1	Nature, origin, transport and deposition of andosol parent material in south-central Chile (36-
2	42°S)
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4	Sébastien Bertrand ^{1,a,*} & Nathalie Fagel ¹
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6	¹ Clays and Paleoclimate Research Unit, Department of Geology, University of Liège, Belgium
7	^a Present address: Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution,
8	Woods Hole, MA 02543, USA

10 Abstract

11 The andosols of south-central Chile (36-42°S) are developed on yellow-brown loams that cover the 12 region with a thickness of several meters. In the literature, several hypotheses concerning the 13 nature, origin, mode of transport and deposition of the andosol parent material have been advanced 14 but no general agreement has been found. In this paper, we test these hypotheses by analyzing new representative outcrops located around Icalma (38°50'S) and Puyehue (40°40'S) lakes by a pluri-15 16 methodological approach. Our data demonstrate that the andosol parent material has the typical 17 mineralogical and geochemical signature of the regional volcanism and that these deposits are post-18 glacial in age. The grain size of the deposits and the morphology of the coarse grains evidence that 19 most of these particles haven't been re-transported by wind but are direct volcanic ash falls 20 deposited throughout the Late Glacial and Holocene. Because of the prevailing westerly winds, 21 most of them have been transported to the East. Following the deposition of the volcanic particles, 22 weathering and pedogenetic processes have transformed part of the volcanic glasses and 23 plagioclases into allophane and have wiped out the original layering. This work demonstrates that 24 most of the andosols that occur in the Andes and in the eastern part of the Intermediate Depression

Telephone: 1-508.289.3410

^{*} Corresponding author: sbertrand@whoi.edu

of south-central Chile are developed on volcanic ashes directly deposited by successive volcanic
eruptions throughout the Late Glacial and Holocene.

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28 Keywords: Andosol, volcanic ashes, volcanic glasses, allophane, Chile

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30 **1. Introduction**

31 Volcanic soils cover over 50% of south-central Chile (36-42°S). Although regional variations exist, 32 these soils are mainly developed on yellow-brown soft deposits covering the area with a thickness 33 of several meters (Laugenie, 1982). These deposits cover the Andes and the eastern part of the 34 Intermediate Depression and constitute a nearly continuous formation between 36° and 47°S 35 (Besoain, 1985). This distribution is imposed by the location of the regional active volcanoes at the 36 western side of the southern Andes, which is part of the Southern Volcanic Zone of Chile (SVZ, 33-37 46°S, Gerlach et al., 1998). The soils developed on these soft deposits are locally called Trumaos, i.e. the Araucanian name for andosols signifying "dust accumulation" (Langohr, 1971). 38

39 The nature, origin and mode of transport and deposition of the Trumaos parent material have often 40 been discussed in the literature but up to today no agreement has been reached (for a review, see Besoain, 1985, Moreno & Valera, 1985 and Veit, 1994). It seems that each author finds his own 41 42 explanation depending on the study location. For south-central Chile, three main hypotheses have been proposed: (1) direct volcanic ash falls (Wright, 1965 In: Besoain, 1985); (2) loess-like deposits 43 44 (Laugenie et al., 1975) or (3) glacial transport with ablation moraine-like deposition (Langohr, 45 1974). Authors sometimes propose a mixed depositional pattern (Besoain, 1985). Locally, pyroclastic flows, lahar deposits and fluvial sediments might have participated to the accumulation 46 of particles on which the andosols further developed (Wright, 1965 In: Besoain, 1985). The main 47 48 objective of this paper is to analyze new representative outcrops located around Icalma and Puyehue 49 lakes by a pluri-methodological approach, in order to test the diverse hypotheses about the nature, 50 origin, transport and deposition of the andosol parent material in south-central Chile.

52 **2. Geological setting**

53 Icalma lake (71°20'W, 38°50'S) is small water body (11.65 km²) located in the Andes at an 54 elevation of 1140 m (Fig. 1). Its watershed covers 147 km² and is flanked westward by three active 55 volcanoes: Longuimay, Llaima and Sollipulli. On the other hand, Puyehue lake (72°20'W, 40°40'S) 56 is a larger lake located at the foothill of the Andes. Its watershed reaches 1267 km² and is 57 characterized by the occurrence of Antillanca and Puyehue-Cordón de Caulle volcanic complexes 58 eastward, with the Osorno volcano being nearby to the south (~ 50 km). The whole region is 59 dominated by westerly winds coming from the Pacific Ocean. Combined to the rough topography of 60 the Andes, these winds are responsible for high precipitation in the area, with an annual rainfall 61 reaching 2000-3000 mm/yr around Icalma (Mardones et al, 1993) and 2000-5000 mm/yr at Puyehue 62 (Muñoz Schick, 1980). Occasionally, a Foehn type easterly wind locally called "Puelche" blows 63 down from the Andes (Aravena et al., 1993).

The watersheds of both lakes are covered by unconsolidated and weakly stratified yellow-brown loams, several meters thick. As in many locations of the Intermediate Depression and the Andes in south-central Chile, andosols – i.e. soils developed on volcanic ashes - are developed on these deposits (Fig. 2). In many locations and particularly at Icalma and Puyehue, these deposits sit on top of glacial or fluvio-glacial sediments.

