



Nicotine in residues of smoking pipes and other artifacts of the smoking complex from an Early Ceramic period archaeological site in central Chile



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ABSTRACT

Consumption of psychoactive substances has been important in the lives of indigenous American people for several millennia. While numerous studies have reported the occurrence of smoking pipes at archaeological sites, only a few have addressed the question of the substances being smoked. The study of smoking pipes is of particular interest at the Early Ceramic period archaeological site La Granja in central Chile (500–1000 A.D.) given its ritual connotation. Analysis by gas chromatography coupled to mass spectrometry showed the presence of nicotine in a large proportion of the residues extracted from a wide variety of grinding and smoking artifacts from La Granja (total $N = 116$). Additionally, the likelihood of finding residual nicotine varied along pipe segments, decreasing from the bowl to the mouthpieces. This research has studied the cultural operative chain of the smoking complex of the Early Ceramic period of central Chile and described *Nicotiana* sp. as a plausible plant source with nicotine as the compound involved in the physiological effect, micromortars and pestles as the artifacts used in the preparation of plants for smoking and finally, the smoking pipe through which the plant compounds were incorporated into the smoker's organism.

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1. Introduction

Consumption of psychoactive substances from natural sources has been important in the lives of indigenous American people for several millennia (Dougherty, 1972; Elferink, 1983; Haberman, 1984; Schultes and Hofman, 1979; Torres, 1999; Torres and Repke, 2006; Wilbert, 1987; Winter, 2000). Tobacco (*Nicotiana* spp.), in particular, was consumed in a variety of ways by different American cultures, e.g., by smoking, chewing, snuffing, drinking or through enemas (Wilbert, 1987). The mode of consumption is usually related to the type of effect pursued, i.e., for medicinal purposes or for the achievement of particular altered states of consciousness (Wilbert, 1987). These effects are likely based on the dose-dependent effects of nicotine, e.g., in small quantities it is a stimulant and painkiller while at large doses it may produce visions, trance and catatonia (Wilbert, 1994).

Numerous studies have reported the occurrence of smoking pipes in the Americas, the earliest pipes being found in archaeological sites some of which are dated as early as the second millennium B.C. (e.g., Aguerre et al., 1973; Fernández Distel, 1980; Pérez Gollán and Gordillo, 1993, 1994; Rafferty, 2004; Winter, 2000). However, only a limited number of studies have directly addressed the question of the substance being smoked. In North America, recent analyses by gas chromatography coupled with mass spectrometry (GC/MS) have shown the presence of nicotine in pipe residues from sites dated as early as 300 B.C. (Rafferty, 2002, 2006; Rafferty et al., 2012; Tushingham et al., 2013). In South America, seeds of *Anadenanthera* sp. were found together with several smoking pipes in a preceramic site at Puna de Jujuy, northwestern Argentina (NWA), dated 2130 B.C. (Fernández Distel, 1980) and GC/MS analysis of residues in smoking pipes revealed the presence of dimethyltryptamine alkaloids, presumably from *Anadenanthera* sp., in a Formative site (ca. 40 A.D.) at Catamarca, also in NWA (Bugliani et al., 2010; Rosso and Spano, 2005–2006). The presence of nicotine was shown in plant material found in a skin pouch at the Niño Korin site near La Paz, Bolivia, dated around 500 A.D. (Bruhn et al., 1976), and archaeobotanical studies of microremains in pipe residues from the Ciénaga period of NWA (650

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B.C.–500 A.D.) revealed the presence of trichomes of *Nicotiana* sp. (Capparelli et al., 2006). Direct evidence of the consumption of nicotine, i.e., the finding of nicotine in the consumers rather than in the objects presumably used for consumption, has only recently been obtained by GC/MS analysis of the hair of prehispanic mummies from the Formative through to the Late Intermediate periods (ca. 100 B.C.–1450 A.D.) of San Pedro de Atacama in northern Chile (Echeverría and Niemeyer, 2013) and from the Inka Period (ca. 1450 A.D.) of the Peruvian coast and Argentina (Musshoff et al., 2009).

The study of smoking pipes is of particular interest at the archaeological site La Granja in central Chile (Fig. 1) due to the high number of pipe fragments found in it (790 pieces in contrast to all other sites in the region which at most have yielded a dozen fragments each); most fragments correspond to inverted T-shaped ceramic pipes with a central bowl and two opposed and open mouthpieces. The site is located in the Cachapoal valley ca. 100 km south of Santiago (34° S, 71° W), at the intersection of ancient north–south and east–west interaction trails (Planella, 1988). Archaeological excavations have shown its occupation by Llolleo groups for a long time interval during the Early Ceramic period of central Chile (500–1000 A.D.). The site contains domestic and ceremonial sectors distinguished mainly on the basis of the nature and concentration of archaeological remains. La Granja 1 and La Granja 2 (Supplementary Figs. 1 and 2) were residential sectors which included a dwelling made with large oval river stones; the materials recovered consisted mainly of grinding stones, bones of *Lama guanicoe* (Camelidae), charred remains of crops (*Zea mays*, *Chenopodium quinoa*, *Phaseolus* sp., *Lagenaria* sp.) and a large number of jug fragments with a variety of decorations. The La Granja 3 sector yielded an exceptionally high number of pipe fragments. In addition, the excavations demonstrated the existence of a system of linear north-south oriented structures made of large river stones; along them, small oven loci and areas with a superimposition of larger burns were found, as well as broken grinding stones embedded in the structure walls. At the north-east end of the system of structures, a 100–110 cm deep vertical pit was found which contained, in addition to pipe fragments, remains of camelid phalanxes, rodents, birds, fish, and sea and fresh water mussels, beads from necklaces, and scarce but selected crop remains. At the bottom of the pit, a pile of river stones was found which covered, as

