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Filling the gap: new precise Early Cretaceous radioisotopic ages from the Andes

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Abstract

Two tuffs in the Lower Cretaceous Agrio Formation, Neuquén Basin, provided U–Pb zircon radioisotopic ages of 129.09 ± 0.16 Ma and 127.42 ± 0.15 Ma. Both horizons are well constrained biostratigraphically by ammonites and nannofossils and can be correlated with the ‘standard’ sequence of the Mediterranean Province. The lower horizon is very close to the base of the Upper Hauterivian and the upper horizon to the Hauterivian-Barremian boundary, indicating that the former lies at c. 129.5 Ma and the latter at c. 127 Ma. These new radioisotopic ages fill a gap of over 8 million years in the numerical calibration of the current global Early Cretaceous geological time scale.

Keywords: Neuquén Basin, Hauterivian, biostratigraphy, ammonoids, calcareous nannofossils, U–Pb CA-ID-TIMS, Argentina.

1. Introduction

The Geological Time Scale for the Phanerozoic has one of its last geochronological gaps in the latest Jurassic – Early Cretaceous interval, where no precise radioisotopic ages are available (Fig. 1) (Cohen et al. 2013). The global Lower Cretaceous ‘standard’ subdivisions (stages) are based on sequences in the Mediterranean Province of the Tethyan Realm and are currently defined by biostratigraphic markers, especially ammonites and calcareous nannofossils (e.g. Channell et al. 2010; Wimbledon et al. 2011; Rebour et al. 2014; Aguado et al. 2014). Unfortunately, one of the main problems is that in most areas where such good biostratigraphic control exists, there are few suitable rocks for modern high-precision geochronology, for example by chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-ID-TIMS) U–Pb zircon dating techniques. As a result, the exact age of stage and substage boundaries remains uncertain (Fig. 1).

Most of the previous tentative numerical age tie-points in the Early Cretaceous (Berriasian–Barremian) of Tethys are indirect, and based upon the correlation of biostratigraphic data with magnetic chron, which, in turn, have very poor and controversial time controls for this time span (see Channell et al. 2010; Ogg & Hinnov, 2012). Some approaches have focused mainly on the Pacific sea-floor spreading numerical model of the M-sequence magnetic-polarity pattern and from limited recent cyclostratigraphic studies (Gradstein et al. 2012). Other authors combined robust nannofossil biostratigraphy and cyclostratigraphy to constrain the numerical dates for stage boundaries based on the accepted magnetochron ages (Sprovieri et al. 2006).

Wan et al. (2011) studied Lower Cretaceous strata exposed in southern Tibet in order to identify the Jurassic/Cretaceous (J/K) boundary using calcareous nannofossil assemblages and to constrain the age of Valanginian nannofossils with U–Pb SHRIMP zircon dating. Based on a single date from a rhyolite, they proposed that the numerical age of the Valanginian/Hauterivian boundary should be no older than 136 ± 3.0 Ma and, by considering sedimentary accumulation rates in the studied sections, the J/K boundary was estimated to be 145 Ma. More recently, Liu et al. (2013) working also in the same general area of Tibet, studied ammonites and nannofossils, integrating their biostratigraphic results with four U–Pb SIMS zircon ages. Their main conclusion was that the J/K boundary should be older than 141–142 Ma.

The first attempt to combine robust biostratigraphic control provided by ammonites and calcareous nannofossils with high-precision CA-ID-TIMS zircon ages was published by Vennari et al. (2014) for the J/K boundary in the Neuquén Basin, a predominantly marine retro-arc basin (Fig. 2a) in the foothills of the Argentine Andes. Higher in the Neuquén sequence, episodic pyroclastic deposits are interbedded with fossiliferous dark shales and limestones of Hauterivian age in the upper part of the Agrio Formation. The ammonite and calcareous nannofossil sequences here are well documented and can be correlated confidently with the ‘standard’ Mediterranean sequence (Section 4 below). A previous study (Aguirre-Urreta et al. 2008) combined this robust biostratigraphy with U–Pb SHRIMP ages in zircons from the Agrio
Formation to provide an isotopic date for the base of the Upper Hauterivian. Our new research follows the recommendations of Gradstein et al. (2012) to use the U–Pb CA-ID-TIMS zircon method to provide more precise age determinations for that level and for the Hauterivian/Barremian boundary.

