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GEOLOGICAL NOTE

First radiometric age (U-Pb, LA-ICP-MS, on detrital zircons) from the Punta Topocalma Formation: insights on Late Cretaceous marine deposition in central Chile

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ABSTRACT. Upper Cretaceous marine rocks crop out along the Pacific coast of central and south-central Chile between 33° and 37°S. These strata constitute an important reference for the Upper Cretaceous of South America due to their diverse fossil fauna and flora. The type unit of these deposits is the Quiriquina Formation, near Concepción. This unit is considered Maastrichtian in age based on ammonites. Upper Cretaceous marine strata from other localities of central and south-central Chile are largely unstudied and their biostratigraphic ages are not precisely known. We present the first radiometric dating (U-Pb on detrital zircons) for Upper Cretaceous marine strata of the Chilean forearc at Punta Topocalma that indicates a probable depositional age of 71.9±0.9 Ma (latest Campanian-earliest Maastrichtian). Provenance analysis indicates that the source of sediments of the Punta Topocalma Formation was plutonic and volcano-sedimentary rocks from the Coastal Cordillera and the Central Depression of central Chile. The Lo Valle Formation, a volcano-sedimentary unit in the Central Depression, recorded deposition of the Upper Cretaceous volcanic arc that was coeval with marine sedimentation in the Topocalma area.

Keywords: Upper Cretaceous, Quiriquina Formation, Punta Topocalma Formation, U-Pb Geochronology.

RESUMEN. Primera datación radiométrica (U-Pb, LA-ICP-MS, en circones detríticos) de la Formación Punta Topocalma: observaciones sobre la sedimentación marina durante el Cretácico Tardío en Chile central. Rocas marinas del Cretácico Tardío afloran a lo largo de la costa pacífica de Chile central y centro-sur entre los 33°-37°S. Estos estratos constituyen una importante referencia para el Cretácico Superior de Sudamérica debido a la diversidad de su fauna y flora fósil. La unidad tipo de estos depósitos es la Formación Quiriquina que aflora en los alrededores de Concepción y es considerada de edad Maastrichtiana sobre la base de ammonites. Depósitos marinos del Cretácico Tardío en otras localidades de Chile central y centro-sur han sido poco estudiados y sus edades bioestratigráficas no se han determinado con precisión. Presentamos la primera edad radiométrica (U-Pb en zircones detríticos) en estratos marinos del Cretácico Superior de Punta Topocalma. Esta indica una probable edad de depósito de 71,9±0,9 Ma (Campaniano terminal-Maastrichtiano basal). El análisis de proveniencia señala que la fuente del sedimento de la Formación Punta Topocalma fueron rocas plutónicas y volcano-sedimentarias de la cordillera de la Costa y en la depresión Intermedia de Chile central. La Formación Lo Valle, unidad volcano-sedimentaria que aflora en la depresión Intermedia, recibió sus aportes de un arco volcánico del Cretácico Tardío contemporáneo con la sedimentación marina en el área de Topocalma.

Palabras clave: Cretácico Superior, Formación Quiriquina, Formación Punta Topocalma, Geocronología U-Pb.

1. Introduction

Campanian?-Maastrichtian (Upper Cretaceous) marine rocks crop out along the Pacific coast of central and south-central Chile between Algarrobo (33°S) and the Arauco Peninsula (37°S) (Stinnesbeck, 1986) (Fig. 1). Upper Cretaceous marine deposits have also been recognized in boreholes drilled on the continental shelf at the same latitudes (Mordojovich, 1981). These strata have been studied since the 19th century (*e.g*., D'Orbigny, 1842; Darwin, 1846; Philippi, 1887; Steinmann *et al*., 1895; Wilckens, 1904; Wetzel, 1930; Biró-Bagóczky, 1982; Stinnesbeck, 1986; Salazar *et al*., 2010; Buatois and Encinas, 2011) and constitute an important reference for the Upper Cretaceous of South America due to their diverse fossil fauna and flora that includes bivalves, gastropods, scaphopods, cephalopods, crustaceans, birds, plesiosaurs, mosasaurs, turtles, fish, pollen, and wood (for references see Salazar *et al*., 2010; Buatois and Encinas, 2011).