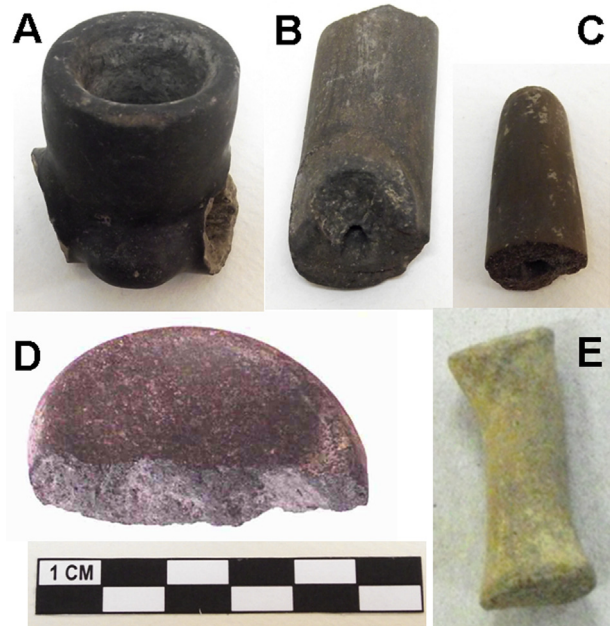


Fig. 2. Examples of artifacts of the smoking complex of Early Ceramic period of central Chile analyzed in this work: bowl (A), pipestem (B), mouthpiece (C), micromortar (D) and pestle (E).

a sort of seal, a number of intentionally buried pipe fragments. The set of elements described support La Granja 3 as a sector with a ritualistic connotation (Planella et al., 2000; Falabella et al., 2001). The wide diversity of smoking pipes found at La Granja is not inconsistent with ethnohistorical accounts of early Spanish chroniclers which describe the existence of places for social congregation of native groups around the XVI century (Valdivia, 1960 [1545]; Vivar, 1979 [1558]). The ceremonial importance of this place is supported by ethnographical studies which show that ceremonial use of smoking pipes has continued amongst natives in southern Chile (Cooper, 1949; Guevara and Oyarzún, 1912; Hilger, 1957), a region strongly linked to central Chile during the Early Ceramic period (Falabella and Planella, 1988–1989).

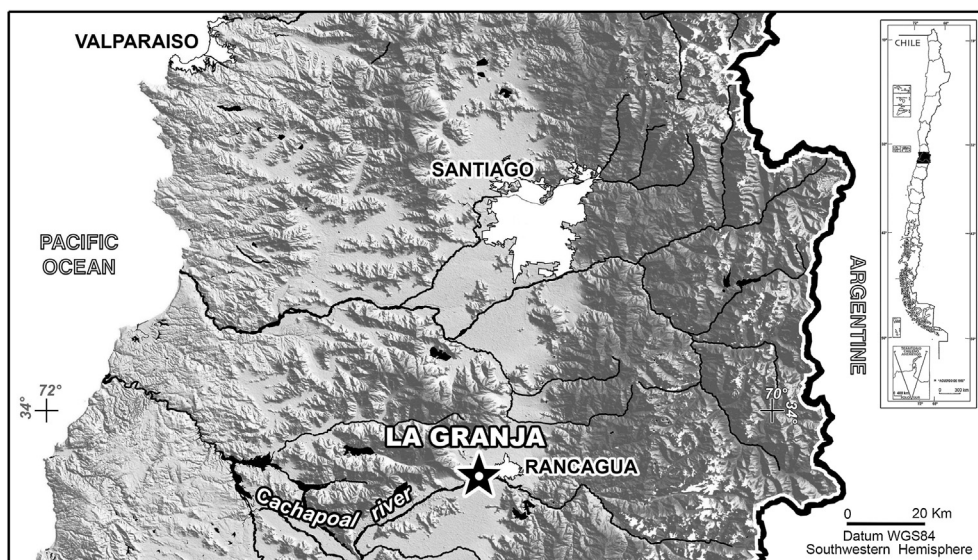


Fig. 1. Map showing the location of the La Granja archaeological site.

The evidence available suggests that smoking practices were an important part of social and ceremonial life of Llolleo as well as other horticulturalist communities of the Early Ceramic period within a vast geographical area (Planella et al., 2012a). Given this importance, the identification of the substances being consumed is a necessary first step to understand these practices, the role they played in social reproduction and the economic systems organized around their provisioning and distribution. In the present paper, we report the chemical analysis of residues in a wide variety of artifacts belonging to the smoking complex at La Granja. The analyses were focused on dimethyltryptamines and nicotine, the two most recurrent psychoactive substances in the archaeological record of the southern cone of South America.