69 In the Icalma region, the andosol parent material reaches a maximum thickness of 6 m and bury all 70 the underlying Pleistocene deposits, whether they are glacial, fluvial or lacustrine (Mardones et al., 71 1993). In addition, the deposits contain two distinct pumice layers that have been attributed to the 72 Holocene explosive eruptions of Sollipulli (Naranjo et al., 1993) and Llaima (Naranjo & Moreno, 1991) volcanoes, respectively dated at 2900 yr BP (Naranjo et al., 1993; De Vleeschouwer et al., 73 74 2005) and 9000 yr BP (9030 yr BP, De Vleeschouwer et al., 2005 or 8830 yr BP, Naranjo & 75 Moreno, 1991). Westward, i.e. closer from Llaima and Sollipulli volcanoes, additional intercalated 76 and well distinct tephra layers occur.

Around Puyehue lake, the yellow-brown soft deposits are thinner (maximum 4 m) with no intercalated distinct tephra layer. They overlay fluvioglacial and glacial deposits. Further to the East the loam deposits are progressively replaced by coarse scoriae particles and volcanic rocks, which is due to the proximity of the Puyehue - Cordón de Caulle and Antillanca volcanic complexes. On the Argentinan side of the Andes, the yellow-brown soft deposits reappear, with the number of distinct tephra layers decreasing eastward.

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84 **3. Material and methods**

85 3.1 Sampling

86 The soft deposits covering the catchments of Icalma and Puvehue lakes have been studied in detail during two fieldwork campaigns in summer 2001-2002 and in December 2003. As a result of a 87 88 preliminary geological investigation of the area, three representative sections were selected for 89 sampling around Icalma and two around Puyehue (Tab. 1, Fig. 1). After sedimentological 90 description and color characterization with a Munsell color chart, the sections were sampled for mineralogical, geochemical and grain size analysis. Moreover, OC2 outcrop has been continuously 91 92 sampled and impregnated for observation in thin section following Boës and Fagel (2005). In this 93 paper, two representative sections are described in detail: OC2 and OC5.

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95 *3.2 Grain size*

Grain size measurements were performed on organic matter-free samples using a laser diffraction particle analyzer Malvern Mastersizer 2000. Organic matter was removed using H_2O_2 10%. The samples were introduced into a 100 ml deionized water tank free of additive dispersant, split with a 2000 rpm stirrer and crumbled with ultrasonic waves. The sample quantity was adjusted in order to obtain a laser beam obscuration between 10 and 20 %. The grain size parameters are averaged over 10,000 scans. Although the grain size analyzer is theoretically capable of measuring particles within a 0.02 - 2000 μ m size range, samples containing particles coarser than 420 μ m were systematically 103 analyzed by a combination of laser diffraction and sieving methods. The distribution parameters 104 have been calculated following Folk and Ward (1957). In order to assess the size of the coarsest 105 grains, the D99 parameter, i.e. the equivalent diameter for which the distribution sum has the value 106 of 99%, has been calculated.

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108 *3.3 Mineralogy*

Bulk and clay mineralogy were achieved by X-ray diffraction (XRD) on a Bruker D8-Advance diffractometer with CuK α radiations. Bulk samples were powdered to 100 μ m using an agate mortar. An aliquot was separated and mounted as unoriented powder by the back-side method (Brindley & Brown, 1980). The powder was submitted to XRD between 2° and 45° 20 and the data were analyzed in a semi-quantitative way following Cook et al. (1975).

Grain size separation of the clay fraction (< 2 µm) was performed by sedimentation in glass vials 114 115 according to the Stokes' law (Moore and Reynolds, 1989). Because the clay fraction obtained after 50 min of sedimentation (< 2 μ m) did not contain enough material for X-ray diffraction, the clay 116 mineralogy was analyzed on the fraction obtained after 20 min of sedimentation ($< 4 \mu m$). Oriented 117 118 mounts of the clay-size fraction were realized by the "glass-slide method" (Moore and Reynolds, 119 1989) and subsequently scanned on the diffractometer. Slides revealing the presence of crystallized 120 clays after air drying (N) were scanned after two additional treatments: ethylene-glycol solvation 121 during 24h (EG) and heating at 500°C during 4h (500). As the mineralogy of the clay-size fraction is dominated by amorphous particles, only a qualitative estimation of the amount of crystallized 122 123 clay minerals is given. It is based on the intensity of the highest clay diffraction peak on the natural (N) diffractogram. 124

125

126 3.4 Geochemistry

127 The major elements of bulk samples from OC3 (5.00 m), OC5 (0.00, 0.75, 1.50 and 2.25 m) and 128 OC6 (-2,00, 1.00 and 3.00 m) sections were determined by X-ray fluorescence (XRF) on fused Li-

129 borate glass beads. Analyses were performed on a ARL 9400 spectrometer. The trace elements of 130 the OC5 (1.50 m) sample were analyzed by ICP-MS. In addition, the chemical composition of 131 individual grains was determined using a Cameca Camebax SX 50 microprobe at Louvain-La-132 Neuve University, Belgium (Tab. 2). Finally, the chemical test of Fieldes and Perrot (1966) was applied to a series of samples. This classical test for andosols is based on the propriety of allophanes 133 134 to produce an alkaline reaction with sodium fluorure (Quantin, 1972). It consists in controlling the 135 variation of pH after mixing 1 g of sediment with 50 ml of NaF 1N solution. In the presence of a 136 high allophane content, the solution reaches a basic pH (10-11) after 1 h.

