) 111 Ca(^{2+}) 140 SO(^{2-}) 512 NO(^{-3}) 234 CI(^-) 73</td>
</tr>
<tr>
<td>Grenzgletscher (^d)</td>
<td>4200</td>
<td>1945–1983</td>
<td>NH(^+_4) 89 Ca(^{2+}) 92 SO(^{2-}) 384 NO(^{-3}) 151 CI(^-) 26</td>
<td>NH(^+_4) 240 Ca(^{2+}) 248 SO(^{2-}) 1037 NO(^{-3}) 408 CI(^-) 70</td>
</tr>
<tr>
<td>Careser (^e)</td>
<td>3090</td>
<td>W–1994</td>
<td>NH(^+_4) 73 Ca(^{2+}) 24 SO(^{2-}) 345 NO(^{-3}) 412 CI(^-) 260</td>
<td>NH(^+_4) 76 Ca(^{2+}) 25 SO(^{2-}) 359 NO(^{-3}) 428 CI(^-) 270</td>
</tr>
<tr>
<td>Stubai (^f)</td>
<td>3106</td>
<td>1992–1995</td>
<td>NH(^+_4) 41 Ca(^{2+}) 42 SO(^{2-}) 163 NO(^{-3}) 329 CI(^-) 39</td>
<td>NH(^+_4) 51 Ca(^{2+}) 53 SO(^{2-}) 204 NO(^{-3}) 411 CI(^-) 49</td>
</tr>
<tr>
<td>Sonnblick Glacier (^g)</td>
<td>2950</td>
<td>1992–1995 (w)</td>
<td>NH(^+_4) 259 Ca(^{2+}) 64 SO(^{2-}) 336 NO(^{-3}) 763 CI(^-) 96</td>
<td>–</td>
</tr>
<tr>
<td>Trentino-Veneto (^h)</td>
<td>1025–3040</td>
<td>1995 (w)</td>
<td>NH(^+_4) – Ca(^{2+}) 510 SO(^{2-}) 530 NO(^{-3}) 900 CI(^-) 162</td>
<td>–</td>
</tr>
<tr>
<td>Dolomites (^i)</td>
<td>1610–2150</td>
<td>2005 (w)</td>
<td>NH(^+_4) 172 Ca(^{2+}) 712 SO(^{2-}) 462 NO(^{-3}) 1297 CI(^-) 300</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Bolius, 2007
\(^b\) Sigl, 2009
\(^c\) Preunkert et al., 1999
\(^d\) Eichler et al., 2004
\(^e\) Novo et al., 1998
\(^f\) Kuhn et al., 1998
\(^g\) Puxbaum et al., 1998
\(^h\) Gabrielli et al., 2008
\(^i\) Gabrielli et al., 2010
Fig. 1. Map of the Alto dell’Ortles glacier, Southern Rhaetic European Alps, (Provincia Autonoma di Bolzano Alto Adige, Italy). In grey the glacialized areas are reported. The star indicates the sampling site while the glacialized areas are reported in grey (adapted from Gabrielli et al., 2010).
Fig. 2. Stratigraphic observations (grain shape and size), density, hardness index, $\delta^{18}$O and NH$_4^+$ profiles inferred from the snow pit dug on the Alto dell’Ortles glacier. The grain shape has been classified in accordance with the International Classification for Seasonal Snow on the Ground (Fierz et al., 2009); in brackets the synthetic crystal shape code is reported.
Fig. 3. Principal Component Analysis (PCA) biplot of all the chemical variables (lines with the variable name) and cases (points indicating the depth of the corresponding sample) on the first two PC which explain 57.1% and 11.6% of the total variance, respectively. The red-written cases correspond to the samples from warm periods while the black those from cold periods, as inferred from the stratigraphic observations.
Fig. 4. Depth profiles of $\delta^{18}$O, major ions concentrations and TOC (a) and of some selected trace elements, and relative enrichment factors (b) in snow samples from the 420 cm snow pit on the Alto dell’Orties glacier. The yellow bars indicate proposed summer layers, as inferred from the stratigraphic analysis and the PCA.
Fig. 5. Summary of seasonal behaviors of air mass back-trajectories, calculated using the NOAA HYSPLIT model, in the three years 2007–2009 time period.
Fig. 6. Monthly averaged maximum boundary layer depth, inferred from the balloon data analysis at the Milano-Linate Airport meteorological station over the 2007–2009 years period.
Fig. 7. Monthly variations of the calculated Pasquill Stability Classes calculated at Milano-Linate Airport meteorological station and at the Alto dell’Ortles glacier, over the 2007–2009 years period. The atmospheric turbulences are categorized into six stability classes from the most unstable to the most stable condition.