Most studies on Upper Cretaceous marine deposits have been carried out on the Quiriquina Formation that crops out in the vicinity of Concepción (~36°45'S) (Fig. 1). Biró-Bagóczky (1982) proposed Las Tablas Bay on Quiriquina Island as a type section for this lithostratigraphic unit and a section at Cocholgüe, on the coast of the bay of Concepción, as a complementary paratype. The Quiriquina Formation overlies plutonic and metamorphic upper Paleozoic rocks and underlies Paleogene fluvial to brackish strata (Stinnesbeck, 1986, 1996). This unit forms a fining-upward succession deposited in a coastal to shallow-marine environment that comprises, from base to top, a transgressive conglomerate, an interval of coarse-grained sandstone with interbedded conglomerate and coquina, and a fine-grained glauconitic sandstone to siltstone interval with calcareous concretions (Stinnesbeck,1986; Buatois and Encinas, 2011). Based on ammonites, a Late Senonian age was originally assigned to the Quiriquina Formation by Steinmann (1895). However, Stinnesbeck (1986, 1996) and Salazar *et al.* (2010) restricted the age of the unit to the Early to Late Maastrichtian, also based on ammonite occurrences.

Upper Cretaceous marine strata from other localities of central and south-central Chile are largely unstudied and their biostratigraphic ages are not precisely known (Fig. 1). They have been reported in the following localities: **1.** the Arauco peninsula (~37°30'S) where strata of the Quiriquina Formation were identified in small outcrops and wells drilled in the area by coal and oil companies (see Stinnesbeck, 1986 and references therein); **2.** Chanco (~35°S), where local strata were defined as the Chanco Formation and assigned to the late Campanian by Tavera (1988[1]) based on stratigraphic correlations and fossil invertebrates. However, Suárez

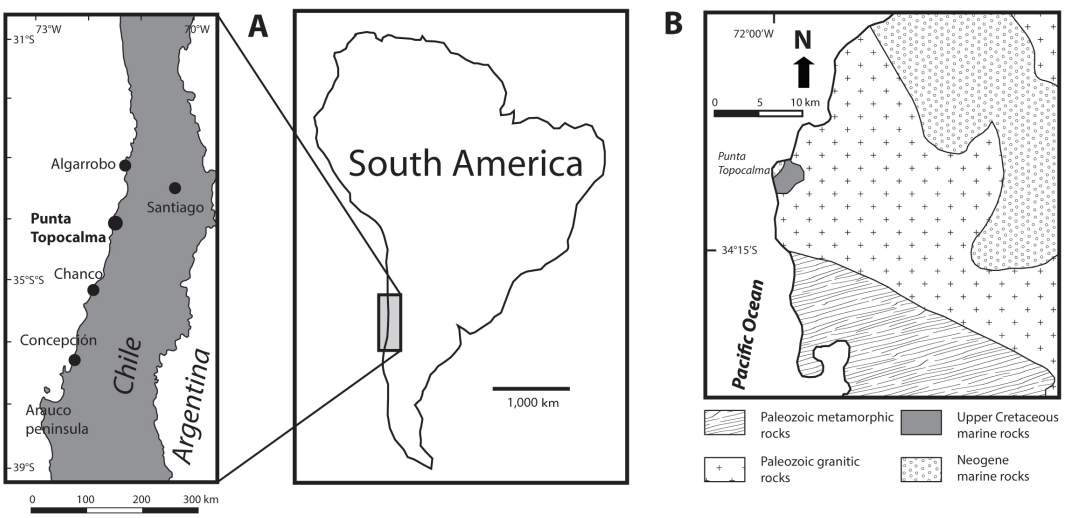

FIG. 1. **A.** Localities with outcrops of Upper Cretaceous marine deposits along the coast of central and south-central Chile; **B.** Geologic map of the study area (modified from Servicio Nacional de Geología y Minería, 2002; Encinas *et al*., 2006).

[1] Tavera, J. 1988. Formación Quiriquina. Localidades para la formación. Estratotipos y fauna (latitudes 33°21'-37°50'). Unpublished monograph, Departamento de Geología, Universidad de Chile: 212 p.

and Otero (2009) tentatively assigned the Chanco strata to the Maastrichtian because their facies and fossil content are similar to those identified in the Quiriquina Formation; **3.** Punta Topocalma (~34°S) where they were defined as the Punta Topocalma Formation by Cecioni (1978) and assigned to the Upper Campanian based on ammonites (Pérez and Reyes,1980); **4.** Algarrobo (~33°S) where they were defined as the Estratos de la Quebrada Municipalidad by Gana *et al.* (1996) and assigned to the early Maastrichtian by Levi and Aguirre (1966) based on ammonites, and by Suárez and Marquardt (2003) based on strontium isotope stratigraphy.