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138 *3.5 Infrared spectrometry*

Infrared spectra of the clay-size fraction of OC3 (5.00 m) and OC5 (1.50 m) samples were recorded with a Nicolet Nexus spectrometer in the 400-4000 cm⁻¹ range. Two milligrams of sediment were mixed with KBr in order to obtain a 150 mg pellet for analysis.

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143 **4. Results**

144 4.1 Description

145 *4.1.1 Icalma*

146 At Icalma OC2 site, the andosol parent material sits on top of a coarse unit (-2 to 0 m, Fig 3a) 147 containing pebbles and sand grains similar in nature to the regional bedrock. The pebbles are 148 composed of granite (Galletue Plutonic Group) and blue-green sedimentary rocks (Icalma Member 149 of Biobio Formation sensu Suarez & Emparan, 1997). Between 0 and 1.30 m, gravel, sand and silt occur with a fining upward texture. Above 1.30 m, the deposits are composed of organic matter rich 150 151 vellow-brown loams with two intercalated pumice layers: the Llaima pumice dated at 9000 yr. BP 152 (1.60 to 1.95 m) and the Alpehue pumice emitted by the Sollipuli volcano in 2900 yr. BP (3.65 to 4.00 m) (De Vleeschouwer et al., 2005). Under both pumice layers, outcrops show brunified buried 153 soils. Apart from the pumice layers and the three brunified horizons (Fig. 3a), no stratification was 154

155 observed. Microscopical inspection of thin sections revealed no lamination (Fig. 4). However, we observed a high porosity, a very poor sorting of particles and we noticed the abundance of highly 156 157 coated grains. This clavey coating has a post-depositional pedogenetic origin and is probably due to 158 the high lixiviation of chemical elements (chitonic structure, sensu Stoops & Jongerius, 1975). It is responsible for the vellow-brown color of the grains. Moreover, the observation of thin sections 159 160 revealed a succession of 5-10 cm thick organic-rich horizons. This indicates that the physical 161 processes controlling the deposition and reworking of particles were not constantly active, therefore 162 allowing enough time for a vegetal cover to develop.

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164 *4.1.2 Puyehue*

From -10 to 0 m, the Puyehue OC5 outcrop shows fluvio-glacial deposits composed of coarse volcanic particles with a grain size ranging from boulder (max 40 cm) to sand (Figs 3 and 5). The andosol-bearing loams occur between 0 and 2.70 m and overlay the fluvio-glacial deposits by a relatively sharp contact (Figs 3 and 5). No stratification was observed and the deposits contain no distinct tephra layer. Pedogenetic processes are responsible for the brunification of the upper part of the outcrop (30 cm).

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172 4.2 Grain size

In volcanic soils, the original grain size distributions can be altered by weathering and illuviation processes, transforming weatherable minerals into very fine-grained amorphous silicates (Buurman et al., 2004). Moreover, the deposits contain 15-20 % of organic matter, which has a significant effect on the bulk grain-size distribution of the samples. To better assess the original grain size of the deposits, the organic matter was dissolved and the results are considered as a minimum of the original grain size.

Icalma. The grain size data of OC2 section show four distinct units (Fig. 3): a) a fining upward unitat the base of the outcrop, b) the two coarse pumice layers and c) a constant grain size for the

andosol parent material (loam to silt loam). Due to the presence of coarse non-weathered particles,
the upper two samples are coarser. The frequency curves characterizing the yellow-brown loams are
bimodal (modes at 15-30 µm and 300-450 µm; fig. 3). Above the pumice layers, the yellow loam
deposits contain a few pumice fragments and are therefore coarser. The D99 values of the andosol
parent material without pumice fragments vary between 506 and 860 µm.

186*Puyehue.* The grain size of OC5 samples does not significantly vary with depth and is typical for silt187loams (Fig. 3b). The base and the top of the outcrop are coarser, which is due to the presence of188coarse fluvio-glacial deposits and coarse non-weathered volcanic particles, respectively. The grain189size distribution curves are bimodal, with the coarse fraction always being less abundant (< 15 % in</td>190volume). The D99 values vary between 87 and 783 μm.

191

192 4.3 Mineralogy

193 Icalma. The bulk mineralogical composition of the coarse unit at the base of OC2 outcrop (0 - 1.3 194 m) clearly differs from the overlying deposits (Fig. 3). It is principally composed of plagioclases, 195 pyroxenes, amphibole, chlorite and quartz, mainly originating from the bedrock. The samples do 196 not contain amorphous particles. Above 1.3 m, the typical vellow loam deposits are characterized by a constant mineralogical composition, largely dominated by plagioclases and amorphous 197 198 particles (volcanic glasses, organic matter and non-crystalline clay minerals). Pyroxenes and quartz 199 are secondary minerals. Smear slides reveal that the amorphous particles are mainly composed of 200 allophane, which is identified by its typical microscopical characteristics: yellow-brown in color 201 and isotropic and amorphous under polarizing microscope. In smear slides, the coarse grains (> 200 202 μ m) of OC2 samples have been identified as typical volcanic particles: scoriae (> 60%), pumices, plagioclase and traces of pyroxene and olivine. 203

Puyehue. The yellow-brown loam deposits of OC5 outcrop are mineralogically similar to OC2
outcrop. They are dominated by amorphous particles, plagioclases and pyroxenes. The coarser than
200 µm fraction is composed of typical volcanic particles: scoriae, plagioclase, volcanic glasses,

207 pyroxene, olivine and amphibole. The sample collected at 0.00 m, i.e. at the limit with the208 underlying fluvio-glacial deposits, is relatively poor in amorphous particles.