2. Materials and methods

2.1. Archaeological samples

The archaeological samples studied were recovered from the La Granja site and are curated at the Museo Regional de Rancagua, Chile. They include (Fig. 2) fragments of smoking pipes (bowls, pipestems and mouthpieces) and grinding artifacts (micromortars and pestles). The number of artifacts studied is shown in Table 1.

2.2. Extraction of residue samples from archaeological artifacts

All sampling implements (Petri dishes, glass funnels, vials and toothpicks) were washed with a mixture of mild soap and water followed by 95% ethyl alcohol, rinsed with distilled water, and finally dried in an oven. Artifacts were carefully manipulated using powder-free gloves (one pair of gloves used for each piece). The interior surface of each artifact was superficially scraped with a plastic toothpick; the powder obtained corresponded to sediment from the immediate surroundings of the object. Further scraping was performed of the cultural remains corresponding to combustion products. Matrix soil samples from the archaeological site were also obtained and analyzed as controls.

2.3. Preparation of extracts from residue samples

Acid-base extractions suitable for the purification of alkaloidal extracts were not attempted because the quantity of starting material was usually exceedingly small (mean: 9.9 mg) and the eventual quantities of alkaloids were suspected to be not far from the limit of detection of the method. This speculation was substantiated by the results which showed that residues analyzed contained a mean of 15 ng of nicotine. Furthermore, since the solubility of nicotine is higher in chloroform than in methanol and that of dimethyltryptamines higher in methanol than in chloroform, both solvents were used sequentially to extract the residues.

The solid residue from an archaeological object was extracted with 500 μ L chloroform (HPLC grade, JTBaker, USA) by maceration in an ultrasonic bath (Power Sonic 405, Hwashin Technology, Korea) at medium intensity for 15 min at 25 °C. The suspension was subsequently vortexed at ambient temperature for 60 min and filtered through cotton wool placed at the tip of a Pasteur pipette using an additional 500 μ L aliquot of chloroform. The extract was collected in a 2 mL amber vial with a teflon-lined screw cap and evaporated to dryness under nitrogen. The solid residue was transferred into a 300 μ L glass insert by means of successive washes with 100, 50 and 20 μ L of chloroform, thus minimizing the amount of extract retained in the vial walls. The solution was evaporated to dryness and the extract reconstituted with 20 μ L chloroform. After chloroform was evaporated from the cotton wool filter, the solid material adhered to it was extracted with 500 μ L methanol (HPLC grade, JTBaker, USA) and collected in a 2 mL amber vial. This methanolic extract was further processed following the same procedure used in the preparation of the chloroformic extract.

2.4. GC/MS analysis

GC/MS analysis was performed in a Shimadzu model GCMS-QP 2010 Ultra gas chromatograph (Shimadzu, Kyoto, Japan) operating in the splitless mode and fitted with a Rtx-5MS crossbond 5% diphenyl – 95% dimethyl polysiloxane (Restek, Bellefonte, PA, USA) capillary GC column (30 m length, 0.25 mm I.D., 0.25 μ m film thickness). The column temperature was held at 30 °C for 3 min, raised at 25° C/min to 230 °C, and maintained for 10 min at 230 °C. The injection volume was 2 μ L and the carrier gas was helium (flow rate: 1.3 mL/min). The mass spectrometer was used in the electron impact ionization mode (70 eV) with an emission current of 250 μ A. The temperatures of the injection port, ion source and transfer line were 250 °C, 250 °C and 280 °C, respectively. The instrument was operated in the scan and SIM (single ion monitoring) modes. In the scan mode, the instrument monitors a wide and continuous range of masses determined by the molecular masses and fragmentation patterns of the potential compounds of interest. In the SIM mode, the instrument gathers data for only a defined set of masses, thus achieving increased selectivity (the masses are chosen to correspond to those of the particular analyte of interest) and sensitivity (the instrument spends time scanning only the few relevant masses chosen). Sensitivity can increase by a factor of 10–100 from scan to SIM modes. In the present study, the main ions of dimethyltryptamines and nicotine were included in the SIM analyses.

3. Results

Dimethyltryptamines were not detected in any of the residues analyzed, whereas nicotine was found in a large proportion of them. An artifact was considered to contain nicotine if either the cultural deposit in it or its associated sediment analyzed positively for nicotine. A positive identification of nicotine was based on the concurrence of two conditions: the chromatogram of the sample showed a peak falling within the time range of pure nicotine (mean = 9.78 min; range = 9.65–9.91 min), and the ratio between ions with m/z 133 and 84, the two most intense mass spectral peaks of nicotine, was within one standard deviation of the mean of reference nicotine samples (Fig. 3).