The Quiriquina Formation is biostratigraphically constrained to the Maastrichtian in its type sections around the bay of Concepción (*e.g*., Las Tablas, Cocholgüe, Tomé; Stinnesbeck 1986, 1996; Salazar *et al*., 2010), but the precise ages of potentially correlative Late Cretaceous units to the north and south of Concepción (Arauco, Chanco, Algarrobo, and Punta Topocalma) are less well known and it remains unclear to date whether deposition in these localities was strictly coeval or may have initiated earlier, during the Campanian (*e.g*., Pérez and Reyes, 1980; Biró-Bagóczky, 1982; Tavera, 1988). The presence of abundant pumice clasts in Upper Cretaceous marine strata at Punta Topocalma prompted us to carry out U-Pb (LA-ICPMS) geochronological analyses on detrital zircons. Here we present the first radiometric age from Upper Cretaceous marine deposit of the Chilean forearc basin and discuss possible stratigraphic implications for the regional geology.

2. The Punta Topocalma Formation

The Punta Topocalma Formation was defined by Cecioni (1978) in the homonymous locality (~34°S; Fig. 1). The unit at the type section is ~16 m thick and overlies Paleozoic granitoids (Fig. 2). The upper contact is a mild angular unconformity with marine Miocene sandstone and siltstone of the Navidad Formation (Tavera, 1979; Encinas *et al*., 2006), which is in turn overlain by cross-bedded sandstone interpreted as Pleistocene? eolian paleodune deposits. The Topococalma Formation comprises a basal interval, ~0.5 m thick, of fossiliferous conglomerate and locally very coarse sandstone, overlain by ~15 m of green to yellow, well-sorted, medium-grained massive sandstone with scarce thin-bedded intercalations of conglomerate and coquina. Pumice clasts are abundant at the top of the succession. Carbonate concretions of diagenetic origin are locally abundant. The unit contains ammonites, bivalves, fishes, reptiles, and wood fragments that are up to one meter long (Pérez and Reyes, 1980; Suárez *et al*., 2003).The poor preservation of sedimentary structures prevents a refined sedimentologic interpretation. However, the presence of well-sorted sandstone with relatively abundant large wood fragments suggests a shallow-marine environment. Thin intercalations of conglomerate and coquina are interpreted as storm deposits. Pumice clasts in the upper part of the succession were probably originated by episodes of explosive volcanism in the arc domain to the east.

3. U-Pb Geochronology

One sample, consisting of ~10 kg of medium-grained sandstone with abundant pumice clasts, was selected for U-Pb zircon geochronology. Heavy mineral concentrates of the <350 μm fraction were separated using traditional techniques at ZirChron LLC, Tucson Arizona. A split of zircons from the non-magnetic fraction was mounted in a 1' epoxy ring and slightly ground and polished previous to laser ablation analysis.

LA-ICP-MS U-Pb analyses were conducted at Washington State University prior to CL imaging (University of Idaho) using a New Wave Nd:YAG UV 213-nm laser coupled to a ThermoFinnigan Element 2 single collector, double-focusing, magnetic sector ICP-MS. Operating procedures and parameters are a modification of Chang *et al.* (2006). Laser spot size and repetition rate were 30 nm and 10 Hz, respectively. He and Ar carrier gases delivered the sample aerosol to the plasma. Each analysis consisted of a short blank analysis followed by 250 sweeps through masses 204, 206, 207, 208, 232, 235, and 238, taking approximately 30 seconds. Time-independent fractionation was corrected by normalizing U-Pb and Pb/Pb ratios to zircon standards (Chang *et al*., 2006). For this study we used two zircon standards: Plesovice, with an age of 338 Ma (Slama *et al*., 2008) and FC-1, with an age of 1,099 Ma (Paces and Miller, 1993). U-Pb ages and plots were calculated using Isoplot (Ludwig, 2003) and systematic and analytic errors (2σ) were included.