209 The andosol parent material of both sections does not contain crystalline clay minerals. The only 210 samples where non-amorphous clay minerals have been detected are samples from the base of Icalma OC2 outcrop (low amounts of kaolinite, illite, chlorite or vermiculite have been identified). 211 212 The clay-size particles of the other samples are only composed of allophane. The allophanic nature 213 of the amorphous clay minerals is confirmed by the infrared (IR) spectrometry analyses. The IR spectra display two broad absorption bands at 3450 and 1000 cm⁻¹ and a weaker band at 1630 cm⁻¹, 214 215 which is typical for allophane (Snetsinger, 1967; Henmi et al., 1981; Wilson, 1994; Gustafson et al., 1999). The broad band near 1000 cm⁻¹ (and its harmonic at 550 cm⁻¹) is due to Al-O and Si-O 216 stretching (Snetsinger, 1967; Gustafson et al., 1999), while the two others are due to absorbed 217 218 molecular water (Snetsinger, 1967; Kawano & Tomita, 1992; Wilson, 1994). In addition, the low 219 amount of $< 2 \mu m$ particles is a typical characteristic for andosols. It is due to the colloidal 220 behaviour of allophanes (Quantin, 1972).

221

222 4.4 Geochemistry

Icalma. The bulk chemical analysis of OC3 (5.00 m) sample reveals a basaltic composition (SiO₂:
51.8%, TAS: 3.5%).

Puyehue. The bulk chemical composition of the samples from OC5 and OC6 outcrops is in the range of basalts to andesites (SiO₂: 49.2 - 63.5 %, TAS: 1.1-3.1 %), with the upper samples being always more silicic.

Due to their abundance and to the petrogenetic significance of their geochemical composition, the plagioclases have been extracted from the host sediment and analyzed by microprobe for major elements (Tab. 2). Their composition varies from anorthite (An 90-100) to andesine (An 30-50) (Fig. 6). The grains from Icalma OC3 outcrop (An 50-91, Or 0-1) tend to be enriched in Anorthite (An) compared to grains from OC5 outcrop (An 42-85, Or 0-6). Analysis of plagioclases from the

- 233 Llaima and Alpehue (Sollipulli) pumice layers show typical Andesine plagioclases: An 28-40, Or 0-
- 1 and An 32-47, Or 1-3 respectively (De Vleeschouwer, 2002; De Vleeschouwer et al., 2005)
 (Fig.6).
- For the OC5 (1.50 m) sample, some volcanic glasses (SiO₂ 75-73 %, TAS: 4.5-5.9 %) and olivine (Fo 75-83) were also analyzed.
- The trace elements of the OC5 (1.50 m) sample are represented in a chrondrite-normalized spidergram (Fig. 7). For comparison, the trace elementary composition of volcanic rocks of the Southern Volcanic Zone (SVZ) and of the Puyehue-Cordon de Caulle volcanic complex has also been plotted. Except for Ba, K and Sr, the composition of the OC5 (1.50m) sample is in perfect agreement with the typical volcanic signature of the SVZ (33-46°S).
- The test of Fieldes & Perrot (1966) shows a pH rising to 10.5 after 30 min and reaching 11.5 after 2 hours (samples OC3 5.00 m and OC5 1.50 m). This confirms the high allophane content of the samples.
- In addition, we also analyzed the density and the pH of the same samples. The pH values are between 6.4 and 6.5 and the bulk density of the samples is 0.85, which are both typical for andosols (Quantin, 1972; Besoain, 1985).
- 249
- 250 4.5 Scanning electron microscope
- Scanning electron microscope (SEM) observations were performed on different grain size fractions
 of samples from OC3 and OC5 outcrops (from bulk sediment to the clay-size fraction). The
 observations reveal that most of the grains are composed of cohesive agglomerates of particles (Fig.
 8). Grains are neither rounded nor dull (Fig. 8a, 8b) and the samples contain fresh volcanic glass
 shards (Fig. 8c).
- 256

257 **5. Discussion**

258 5.1. Age of the andosol parent material

Around Icalma and Puyehue, the yellow-brown loam deposits on which the andosols developed overlay glacial and fluvio-glacial deposits. These deposits occurring at the base of the outcrops are believed to date from the last glacial period (Llanquihue phase *sensu* Mercer, 1976 and Porter, 1981) and the last deglaciation (Laugenie et al., 1982; Mardones et al., 1993). Therefore, the unconsolidated deposits on which the andosols developed are post-glacial in age.