2. The geological setting

The Agrio Formation (Weaver, 1931) covers extensive areas of the Neuquén Basin in west-central Argentina (Fig. 2a). It is up to 1300 m thick and is divided into three members (Leanza & Hugo, 2001). Both the Pilmatué and Agua de la Mula members are marine, mainly composed of dark shales and paler, silty shales interbedded with limestones that contain an abundant invertebrate fauna. The middle Avilé Member is a 30–40 m thick package of yellowish coarse sandstones, often with cross-bedding of fluvial and aeolian origin (Gulisano & Gutiérrez Peimling, 1988). The Agrio Formation represents a storm-dominated, shallow-marine environment, with mixed siliciclastic and carbonate sedimentation (Brinkmann, 1994; Spalletti et al. 2001). Ammonoids and calcareous nannofossils together indicate that the formation is of late Early Valanginian to earliest Barremian age. Detailed ammonite zonation of the Neuquén Basin is based on Aguirre-Urreta & Rawson (1997) with subsequent modifications in Aguirre-Urreta et al. (2005, 2007) and Aguirre-Urreta & Rawson (2012). Nannofossil zones and events are documented by Bown & Concheyro (2004) and Concheyro et al. (2009). Integration of the two zonal schemes is presented by Aguirre-Urreta et al. (2005) and Concheyro et al. (2009).

One of the key factors of the Agrio Formation is that it is associated with a volcanic arc that is mainly exposed in the Chilean slope of the Andean Cordillera at these latitudes. Jurassic–Cretaceous magmatic activity along the arc was clearly episodic (Parada et al. 2007; Morata et al. 2008). This calcalkaline volcanic activity, frequently of an explosive nature, shows pyroclastic pulses that peaked in Early Tithonian (Naipauer et al. 2014), Middle–Late Berriasian (Vennari et al. 2014) and Late Hauterivian (this study) times to reach a maximum in Aptian–Albian times (Charrier, Pinto & Rodríguez, 2007). These magmatic pulses may be related to the intermittent nature of the subduction and to variation in the convergence rates associated with migration and expansion of the volcanic front (Ramos, 2010; Folguera & Ramos, 2011). Because the volcanism was intermittent there are only scattered ash-fall horizons within the Agrio Formation. In the study area, tuffs are very rare and thin in the Lower Hauterivian sequence but frequent in the Upper Hauterivian succession, in the Agua de la Mula Member. Two tuffs were sampled from this member, one at Caepe Malal and the other at Agrio del Medio, where two detailed partial sections were measured (Fig. 2c, d). A complete section through the member was studied at Mina San Eduardo, to provide a valuable reference section to which the two tuff-bearing sequences can be correlated (Fig. 2b).
Figure 2. (Colour online) (a) The Neuquén Basin in west-central Argentina showing outcrops of the Agrio Formation, basin borders and location of studied localities. (b) Lithic log of the Agua de la Mula Member of the Agrio Formation in Mina San Eduardo with ammonoid zonation and nannofossil bioevents. B. – Barremian. (c) Lithic log of lower part of the Agua de la Mula Member in Caepe Malal with location of the tuff layer. (d) Lithic log of upper part of the Agua de la Mula Member in Agrio del Medio with location of the tuff layer.
underlying shales are very poor and badly preserved, only characterized by the presence of *C. cuvillieri* (BAFC-NP 3119). Higher in the sequence, several subaqueous volcanioclastic debris-flow deposits occur interbedded in the dark shales. Zircons in the vitric tuff gave an age of 132.08 ± 1.3 Ma by U–Pb SHRIMP dating (Aguirre-Urreta et al. 2008), but we present here a new, more precise U–Pb zircon age using the CA-ID-TIMS method (Section 3 below).

2.c. Agrio del Medio section (38° 20′ S, 69° 57′ W)

The Agua de la Mula Member here reaches 420 m in thickness. The topmost part of the section (Fig. 2d) starts with an orange oyster floatstone followed by a thick greenish shale package interbedded with thin fine onudlitic sandstones. Up sequence, greenish shales with thin fine sandstone include ten prominent levels of floatstones and rudstones with a highly diverse marine fauna (bivalves, ammonoids, serpulids, crinoids, sponges and gastropods) and one conspicuous, 15 cm thick, whitish vitric tuff dated here by the U–Pb zircon CA-ID-TIMS method. In the vitric tuff, shards are the main component of the glass that is highly altered to carbonate. Crystals are less than 10%; angular quartz grains with engulfments and plagioclase are dominant, followed in abundance by biotite and K-feldspar. Volcanic lithic particles are rare and zircons are present as accessory minerals. Two channelized oolitic grainstones reveal the somerization of the succession. The grainstones are overlain by shales with another conspicuous bioclastic grainstone. The contact with the overlying Huitrin Formation is covered.