Zircon crystals in the sample analyzed are mainly magmatic based on the Th/U ratio (1.0-0.4:1),

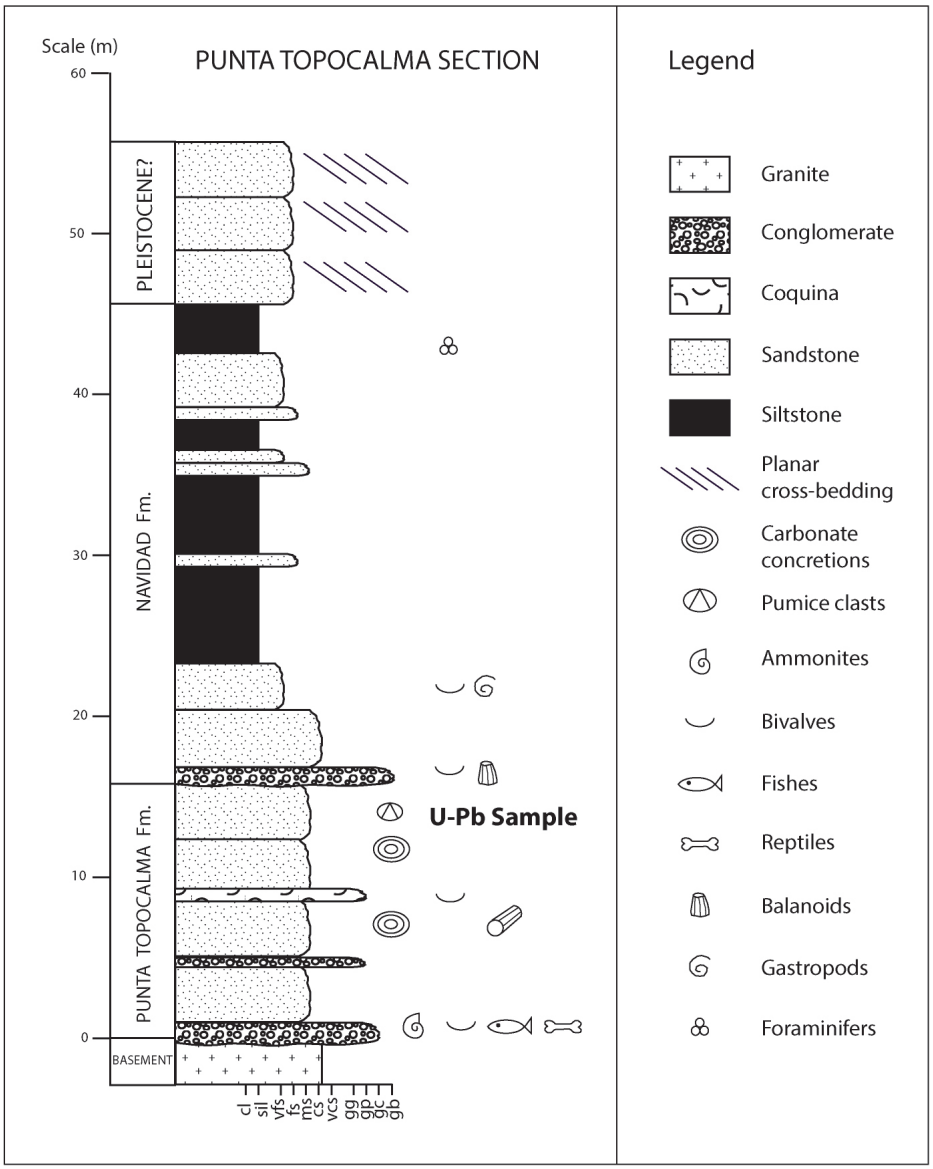

FIG. 2. Punta Topocalma section. Grain size: **cl:** clay; **sil:** silt; **vfs:** very fine sandstone; **fs:** fine s.; **ms:** medium s.; **cs:** coarse s.; **vcs:** very coarse s.; **gg:** gravel (granules); **gp:** gravel (pebbles); **gc:** gravel (cobbles); **gb:** gravel (boulders). The position of the U-Pb sample is indicated in the column.

oscillatory and sector zoning, and morphology. Zircons are pink colored and crystals mostly prismatic in shape, CL image shows predominantly long and thin zircons with broad to narrow oscillatory growth zoning (3-6:1 c/a axial ratio), which is common in evolved volcanic rocks (Fig. 3). Detrital zircon grains used here, however, were randomly selected and not by shape, size, clarity, or other attributes.