The results of these analyses provided conclusive evidence for the presence of nicotine both in smoking and grinding artifacts (Table 1). Statistical analysis showed that the proportion of artifacts with and without nicotine differed significantly between the three sectors of a smoking pipe (CHI-2 = 6.055; df = 2; P = 0.048). Pairwise comparisons showed the proportions to differ between the bowl and the other two sectors (bowl-pipestem: CHI-2 = 5.11,

Table 1
Presence and absence of nicotine in the different types of artifacts analyzed.

| Artifact | Nicotine in artifact | | | |
|-----------------------------------|----------------------|-----------|------------|--------------|
| | Present | Absent | Total | % Presence |
| Bowl | 14 | 10 | 24 | 58.33 |
| Pipestem | 19 | 41 | 60 | 31.67 |
| Mouthpiece | 5 | 13 | 18 | 27.78 |
| Summary smoking artifacts | 38 | 64 | 102 | 37.25 |
| Micromortar | 5 | 6 | 11 | 45.45 |
| Pestle | 2 | 1 | 3 | 66.67 |
| Summary grinding artifacts | 7 | 7 | 14 | 50.00 |
| All artifacts | 45 | 71 | 116 | 38.79 |

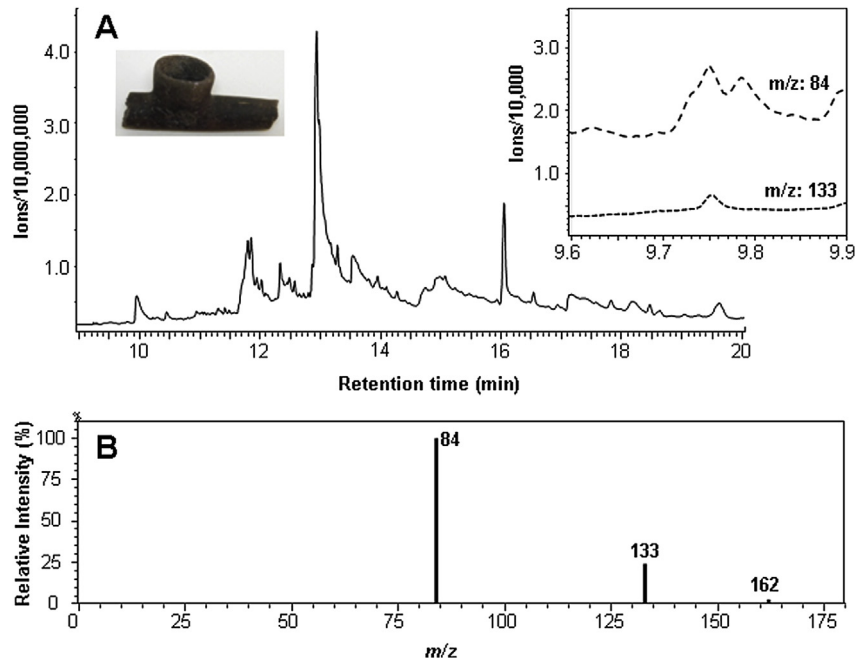


Fig. 3. Analysis of nicotine in fragments of smoking pipes. A: Scan chromatogram of the smoking pipestem 46-RT with inset showing SIM chromatogram with ions m/z 84 and 133 around the retention time of nicotine; B: Mass spectrum of peak in chromatogram A at the retention time of nicotine.

$df = 1, P = 0.024$; bowl-mouthpiece: $CHI-2 = 3.88, df = 1, P = 0.049$; pipestem-mouthpiece: $CHI-2 = 0.098, df = 1, P = 0.754$ (Fig. 4). Furthermore, the proportion of artifacts with and without nicotine did not differ between grinding and smoking artifacts ($CHI-2 = 0.391; df = 1; P = 0.532$).

4. Discussion

The sampling method was designed in such way that both chemical and archaeobotanical analyses could be performed on the pipe residues. Since starch grains have high diagnostic value for psychoactive plants at the genus or species levels (Cortella and Pochettino, 1994; Planella et al., 2014), and they may be affected by organic solvents (Babot, 2007), the samples for analysis were obtained by scraping solid residues from the pipes rather than by direct extraction with an organic solvent, as has been done in other analyses of pipe residues (Tushingham et al., 2013). Additionally, parallel analyses of sediments attached to the archaeological objects were undertaken based on the presumption that if chemicals leached from the object during the time it was buried, they may be unapparent in cultural deposits but be detectable in associated sediments. This may be an important consideration at the La Granja site given the weather patterns in the area and the nature of its soil; thus, an average yearly rainfall of ca. 400 mm and the acidic soils of the Cachapoal valley (Ginocchio et al., 2002) are factors which favor the leaching of a basic and water-soluble compound such as nicotine. Indeed, nicotine was found in the sediments four times as often as in the cultural deposition residues, while samples of the soil matrix gave consistently negative results.

Previous analyses of fragments of ceramic pipes from the La Granja site showed the presence of alkaloids; however, identification of nicotine was not achieved (Hairfield and Hairfield, 2002). The study mentions identifications based on comparisons with library mass spectra, i.e., the instrument was most likely operated in the scan mode, a method less sensitive than the SIM mode used in the present study. In fact, when the nicotine-containing samples of

the present study were re-analyzed in the scan mode, nicotine could not be detected in any of them (Fig. 3).