Near Icalma, the andosol parent material does not directly overlay the glacial sediments. Both units are separated by an intermediate fining-upward deposit, composed by a mixture of yellowish loam particles and rock fragments similar in nature to the geological bedrock (e.g., OC2 outcrop 0.00 -1.30 m). Because of the non-volcanic nature of the rock fragments this deposit cannot be confused with the Curacautin ignimbrite, which is composed of ashes and basaltic scoriae (Naranjo & Moreno, 1991). This layer probably originates from solifluction movements, which are frequent in periglacial environments. Therefore, it probably dates from the last deglaciation.

Veit (1994) assumes that the andosol parent material accumulated during the Late Glacial and Early
Holocene, which would have left enough time for soils to develop during the rest of the Holocene.
However, around Icalma, the two pumice layers intercalated in the yellowish soft deposits, and
especially the upper pumice layer dated at 2900 BP (Naranjo et al., 1993; De Vleeschouwer et al.,
2005), indicate that these sediments accumulated during most of the Holocene.

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277 5.2. Allophane formation

The investigated soils bear all the typical characteristics for andosols (amorphous bulk and clay minerals, slightly acid pH, low density...) (Quantin, 1972; Besoain, 1985). As evidenced by microscopic observations (SEM and smear slides), the amorphous particles detected in the bulk samples are mainly non-crystalline clay minerals and volcanic glasses. Similarly, the clay-size fraction is dominated by non-crystalline minerals and traces of plagioclase. The IR spectrometry analyses have proved that these non-crystalline clay-size particles are allophane, a typical secondary product of volcanic ashes under humid, temperate or tropical climatic conditions (Quantin, 1972; 285 Righi & Meunier, 1995). Although allophane can also derive from the weathering of plagioclases (Aomine & Wada, 1962; Besoain, 1963; Snetsinger, 1967), it is mainly produced by hydrolysis of 286 287 volcanic glasses (Henmi & Wada, 1976; Laugenie, 1982). In the investigated samples, halloysite 288 and imogolite, which are clay minerals frequently observed in association to allophane in andosols, 289 have never been detected. However, it is known that hallovsite forms by neoformation of allophane 290 (Laugenie, 1982, Besoain et al., 1992a) in a minimum time range of 8000 to 9000 years (Aomine & 291 Miyauchi, 1963) and that imogolite is a frequent intermediate product appearing during the 292 crystallization of allophane into halloysite (Besoain, 1968). However, due to the humid 293 mediterranean climate conditions of south-central Chile, allophane can regionally remain stable for up to 18,000 to 22,000 years (Besoain, 1985). Because the transformation of allophane into 294 halloysite requires 18,000 to 22,000 years, its absence in our samples indicates that the investigated 295 296 deposits are younger than the Last Glacial Maximum, which is in agreement with the stratigraphic 297 evidence. This argument is supported by the detection of halloysite and imogolite in older andosol 298 samples from south-central Chile (Besoain, 1968; Laugenie et al., 1975).

299

300 5.3 Volcanic origin

301 Due to their relative young age, the investigated andosols still contain a lot of primary minerals and 302 non-altered volcanic glasses. Their mineralogical and geochemical composition clearly evidences 303 the volcanic origin of their parent material:

(1) The bulk mineralogy of the outcrops is dominated by plagioclases, amorphous particles
(original volcanic glasses and secondary allophane products) and pyroxenes (Fig. 3). These
minerals are typical for the regional volcanism (Laugenie, 1982). Similar conclusions were obtained
by Laugenie et al. (1975) when studying the heavy minerals of regional andosols.

308 (2) The trace elemental composition of the representative OC5 (1.50 m) sample shows a
309 typical SVZ signature (Fig. 7). The only elements deviating from the SVZ signature are Ba, K and

310 Sr. This depletion is due to the high mobility of Ba, K and Sr during weathering processes311 (Martínez Cortizas et al., 2003).

312 (3) The nature of the plagioclases in OC3 and OC5 outcrops is characteristic for plagioclases
313 associated to basaltic and andesitic magma, which are typical for the regional volcanoes of the SVZ
314 (Fig. 6).

315 However, the nature of the plagioclases from Icalma OC3 outcrop (An 50-91) differs from the 316 plagioclases associated to the Llaima and Sollipulli pumice layers (An 28-40 and An 32-47 317 respectively; De Vleeschouwer, 2002) (Fig. 6). This difference is due to the relation between the 318 plagioclase composition and the magma chemistry, itself characteristic for the type of eruption (Fig. 319 6). Because of the dacitic (Si-rich) composition of the magma at the origin of the Llaima and 320 Sollipulli pumice layers (De Vleeschouwer et al., 2005), the plagioclases associated to these 321 pumices are enriched in Ab (Andesine-Oligoclase). However, the magma generally emitted by 322 Llaima, Sollipulli and Longuimay volcanoes has a basaltic to andesitic composition (Besoain et al., 1992b, Naranjo & Moreno, 1991, Suarez & Emparan, 1997), which means that most of the 323 324 plagioclases emitted by these volcanoes are An-rich, as they occur in the andosol parent material of OC3 outcrop. 325