The maximum depositional age of the Punta Topocalma Formation sample is ~71.9±0.9 Ma (2 sigma, n=42) (Fig. 4). An abundant Mesozoic main detrital zircon population is present and ranges from 68-75 Ma (53% of the dated zircons). Other peak populations show ages of ~89-105 Ma (8%), ~288-314 Ma (22%) and 321-352 Ma (10%). Single analyses at 572 Ma and 1,086 Ma are also present (Fig. 4).

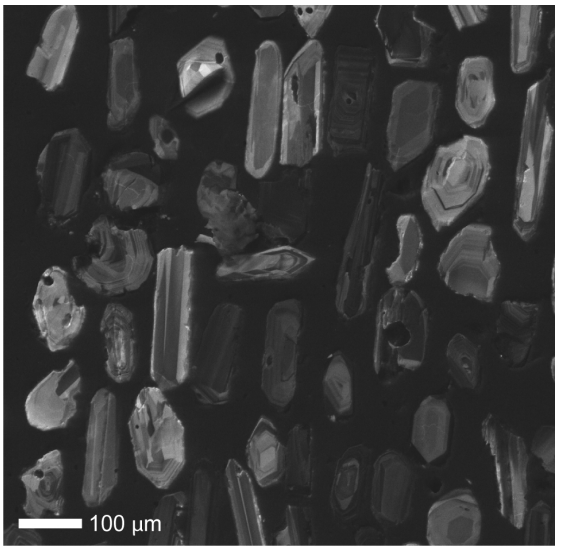

FIG. 3. Cathodoluminiscence image from the analyzed zircons.

4. Discussion

The age of Upper Cretaceous marine rocks of the Chilean forearc is mainly based on the study of ammonites from the Quiriquina Formation in the area of Concepción bay. In this unit, the assemblage is exceptionally diverse (30 taxa assigned to 17 genera) and shows affinities with Indo-Pacific and European assemblages (Stinnesbeck, 1986; Salazar *et al*., 2010). Biró-Bagóczky (1982) proposed a Campanian-Maastrichtian age for the formation, but subsequently, Stinnesbeck (1986, 1996) and Salazar *et al.* (2010) restricted the age of the Quiriquina Formation to the Maastrichtian. Salazar *et al.* (2010) refined the biostratigraphic scheme proposed by Stinnesbeck (1986) and divided the Quiriquina Formation into three biozones: **1.** the *Baculites anceps* biozone, assigned to the late Early Maastrichtian; **2.** the *Eubaculites carinatus* biozone,