Nicotine was identified in a high proportion of the artifacts studied. The most likely sources of nicotine are species of the genus *Nicotiana*. Several native *Nicotiana* species grow in central Chile, the most common being *Nicotiana corymbosa* and *Nicotiana acuminata* (Goodspeed, 1954). Archaeobotanical studies of the cultural rock-shelter deposits at levels corresponding to the Early Ceramic period in the Las Morrenas 1 site in the Andes of central Chile showed the presence of desiccated and charred seeds originally attributed to a species of the genus *Nicotiana* (Planella et al., 2005) and later identified as *N. corymbosa* (Planella et al., 2012b), while pipe residues from La Granja yielded starch grains similar to those of species of the genus *Nicotiana* (Planella et al., 2012a). One may wonder, however, whether an important communal ceremonial activity

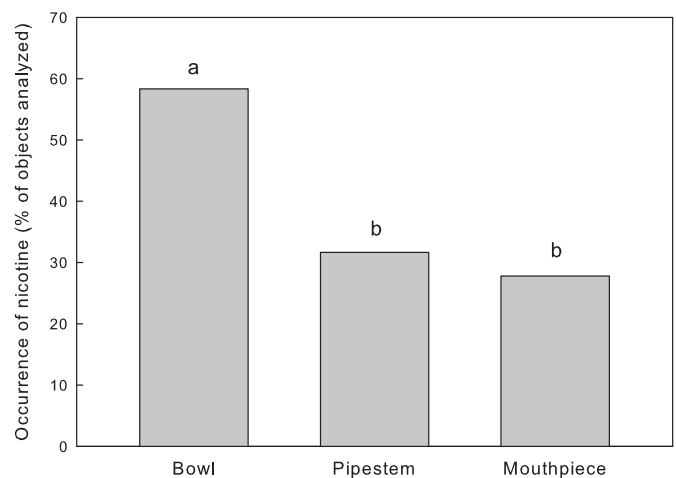


Fig. 4. Frequency of occurrence of nicotine in different parts of a smoking pipe. Different letters above bars indicate significant differences (multiple proportion tests, $P < 0.05$).

such as tobacco smoking appears to be at La Granja, could have depended solely on the collection of a wild species of tobacco, whose natural abundance was likely to be low since their preferred habitats are strongly disturbed environments which must have been scarce in prehispanic times. It appears more likely that micro-scale cultivated or domesticated tobacco was smoked, whose production could be controlled. Tobacco is among the oldest cultigens of the Americas (Wilbert, 1987), the two most important cultivated varieties being *Nicotiana tabacum*, whose cultivation is believed to have begun in the central Andes and spread into northern South America and the Amazonia, and *Nicotiana rustica*, probably a hybrid between species from Bolivia and Argentina which spread into the whole American continent (Pérez Gollán and Gordillo, 1993). Hence, the trade routes linking central Chile to areas across the Andes (Neme and Gil, 2010; Planella et al., 2005, 2011; Sanhueza et al., 2004) or to the semiarid north of Chile (Troncoso et al., 2012) make it possible that cultivated or domesticated tobacco was brought to central Chile; alternatively, cultivated or domesticated tobacco may have been produced locally by horticultural communities of the Early Ceramic period. Clearly, species-specific markers for *Nicotiana* are needed to determine the species smoked. Chemical markers are unlikely to be reliable because of the instability of nicotinic alkaloids in the bowl of a smoking pipe (Seeman, 2005; Tyrpień et al., 2003); however, archaeobotanical markers show great promise: seeds of *Nicotiana* from 12 species growing in Chile (7 native, 4 introduced, and one cultivated species) showed marked interspecific differences (Planella et al., 2012b), and microfossils (Quiroz, personal communication), pollen (Bryant et al., 2012; Collao-Alvarado, personal communication) and epidermal structures (Naulin and Valenzuela, personal communication) are also promising candidates.

The likelihood of finding nicotine was higher in the bowl than in the pipestem and mouthpiece. When ground tobacco leaves were burned in the bowl, the nicotine-containing vapors were guided through the pipestem by suction at either of the mouthpieces, making it likely that concentration of residual nicotine – and hence the likelihood of finding it – decreased as the distance from the bowl increased. Comparable results were obtained by Eerkens et al. (2012) who did not find nicotine in the mouth section of a prehistoric tubular pipe from North America whose bowl section had indeed shown the presence of nicotine.

The absence of dimethyltryptamines in the pipe residues analyzed merits a comment. The main sources of these compounds in southern South America are the seeds of the tree *Anadenanthera colubrina*, whose southernmost distribution are the forests near Córdoba, Argentina (Hunziker, 1973), distant some 1000 km from the La Granja site. Seeds of this species have been found in archaeological sites of NWA (Fernández Distel, 1980) and dimethyltryptamines have been found in pipe residues from sites also of NWA (Bugliani et al., 2010; Rosso and Spano, 2005–2006). The lack of evidence for the use of this plant in central Chile could be accounted for by distance from the source or by cultural preferences of its inhabitants.