326 The plagioclases occurring in the OC5 (1.50 m) sample show an An content ranging from 42 to 85 327 %. This composition is roughly similar to the plagioclases associated with the post-glacial andesitic rocks emitted by the Puyehue volcano (Fig. 6). As a general rule for the Puyehue - Cordon de 328 329 Caulle volcanic complex, the An content of the plagioclases decreases with an enrichment of the 330 magma in silica (Gerlach et al., 1988; Fig. 6). The best example is the Ab-rich plagioclases associated to the exceptional rhyodacitic eruption of 1960. However, the Puyehue - Cordon de 331 Caulle is not the only volcano at the origin of the volcanic particles deposited around Puyehue lake. 332 333 A large part of the particles may originate from Antillanca and Osorno volcanoes which are typical for the SVZ and basaltic or andesitic in composition (Gerlach et al., 1988). Although there is no 334 335 data available for Antillanca and Osorno in the literature, the relation between the plagioclase composition and magma chemistry evidence that the volcanic products emitted by the volcanoes
located around Puyehue lake mainly contain An-rich plagioclases, as they occur in the OC5
outcrop.

In agreement with the results of Laugenie (1982), these new data demonstrate that the particles composing the andosol parent material in south-central Chile have the same geochemical and mineralogical characteristics than the regional volcanic products. They can therefore be considered as volcanic ashes.

343

344 5.4 Mode of transport and deposition

345 The previous arguments have demonstrated that the andosol parent material is composed of volcanic ashes that bear the mineralogical and geochemical signature of the SVZ volcanoes. Our 346 347 field observations demonstrate that these deposits cover the region whatever the elevation, with a 348 relatively uniform thickness draping all but the steepest topography. This argument is incompatible 349 with the glacial (Langhor, 1974) and pyroclastic flow (Wright 1965 In: Besoain 1985) origins that 350 would have concentrated the volcanic particles in valleys and local depressions. On the contrary, the 351 above-cited characteristics appear to be typical for pyroclastic fall (Orton, 1996) or loess-like 352 (Laugenie et al., 1975) deposits.

353

5.4.1. Relation between the grain size and thickness of the deposits and their location to volcanoes 354 The grain size and the thickness of the andosol parent material in Icalma and Puyehue outcrops are 355 356 significantly different. Around Icalma, the deposits are thick (4 to 7 m), they contain coarse intercalated pumice layers and they are characterized by an average mean grain size of 25 µm (Fig. 357 358 3). Near Puyehue lake, the deposits are typically less than 3 m thick and the average mean grain size 359 is 18 µm (Fig. 3). These differences are due to the relative position of the outcrops compared to the 360 regional volcanoes. Because of the dominant westerly winds, the volcanic particles are mainly 361 transported from the volcanoes to the East. Therefore, the Icalma outcrops, which are located east of Llaima, Lonquimay and Sollipulli volcanoes (Fig. 1), receive more and coarser particles than the
 outcrops selected around Puyehue, which are located west of Puyehue and Antillanca volcanoes.

364 Within individual watersheds, a clear relation between the grain size and the thickness of the 365 deposits and their relative position to volcanoes has been noticed. In Icalma watershed the sediments of OC4 outcrop contain 6 distinct tephra layers and are significantly coarser that in OC2 366 367 and OC3 outcrops which are located east of OC4 and therefore further away from the local 368 volcanoes (De Vleeschouwer, 2002). In the watershed of Puyehue lake, a significant fining and 369 thinning westward was deduced from the analysis of 7 outcrops located at various distances from 370 the Puyehue and Antillanca volcanoes (Bertrand, 2005). Laugenie (1982) made similar observations 371 around Villarica volcano.

These data evidence that since the end of the last glaciation the westerly winds are responsible for the spatial distribution of the volcanic ashes and that they strongly influence the grain size and thickness of the andosol parent material. These results are confirmed by the observations made during historical eruptions, which show that most of the emitted particles have been transported eastward, as far as Argentina (Wright & Mella, 1963; Moreno & Valera, 1985; Gonzàles-Ferràn et al., 1989; Naranjo & Moreno, 1991; Naranjo et al., 1993; Gonzàles-Ferràn, 1994). Similar conditions probably prevailed during most of the Quaternary period (Moreno & Varela, 1985).

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380 5.4.2. Grains morphology

In order to characterize the type of aeolian transport which is responsible for the delivery of volcanic ashes in south-central Chile (pyroclastic fall vs loess-like deposition), we compared the size (using the D99 factor) and the morphology of the coarsest volcanic particles to typical loess and pyroclastic deposits.

The occurrence of high D99 values, i.e. very coarse particles, in both outcrops is a new argument for rejecting the sole loess-like origin of the andosol parent material. Indeed, the D99 values of the andosol parent material range between 91 and 860 μ m (506-860 μ m for OC2 and 91-783 μ m for 388 OC5), which is much higher than the typical D99 values for loess deposits (typically lower than 100μ m; Manil & Delecour, 1957; Sun et al., 2000). Grains coarser than ~100 μ m can not travel on large distances by wind only.

The morphology of the volcanic ash soil particles are in agreement with a very limited transport of the particles by wind. Indeed, the MEB observations display grains with a rough, not rounded morphology (Fig. 8). The rough morphology is due to the agglomeration of smaller volcanic particles during volcanic eruptions, which leads to the formation of strongly cohesive agglomerates. These observations evidence that the particles composing the andosol parent material have been directly deposited after volcanic eruptions. Because of their coarse grain-size and rough, non abraded morphology, we can argue that these particles have virtually never been reworked by wind.