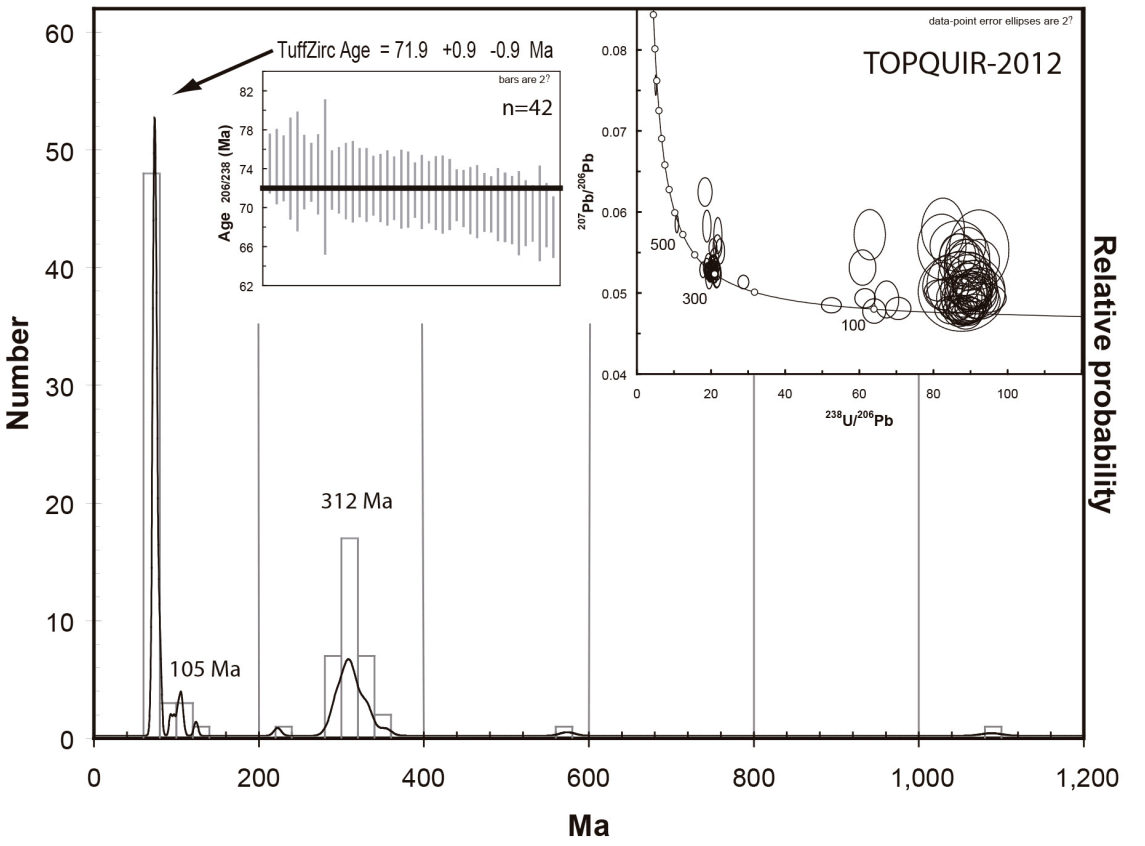

FIG. 4. U-Pb plots from analyzed sample including the Tera-Wasseburg diagram (right inset), the probability density plot with the main age peaks and the youngest age calculated with the Tuff-Zirc algorithm (Ludwig, 2003).

which is further divided into the *Menuites fresvillensis* subzone (early Late Maastrichtian) and the *Kitchinites (K.) darwini* subzone (middle to late Late Maastrichtian); and **3.** a biozone without Baculitids tentatively assigned to the latest Late Maastrichtian. The Quiriquina ammonite assemblage correlates well with the top of the López de Bertodano Formation in Seymour Island, Antarctica, the Miria Formation in Western Australia, the top of Valudayur Formation in the Pondicherri district of southern India, and sections in the Biscay region in SW France and Spain. These units are mainly Late Maastrichtian in age, which is also indicated by the presence of planktonic foraminifers assigned to the *Gansserina gansseri* and *Abathomphalus mayaroensis* zones (Stinnesbeck, 1986, 1996; Salazar *et al.,* 2010 and references therein).

Direct correlation between the Quiriquina Formation and reference successions for the Maastrichtian stage in Europe, however, must be taken with caution as there is no world-wide ammonite zonation for this period and planktonic index fossils such as foraminifers or coccolithophorids are not preserved in strata of the Quiriquina Formation and correlative units (Stinnesbeck, 1986, 1996; Salazar *et al.,* 2010). In addition, the use of independent radiometric dating methods to test the accuracy of correlations based on ammonite biostratigraphy is hampered, in the area of Concepción bay, by the absence of interbedded volcanic rocks.

As noted above, deposition of Upper Cretaceous marine rocks in other localities of the Chilean forearc could have started earlier, in the Campanian or the Early Maastrichtian (Levi and Aguirre, 1966; Pérez and Reyes, 1980; Tavera, 1988; Suárez and Marquardt, 2003). Studies on the precise age of these successions, however, are scarce and their conclusions must be taken with some caution as they were likely skewed by insufficient fossil sampling and sparse documentation. The Punta Topocalma Formation was assigned to the Late Campanian by Pérez and Reyes (1980) based on the presence of the ammonites *Gunnarites* sp. and *Grossouvrites* sp. Pérez and Reyes (1980) cited the presence of the following taxa in strata of the Punta Topocalma Formation: *Baculites* sp., *Gunnarites* sp., *Grossouvreites* sp., *Buchotrigonia* (*B.*) *topocalmensis* sp. nov., *Pacitrigonia banetiana* (D' Orbigny), *Cardium* (*B.*) *acuticostatum* (D' Orbigny) and *lnoceramus* sp. The fossils collected by Pérez and Reyes (1980) were briefly revised by Stinnesbeck (1986) who was given access to the collection at Servicio Nacional de Geología y Minería, in Santiago. Stinnesbeck (1986, p. 124) states the presence of *Maorites* aff. *tenuicostatus, Nostoceras* sp., *Baculites* sp., *Inoceramus (Endocostea) biroi*, *Pacitrigonia hanetiana, Buchotrigonia topocalmensis, Cardium (Bucardium) acuticostatum, Aphrodina quiriquinae*, ?*Mytilus* sp., *Nucula* aff. *N. (Leionucula) ceciliana, Perna* sp., *Turbo ovallei,* and *Calyptraea* sp. Suárez *et al.* (2003) also noted the occurrence of *Centrophoroides* sp., *Charcharias* sp., *Ischirhiza chilensis* sp., Teleostei indet., and Elasmosauridae indet.