Nicotine was not detected in all the artifacts analyzed. However, this should not necessarily be taken to indicate that tobacco was not ground in the micromortars or smoked in the pipes analyzed since, in spite of the high sensitivity of GC/MS analysis in the SIM mode, quantities of nicotine in some artifacts may be below the detection level of this analytical method. Several arguments may be put forward to explain particularly low levels of nicotine in smoking pipes: i) since the La Granja site was occupied for nearly 500 years, some of the pipes will have experienced longer leaching processes than others eventually leading to larger losses of nicotine from their residues; ii) smoking pipes with a relatively thicker bowl could have led to higher combustion temperatures and hence to a higher

extent of nicotine degradation (Hairfield and Hairfield, 2002; Rodgman and Perfetti, 2009), iii) differential leaching due to different microenvironments where pipe fragments were deposited could determine different degrees of dilution of nicotine in the residues sampled, and iv) pipes could have been used only a few times leading to little cultural deposition of nicotine. This latter situation may arise, for example, if pipes were used for ceremonial purposes, i.e., during a limited time period. This argument is supported by the finding of only pipe fragments in the La Granja site, i.e., not a single complete pipe was recovered (Falabella et al., 2001; Planella et al., 2000), pointing to the ritual breaking of the pipes. This is consistent with the tradition of symbolic destruction of ceramic containers by making a hole in them noticed at Early Ceramic period sites of central and southern Chile (Dillehay and Gordon, 1979; Falabella and Planella, 1980; Gordon, 1985), and also the intentional destruction of smoking pipes characteristic of Early Woodland Period (1000–0 B.C.) archaeological sites in North America, a practice that persists in later periods (Rafferty, 2004). In other words, it is likely that pipes of the La Granja site were not used extensively before breaking and deposition in the ground.

Nicotine was present in a high proportion of micromortars and pestles found together with pipe fragments. These artifacts were presumably used in grinding and homogenizing dried plant material prior to smoking. These micromortars are considerably smaller than those which served domestic purposes and which were found associated with macroremains of edible species such as corn (*Zea mays*), quinoa (*C. quinoa*), squash (*Cucurbita* sp.) and beans (*Phaseolus vulgaris*) (Planella and Tagle, 1998). Hence, the cultural operative chain of the smoking complex (Planella et al., 2012a) has now been described to include species of *Nicotiana* as a plausible plant source with nicotine as the compound involved in the physiological effect, micromortars and pestles as the artifacts used in the preparation of plants for smoking and finally, the smoking pipe through which the plant compounds were taken up by the smoker. Future efforts should be directed at identifying the species of *Nicotiana* used, particularly since such information will shed light on patterns of exchange and mobility during the Early Ceramic period in central Chile.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jas.2014.01.016>.

References

- Aguerre, A., Fernández, A., Aschero, C., 1973. Hallazgo de un sitio acerámico en la Quebrada de Inca Cueva (Provincia de Jujuy). *Relac. Soc. Argent. Antropol.* 7, 197–235.
- Babot, M.P., 2007. Granos de almidón en contextos arqueológicos: posibilidades y perspectivas a partir de casos del noroeste argentino. In: Marconetto, B., Olszewsky, N., Babot, M.P. (Eds.), *Paleoetnobotánica del Cono Sur: Estudios de*