398

399 5.5. Unique event of successive eruptions?

400 The previous arguments demonstrate that most of the andosol parent material is composed of volcanic ashes originating from eruptions of regional volcanoes and directly deposited by gravity. 401 402 However, whether these particles accumulated rapidly during the Late Glacial and early Holocene 403 (Veit, 1994) or continuously since the last glaciation remained unclear. The only macroscopical 404 chronological markers occurring in the investigated outcrops are the two intercalated pumice layers 405 described in Icalma outcrops, which indicate that the andosol parent material around Icalma 406 accumulated during several volcanic eruptions throughout the Holocene. Several additional 407 arguments evidence that these particles accumulated during successive volcanic eruptions: (1) the 408 heavy minerals study of Laugenie (1982) shows that the mineral sources of the andosol parent 409 material were frequently renewed by successive magmatic eruptions; (2) the tephra record of Puyehue lake sediments attest that at least 78 tephras reached the region since the Last Glacial 410 411 Maximum (Bertrand et al., 2007b); (3) the Icalma lake and peat deposits contain a large number of 412 Holocene tephra layers, representing 40% of the lake sedimentary infill at certain locations (De 413 Vleeschouwer, 2002; Bertrand et al., 2007a); (4) the high resolution geochemical analyses realized 414 by McCurdy (2003) on andosols from Calafquen (39°S) and Ensenada (41°S) evidence that those 415 outcrops are composed of several superimposed paleosoils. Therefore, we argue that most of the 416 particles composing the andosol parent material are typical fall-out ashes deposited by successive 417 volcanic eruptions throughout the Late glacial and Holocene.

418

419 5.6 Layering and pedogenesis

420 If the andosol parent material has been deposited during successive volcanic eruptions, one can 421 expect for it to be stratified. Our field observations have demonstrated that the only macroscopically 422 visible layering is caused by the Sollipulli and Llaima pumice layers in outcrops around Icalma and 423 by several distinct tephra layers in outcrops located at the vicinity of regional volcanoes. In thin 424 section, the OC2 deposits are not stratified either but they appear structurally homogeneous (Fig. 425 4a). The absence of stratification seems to be the result of intense weathering processes during the 426 soil formation, as they typically occur under the very humid climate of south-central Chile (Laugenie et al., 1975). Moreover, previous studies have demonstrated that the biological activity is 427 428 able to generate a deep pedoturbation in the andosols of south-central Chile, especially by roots and worms (Langohr, 1971). Therefore, we argue that the andosol parent material was initially layered, 429 430 but weathering and pedogenesis processes have rapidly wiped out the internal structures. Because 431 the development of andosols can only be interrupted by the deposition of thick volcanic sediments 432 (Buurman et al., 2004), only the two pluridecimetric Sollipulli and Llaima pumice layers have interrupted the soil formation and buried older soils. All the thinner tephra layers have been 433 434 incorporated into previously deposited particles, although some of them have probably affected the soil development during short periods of time, as evidenced by the occurrence of successive 435 436 organic-rich layers (5-10 cm) in thin sections.

437

438 **6.** Conclusion

439 The andosols of south-central Chile are developed on plurimetric vellow-brown loams mainly composed of plagioclases and (bulk and clay-) amorphous particles. The mineralogy and 440 441 geochemistry of these particles is typical for the regional volcanism, except for allophane which 442 originates from the post-depositional weathering of volcanic glasses and plagioclases. The 443 stratigraphy of the andosol parent material and the tephra record of regional lake and peat deposits 444 demonstrate that the andosol parent material accumulated during successive volcanic eruptions 445 throughout the Late glacial and Holocene. Moreover, the presence of very coarse particles and the 446 rough morphology of the coarse grains evidence that these deposits haven't been re-transported by 447 wind. Therefore, even if a small fraction of the fine particles may have been re-transported by wind, 448 these deposits can not be considered as typical loess sediments. Our results evidence their direct 449 volcanic ash fall origin. Because of the prevailing westerly winds, most of the particles have been 450 transported to the East. Very locally, andosols might have developed on volcanic ashes re-451 transported by glaciers, lahars or rivers.

452

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	Outcrop n°	Latitude	Longitude	Thickness (m)	Sampling step (cm)	Number of samples
Icalma	OC2	S38°47.079'	W71°17.062'	4.90	50 - 10	10 - 50
	OC3 S38°47.959'		W71°16.015'	6.15	50	10
	OC4	\$38°50.237'	W71°22.377'	4.60	50	8
Puyehue	OC5	S40°42.974'	W72°24.312'	2.70	25 - 10	11 – 28
	OC6	S40°38.111'	W72°22.392'	4.30	50	9

Table 1 – Location, size and sampling intervals of the 5 investigated outcrops. See figure 1 for map location. The geographic coordinates are referenced to the WGS84 datum. The thickness of the andosol parent material doesn't take into account the underlying glacial or fluvio-glacial sediments. For OC2 and OC5 outcrops, the two sampling steps represent samples collected for mineralogical and grain size analysis, respectively.