The interpretation of Pérez and Reyes (1980) that the Punta Topocalma Formation is older than the classical sections of the Quiriquina Formation is based on the absence of unequivocal Maastrichtian index fossils, such as *Eubaculites carinatus, Fresvillia constricta, Hoploscaphites constrictus, Pachydiscus.* (*P.*) *jacquoti*, and *Menuites fresvillensis*. These ammonites are characteristic faunal elements in the type sections of the Quiriquina Formation at Las Tablas and at Cocholgüe and are well known from Maastrichtian strata outside South America (*e.g.*, Europe). However, they have never been reported in the Punta Topocalma Formation. The faunal ranges of the Punta Topocalma ammonites *Gunnarites, Grossouvrites*, and *Baculites* are not well known at generic level, but clearly include both the Campanian and Maastrichtian, at least for the Austral realm (Patagonia, Antarctica) (Macellari, 1985, 1988; Stinnesbeck *et al.,* 2012). *Nostoceras*, determined by Stinnesbeck (1986, p. 124) in the Punta Topocalma collection of Pérez and Reyes (1980), is known to range from the Late Campanian to Early Maastrichtian (Ifrim *et al.,* 2004). Tentatively, *Maorites* aff. *tenuicostatus* (determined by Stinnesbeck, 1986, p. 124) may correspond to *Maorites densicostatus* (Marshall; see Salazar *et al*., 2010), a taxon described from the Santonian to Maastrichtian of New Zealand; elsewhere in the southern South Pacific region. *M. densicostatus* may be restricted to the Maastrichtian (Salazar *et al*., 2010).

The bivalve assemblage at Punta Topocalma includes trigoniids and inoceramids which have variously been interpreted to be of biostratigraphical significance. *Buchotrigonia (B.) topocalmensis*, a characteristic faunal component at Punta Topocalma, was never identified in the Concepción area, while

Pacitrigonia hanetiana is known from both localities. Inoceramids are abundant throughout the Late Cretaceous, but a global extinction of this important bivalve genus was registered within the Early Maastrichtian (MacLeod *et al*., 1996). The Punta Topocalma species determined as *Inoceramus* sp. by Pérez and Reyes (1980) was assigned to *I. (Endocostea) biroi* by Stinnesbeck (1986, p. 124). This taxon was established by Stinnesbeck (op. cit.) in the basal Quiriquina Formation of the Concepcion area (*e.g*., Las Tablas), where it is constrained to the unit of 'yellow cross-bedded sandstone' near the base of the formation. *I. (Endocostea) biroi* is there associated with *Baculites anceps*, an Early to Late Maastrichtian taxon (Salazar *et al*., 2010).

According to these arguments, the Punta Topocalma Formation could be Late Campanian or Early Maastrichtian in age. Faunal differences between the Punta Topocalma and the Quiriquina formations are clearly stated by the presence of *Buchotrigonia topocalmensis* and *Nostoceras* in the first unit and may reflect earlier deposition of the Punta Topocalma Formation, or a stratigraphic overlap with the basal Quiriquina Formation at Concepcion bay (*e.g*., the unit of yellow cross-bedded sandstone at Las Tablas section).

Alternatively, however, other causes may also exist to explain faunal differences between the two outcrop areas, such as insufficient sampling and poor fossil preservation at Punta Topocalma, or differences in paleoecological setting. Future paleontological and biostratigraphical research is clearly needed for Punta Topocalma to decide whether these sediments are Early Maastrichtian in age and thus coeval to the basal Quiriquina Formation, or Late Campanian and thus slightly older.