- Casos y Propuestas Metodológicas. Centro Editorial de la Facultad de Filosofía y Humanidades, Universidad Nacional de Córdoba, pp. 95–125.
- Bruhn, J.G., Holmstedt, B., Lindgren, J.E., Wassén, S.H., 1976. The Tobacco from Niño Korin: Identification of Nicotine in a Bolivian Archaeological Collection. In: Göteborgs Etnografiska Museum Årstryk, pp. 45–48.
- Bryant, V.M., Kampbell, S.M., Hall, J.L., 2012. Tobacco pollen: archaeological and forensic applications. *Palynology* 36, 208–223.
- Bugliani, M.F., Calo, C.M., Scattolin, M.C., 2010. Fumando en la cocina. Determinación de contenidos por técnicas fisicoquímicas en dos pipas cerámicas del sitio Cardonal. In: La arqueometría en Argentina y Latinoamérica, pp. 231–236.
- Capparelli, A., Pochettino, M.L., Andreoni, D., Iturriza, R.D., 2006. Differences between written and archaeological record: the case of plant micro remains recovered at a Northwestern Argentinean pipe. In: Proceedings of the IVth International Congress of Ethnobotany (ICEB 2005), pp. 397–406.
- Cooper, J., 1949. Stimulants and narcotics. In: Steward, H. (Ed.), *Handbook of South American Indians*, vol. 5. Smithsonian Institution, Washington, pp. 525–558.
- Cortella, A.R., Pochettino, M.L., 1994. Starch grain analysis as a microscopic diagnostic feature in the identification of plant material. *Econ. Bot.* 48, 171–181.
- Dillehay, T., Gordon, A., 1979. El simbolismo en el ornitomorfo mapuche. La mujer casada y el "ketru metawe". In: Proceedings of the VII Congreso Nacional de Arqueología Chilena. Altos de Vilches. Ediciones Kultrún, pp. 303–316.
- Dougherty, B., 1972. Las pipas de fumar arqueológicas de la Provincia de Jujuy. *Relac. Soc. Argent. Antropol.* VI, 83–89.
- Echeverría, J., Niemeyer, H.M., 2013. Nicotine in the hair of mummies from San Pedro de Atacama (Northern Chile). *J. Archaeol. Sci.* 40, 3561–3568.
- Eerkens, J., Tushingham, S., Lentz, K., Blake, J., Ardura, D., Palazoglu, M., Fiehn, O., 2012. GC/MS analysis of residues reveals nicotine in two late prehistoric pipes from CA-ALA-554. *SCA Proc.* 26, 212–219.
- Elferink, J.G., 1983. The narcotic and hallucinogenic use of tobacco in Pre-Columbian Central America. *J. Ethnopharmacol.* 7, 111–122.
- Falabella, F., Planella, M.T., 1980. Secuencia cronológica cultural para el sector de desembocadura del río Maipo. *Rev. Chil. Antropol.* 3, 87–106.
- Falabella, F., Planella, M.T., 1988–1989. Alfarería temprana en Chile central: un modelo de interpretación. *Paleoetnología* 5, 41–64.
- Falabella, F., Planella, M.T., Tagle, B., 2001. Pipes and smoking tradition in the pre-hispanic societies of the Early Ceramic period of the central region of Chile. *Eleusis* 5, 137–151.
- Fernández Distel, A.M., 1980. Hallazgos de pipas en complejos precerámicos del borde de la Punajujeña (República Argentina) y el empleo de alucinógenos por parte de las mismas culturas. *Estud. Arqueol.* 5, 55–75.
- Ginocchio, R., Rodríguez, P.H., Badilla-Ohlbaum, R., Allen, H.E., Lagos, G.E., 2002. Effect of soil copper content and pH on copper uptake of selected vegetables grown under controlled conditions. *Environ. Toxicol. Chem.* 21, 1736–1744.
- Goodspeed, T.H., 1954. The Genus *Nicotiana*. *Chronica Botanica*, Waltham, Massachusetts, USA.
- Gordon, A., 1985. El potencial interpretativo de la fractura y perforación intencionales de "Artefactos Símbolos". *Chungará* 15, 59–66.
- Guevara, T., Oyarzún, A., 1912. El tabaco y las pipas prehistóricas de Chile. In: *Actas del XVII Congreso Internacional de Americanistas*, Buenos Aires, Argentina, pp. 414–437.
- Haberman, T.W., 1984. Evidence for aboriginal tobaccos in eastern North America. *Am. Antiq.* 49, 269–287.
- Hairfield, H.H., Hairfield, E.M., 2002. Smoking out the Past. *Anthropology uses GC–MS to determine the botanical origins of residue in ancient clay pipes from Chile*. *Today's Chem. Work*, 27–31. American Chemical Society. <http://pubs.acs.org/tcaw>.
- Hilger, S.M.I., 1957. Araucanian Child Life and its Cultural Background. In: *Smithsonian Miscellaneous Collections*, vol. 133 (Washington, USA).
- Hunziker, A.T., 1973. El "cebil" (*Anadenanthera colubrina* var. *cebil*) en la Provincia de Córdoba. *Kurtziana* 7, 265.
- Musshoff, F., Rosendahl, W., Madea, B., 2009. Determination of nicotine in hair samples of pre-Columbian mummies. *Forensic Sci. Int.* 185, 84–88.
- Neme, G., Gil, A., 2010. Discusiones Teórico-metodológicas y el desarrollo de la investigación en la macroregión Cuyo-Chile central. In: *Proceedings of the XVII Congreso Nacional de Arqueología Chilena*. Valdivia, vol. 1, pp. 373–382.
- Pérez Gollán, J.A., Gordillo, I., 1993. Alucinógenos y sociedades indígenas del noroeste argentino. *An. Antropol.* 30, 299–345.
- Pérez Gollán, J.A., Gordillo, I., 1994. Vilca/Uturuncu. Hacia una arqueología del uso de alucinógenos en las sociedades prehispánicas de los Andes del Sur. *Cuicuilco* 1, 99–140.
- Planella, M.T., 1988. La propiedad territorial indígena en la cuenca de Rancagua, siglos XVI y XVII. Tesis para optar al título de Magister en Historia, mención Etnohistoria. Departamento de Ciencias Históricas, Universidad de Chile, Santiago, Chile.