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total	An	Ab	Or
	16.6	0.00	22.0	0.47	0.11	17.0	1.77	0.00	00.12	04.0	15.0	0.0
	46.6	0.00	32.0	0.6/	0.11	17.9	1.//	0.00	99.13	84.8	15.2	0.0
	45.1	0.00	33.0	0.52	0.11	19.3	1.27	0.05	99.31	89.1	10.6	0.3
PI	49.0	0.07	30.5	0.63	0.10	16.2	2.86	0.00	99.34	75.8	24.2	0.0
agic	55.3	0.00	26.5	0.56	0.09	10.8	5.64	0.12	98.92	50.9	48.4	0.7
ocla	46.1	0.00	32.8	0.48	0.10	18.5	1.57	0.00	99.48	86.7	13.3	0.0
ses	55.7	0.00	26.6	0.38	0.06	10.6	5.70	0.12	99.19	50.3	49.0	0.7
0C	47.9	0.00	31.6	0.65	0.13	17.4	2.23	0.04	99.93	81.0	18.8	0.2
3 5.	51.2	0.09	29.1	0.55	0.17	14.4	3.69	0.08	99.33	68.1	31.4	0.5
00 1	49.4	0.00	30.2	0.71	0.08	16.0	3.05	0.06	99.50	74.1	25.6	0.3
н	45.9	0.00	32.9	0.51	0.08	18.9	1.34	0.00	99.59	88.6	11.4	0.0
	45.1	0.00	33.5	0.48	0.06	19.7	1.05	0.00	99.88	91.2	8.8	0.0
	47.6	0.00	31.2	0.68	0.13	17.1	2.28	0.00	99.04	80.6	19.4	0.0
	44.9	0.00	33.2	0.48	0.08	19.2	1.22	0.00	99.14	89.7	10.3	0.0
	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	Total	An	Ab	Or
	56.0	0.00	26.5	0.33	0.03	10.6	5.71	0.20	99.35	49.9	49.0	1.1
Pla	59.9	0.20	21.7	1.91	0.30	7.86	5.40	0.86	98.03	42.1	52.4	5.5
gioc	52.4	0.00	28.7	0.53	0.18	13.7	4.09	0.19	99.73	64.2	34.7	1.1
clase	56.0	0.00	26.8	0.19	0.03	10.6	5.80	0.10	99.52	49.8	49.6	0.6
es C	46.6	0.00	32.4	0.55	0.08	18.2	1.81	0.00	99.64	84.8	15.2	0.0
Č5	52.7	0.08	28.3	0.71	0.21	13.9	3 95	0.15	99 97	65.4	33.8	0.8
1.5	51.6	0.06	28.9	0.89	0.16	14.1	3 76	0.16	99.66	66.9	32.2	0.9
) m	55.5	0.00	27.0	0.32	0.00	11.1	5 51	0.16	99.58	52.3	46.8	0.9
	55.6	0.00	27.0	0.25	0.00	10.9	5 49	0.16	99.68	52.0	47.1	0.9
	55.0	0.00	21.5	0.25	0.00	10.7	5.77	0.10	JJ.00	52.0	T/.1	0.9

601 Table 2 - Microprobe analyses of plagioclases separated from the sediments of OC3 (5.00m) and OC5 (1.50m) samples. An, Ab and Or represent the

602 Anorthite, Albite and Orthose content of each sample, respectively.

603 **Figure captions**

604

605 Figure 1 – Study area and sampling sites.

606

Figure 2 - Simplified pedological map of south-central Chile (FAO-UNESCO, 1971 In: Aravena etal., 1993).

609

610 Figure 3 - Mineralogical composition and grain size of samples collected in OC2 and OC5 outcrops 611 (see Figure 1 for location). The grain size distribution has been measured on organic matter free 612 samples and the mean grain size has been calculated following Folk & Ward (1957). The minerals 613 detected in the bulk samples by x-ray diffraction were semi-quantified using the intensity of the 614 principal diffraction peak of each mineral corrected by a multiplication factor from Cook et al. 615 (1975) (pyroxenes: 5; chlorite: 4.95; plagioclases: 2.8, amphibole: 2.5 and guartz: 1). For the amorphous material, we used a correction factor of 75, which has been calculated from diffraction 616 617 results on mixtures of known quantities of amorphous material and quartz. It applies to the maximum of the broad diffraction band at 3.7 Å. 618

619

Figure 4 – Microscope images of some thin sections of OC2 outcrop sediments. Both images show
coated and very poorly sorted grains. a) bulk sediment (OC2 3.20 m); b) detail of the grain coating
(OC2 3.05 m).

623

Figure 5 - Picture of OC5 outcrop located in the watershed of Puyehue lake. The picture shows the
andosol parent material overlying fluvio-glacial sediments. The volcanic deposits are 2.70 m thick.

Figure 6 - Plagioclase composition of samples from Icalma (OC3 5.00m) and Puyehue (OC5 1.50
m) outcrops plotted in an Ab-An binary diagram. The An content is calculated as An/(An+Ab). For
comparison, results obtained on plagioclases from the Llaima and Sollipulli pumice layers are

630 presented (De Vleeschouwer, 2002). The data from the Puyehue-Cordon de Caulle volcanic631 complex are from Gerlach et al. (1988).



641 Figure 8 - Scanning electron microscope (SEM) images of particles from OC3 (5.00 m) sample. a,642 b) coarse grains with a typical rough morphology; c) glass shard.









B