These uncertainties regarding the biostratigraphical interpretation of the Punta Topocalma section are well reflected by the U-Pb radiometric age of 71.9±0.9 Ma for the youngest zircon population of the sample analyzed in this study. This age is close to the Campanian-Maastrichtian boundary which has been established at 72.1±0.2 Ma (Cohen *et al*., 2013). The Punta Topocalma age of 71.9±0.9 Ma is considered as a maximum depositional age because it was calculated from detrital zircons. However, the rock sample was obtained from an interval with abundant pumice clasts which were likely derived from explosive volcanism coeval with sediment deposition and are the probable source of the Late Cretaceous zircon population. The ammonites reported by Pérez and Reyes (1980) were obtained from the basal conglomerate of the Punta Topocalma section and must therefore be older than the rock sample used for U-Pb geochronology, which was obtained from the upper part of the succession. On the other hand, thickness of the Punta Topocalma section is only ~16 m and depositional rates for shallow-marine settings are generally high. Therefore, the difference in age between the base and top of the succession may not differ significantly. The 71.9±0.9 Ma U-Pb age reported here does neither prove nor refute the late Campanian age assigned by Pérez and Reyes (1980) for the Punta Tococalma Formation.

The sample analyzed by U-Pb geochronology shows four distinct detrital zircon populations of ~68-75 Ma (Maastrichtian- Campanian), ~89-105 Ma (Coniacian-Albian), ~288-314 Ma (Artinskian-Moskovian), and 321-352 (Bashkirian-Tournaisian) which allows for some paleogeographic interpretations. Radiometric ages of 308±15 Ma (Rb/Sr), 299±10 Ma (U-Pb), and 309 Ma (U-Pb) were obtained from Paleozoic granitoids that crop out in the Coastal Cordillera of central Chile (Godoy and Loske, 1988; Wall *et al*., 1996 and references therein). These plutonic rocks are the most likely source for the Permian-upper Carboniferous populations of detrital zircons from the Punta Topocalma section. The oldest group of zircons (321-352) could have also been derived from upper Paleozoic metamorphic rocks that crop out in the same area (Wall *et al*., 1996).

K-Ar radiometric ages between 118 and 91 Ma where obtained from plutonic rocks (granitoids and gabbros) of the western Coastal Cordillera near Valparaíso (~33°S) (Gana *et al*., 1996). An age of 107±0.62 Ma ($^{40}Ar/^{39}Ar$) was obtained for granitoids from the eastern Coastal Cordillera, south of Santiago (~33°30'S, Sellés and Gana, 2001). Radiometric (U-Pb) ages between 106 and 110 Ma were obtained by Wall *et al*. (1999) from basal strata of the Las Chilcas Formation, a volcano-sedimentary unit in the eastern part of the Coastal Cordillera near Santiago. In addition, Martínez-Pardo *et al*. (1994) assigned an Albian age to a limestone unit that forms part of this formation, based on benthic foraminifers. Thus, the ~89-105 Ma zircon population from the Punta Topocalma Formation was likely derived from plutonic rocks of the Coastal Cordillera of central Chile, or from volcano-sedimentary strata of the Las

Chilcas Formation exposed in the eastern Coastal Cordillera and Central Valley.

Three $^{40}Ar/^{39}Ar$ ages of 72.4±1.4, 71.9±1.4, and 71.4±1.4 Ma were obtained by Gana and Wall (1997) from tuffs and ignimbrites of the Lo Valle Formation, a volcano-sedimentary unit that crops out in the Central Depression in the vicinity of Santiago. In addition, a K-Ar age of 72±3 Ma was obtained by Sellés and Gana (2001) from volcanic rocks (lavas) that crop out in the eastern Coastal Cordillera south of Santiago (~34°S), but these were assigned to the upper Las Chilcas Formation by the authors. These radiometric ages are similar to, or even indistinguishable from the U-Pb age of 71.9±0.9 Ma obtained here for the Punta Topocalma Formation. We therefore suggest that the Lo Valle and the upper Las Chilcas formations were deposited coeval to marine sediments of the Punta Topocalma Formation.

5. Conclusions

The first radiometric dating (U-Pb on detrital zircons) for Upper Cretaceous marine strata of the Chilean forearc was carried out at Punta Topocalma and indicates a probable depositional age of 71.9±0.9 Ma (latest Campanian-earliest Maastrichtian). Provenance analysis based on the age of detrital zircon populations suggests that the source of sediments of the Punta Topocalma Formation was plutonic and volcano-sedimentary rocks from the Coastal Cordillera and the Central Depression of central Chile. The Lo Valle Formation, a volcano-sedimentary unit in the Central Depression, recorded deposition of the Upper Cretaceous volcanic arc that was coeval with marine sedimentation in the Punta Topocalma area.

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