- Planella, M.T., Tagle, M.B., 1998. El sitio agroalfarero de La Granja: un aporte desde la perspectiva arqueobotánica. Museo Nacional de Historia Natural de Chile. Ediciones de la Dirección de Bibliotecas, Archivos y Museos DIBAM. *Publicación Ocasional* N° 52.
- Planella, M.T., Belmar, C., Quiroz, L., Estévez, D., 2012a. Propuesta integradora para un estudio del uso de plantas con propiedades psicoactivas en pipas del Período Alfarero Temprano y sus implicancias sociales. *Rev. Chil. Antropol.* 25, 93–119.
- Planella, M.T., Belmar, C.A., Quiroz, L.D., Falabella, F., Alfaro, S.K., Echeverría, J., Niemeyer, H.M., 2014. Towards the reconstruction of the ritual expressions of societies of the Early Ceramic period in central Chile: social and cultural contexts associated to the use of smoking pipes. In: *Bollwerk, E., Tushingham, S. (Eds.), Perspectives on the Archaeology of Pipes, Tobacco and other Smoke Plants in the Ancient Americas*. (submitted for publication).
- Planella, M.T., Collao-Alvarado, K., Niemeyer, H.M., Belmar, C., 2012b. Morfometría comparada de semillas de *Nicotiana* (Solanaceae) e identificación de semillas carbonizadas provenientes de un sitio arqueológico en Chile central. *Darwiniana* 50, 207–217.
- Planella, M.T., Cornejo, L., Tagle, B., 2005. Alero Las Morrenas 1: evidencias de cultígenos entre cazadores recolectores de finales del Período Arcaico en Chile Central. *Chungara* 37, 59–74.
- Planella, M.T., Falabella, F., Tagle, B., 2000. Complejo fumatorio del período Alfarero Temprano en Chile central. *Contrib. Arqueol.* 5, 895–909.
- Planella, M.T., Scherson, R., McRostie, V., 2011. Sitio El Plomo y nuevos registros de cultígenos iniciales en cazadores del Arcaico IV en Alto Maipo, Chile central. *Chungará* 43, 189–202.
- Rafferty, S.M., 2002. Identification of nicotine by gas chromatography/mass spectrometry analysis of smoking pipe residue. *J. Archaeol. Sci.* 29, 897–907.
- Rafferty, S.M., 2004. They pass their lives in smoke, and at death fall into the fire: smoking pipes and mortuary ritual during the Early Woodland Period. In: *Rafferty, S.M., Mann, R. (Eds.), Smoking and Culture: the Archaeology of Tobacco Pipes in Eastern North America*. University of Tennessee Press, Knoxville, pp. 1–41.
- Rafferty, S.M., 2006. Evidence of early tobacco in Northeastern North America? *J. Archaeol. Sci.* 33, 453–458.
- Rafferty, S.M., Lednev, I., Virkler, K., Chovanec, Z., 2012. Current research on smoking pipe residues. *J. Archaeol. Sci.* 39, 1951–1959.
- Rodgman, A., Perfetti, T.A., 2009. *The Chemical Components of Tobacco and Tobacco Smoke*. CRC Press, Taylor and Francis Group, New York.
- Rosso, C., Spano, R., 2005–2006. Evidencias del uso de alucinógenos en pipas halladas en dos sitios tempranos de los Valles Calchaquíes. *Arqueología* 13, 79–99.
- Sanhueza, L., Falabella, F., Fonseca, E., Andonje, O., 2004. Aplicación de análisis de pastas macroscópicas, petrográficas y de composición de elementos químicos al problema de la procedencia de la cerámica en el Período Alfarero Temprano de Chile central y Cuyo, Argentina. *Estud. Atacameños* 28, 121–132.
- Schultes, R.E., Hofmann, A., 1979. *Plants of the Gods: Origins of Hallucinogenic Use*. McGraw-Hill, New York.
- Seeman, J.I., 2005. Using 'basic principles' to understand complex science: nicotine smoke chemistry and literature analogies. *J. Chem. Educ.* 82, 1577–1582.
- Torres, C.M., 1999. Psychotropic substances in the archaeology of Northern Chile and NWArgentina. A comparative review of the evidence. *Chungara* 30, 49–63.
- Torres, C.M., Repke, D.B., 2006. *Anadenanthera*. Visionary Plant of Ancient South America. The Haworth Herbal Press, NY.
- Troncoso, A., Larach, P., Alfaro, S., Pascual, D., Pavlovic, D., 2012. Nuevos antecedentes para el período Alfarero Temprano en el valle del Choapa: el sitio Los Mellizos (Cuenca superior del río Illapel). In: *Actas del XVIII Congreso Nacional de Arqueología Chilena*. Sociedad Chilena de Arqueología, pp. 309–327.
- Tushingham, S., Ardura, D., Eerkens, J.W., Palazoglu, M., Shahbaz, S., Fiehn, O., 2013. Hunter-gatherer tobacco smoking: earliest evidence from the Pacific northwest coast of North America. *J. Archaeol. Sci.* 40, 1397–1407.
- Tyrpień, K., Dobosz, C., Chróściewicz, A., Ciotecka, M., Wielkoszyński, T., Janoszka, B., Bodzek, D., 2003. Investigation of nicotine transformation products by densitometric TLC and GC–MS. *Acta Chromatogr.* 13, 154–160.
- Valdivia, Pedro de, 1960 [1545]. *Cartas al Emperador Carlos V*. Biblioteca de Autores Españoles. In: *Crónicas del Reino de Chile*, Tomo 131, pp. 1–74.
- Vivar, Gerónimo de, 1979 [1558]. *Crónica y relación copiosa y verdadera de los Reinos de Chile*. In: *Saez-Godoy, L. (Ed.), Bibliotheca Ibero-Americana*. Colloquium Verlag, Berlin.
- Wilbert, J., 1987. *Tobacco and Shamanism in South America*. Yale University Press.
- Wilbert, J., 1994. The cultural significance of tobacco use in South America. In: *Seaman, G., Day, J.S. (Eds.), Ancient Traditions: Shamanism in Central Asia and the Americas*. University Press of Colorado & Denver Museum of Natural History, Denver, pp. 47–76.
- Winter, J.C., 2000. Tradicional uses of tobacco by native Americans. In: *Winter, J.C. (Ed.), Tobacco Use by Native North Americans*. University of Oklahoma Press, Norman, pp. 9–58.