Ammonites characteristic of the *Parastephanoceras groheri* Zone occur at four horizons, the highest just above the tuff level. Moderately preserved nannofossils have been recovered from ten horizons. Two bioevents, FO and LO of *Nannocysta ligia* (BAFC-NP 3940 and BAFC-NP 3943, respectively), have been recorded (Fig. 2d), both within the *Parastephanoceras groheri* Zone. These bioevents occur in the CC4-B nannofossil subzone and CC5 nannofossil zone of the Neuquén Basin zonation, respectively.

3. U–Pb CA-ID-TIMS results

Abundant populations of relatively large (c. 100–300 microns in long dimension), elongate, prismatic zircon crystals were separated from both tuff hand samples by conventional density and magnetic methods. The entire zircon separate from each sample was placed in a muffle furnace at 900°C for 60 hours in quartz beakers to anneal minor radiation damage; annealing enhances cathodoluminescence (CL) emission and prepares the crystals for subsequent chemical abrasion (Mattinson, 2005). Following annealing, individual grains were hand-picked, mounted, polished and imaged by CL on a scanning electron microscope. From these compiled images, grains with consistent and dominant CL patterns were selected for further isotopic analysis (see Figs S1 & S2 in the online Supplementary Material available at http://journals.cambridge.org/geo).

Selected crystals were plucked from grain mounts, chemically abraded using a single aggressive abrasion step in concentrated HF at 195°C for 12 hours, and the residual crystals processed for ID-TIMS. The details of ID-TIMS analysis are described by Davydov et al. (2010) and Schmitz & Davydov (2012). U–Pb dates and uncertainties for each analysis were calculated using the algorithms of Schmitz & Schoene (2007), the U decay constants of Jaffey et al. (1971) and values of $^{235}U/^{208}Pb = 100.2329$ and $^{233}U/^{238}U = 0.99506$ for the ET535 tracer. Other details of analytical parameters can be found in the notes to Table S1 in the online Supplementary Material available at http://journals.cambridge.org/geo.

Propagated age uncertainties are based upon non-systematic analytical errors, including counting statistics, instrumental fractionation, tracer subtraction and blank subtraction. These error estimates should be considered when comparing our $^{208}Pb–^{238}U$ dates with those from other laboratories that used tracer solutions calibrated against the EARTHTIME gravimetric standards. When comparing our dates with those derived from other decay schemes (e.g. $^{40}Ar–^{39}Ar$, $^{176}Re–^{177}Os$), the uncertainties in tracer calibration (0.05%; Condon et al. 2007) and U decay constants (0.108%; Jaffey et al. 1971) should be added to the internal error in quadrature. Quoted errors for calculated weighted means are thus of the form ±XY[Z], where X is solely analytical uncertainty, Y is the combined analytical and tracer uncertainty, and Z is the combined analytical, tracer and $^{238}U$ decay constant uncertainty.

3.a. Caepe Malal tuff

CL-imaging of the 47 zircon crystals from the Caepe Malal tuff sample revealed a consistent population of moderately to brightly luminescent, oscillatory zoned crystals (Fig. S1 in the online Supplementary Material available at http://journals.cambridge.org/geo). A minority of crystals have irregularly shaped, uniform to complexly zoned cores overgrown by these luminescent, oscillatory rims. Six of the largest zircon grains were selected for CA-TIMS analysis on the basis of CL pattern (Table S1 in the online Supplementary Material available at http://journals.cambridge.org/geo). Five of the six analyses are concordant and equivalent, with a weighted mean $^{208}Pb–^{238}U$ date of 129.09 ± 0.04(0.08)[0.16] Ma (MSWD = 0.19) (Fig. 3a), which is interpreted as dating the eruption and deposition of this tuff. A single crystal yielded a resolvable older $^{208}Pb–^{238}U$ date of 129.26 ± 0.09 Ma, which is interpreted to contain a small nucleus of inherited zircon in its core.
3.b. Agrio del Medio tuff

CL-imaging of the 74 largest zircon crystals from the Agrio del Medio tuff sample revealed a consistent population of moderately to brightly luminescent, oscillatory zoned crystals (Fig. S2 in the online Supplementary Material available at http://journals.cambridge.org/geo). A prominent thin non-luminescent (dark) zone occurs approximately two-thirds to three-quarters of the radius from the centre of most crystals. A lesser number of crystals have irregularly shaped, relatively non-luminescent cores overgrown by the luminescent, oscillatory rims. Six grains were selected for CA-TIMS analysis on the basis of the uniform, predominant CL pattern, avoiding those crystals with resorbed non-luminescent cores. All six analyses are concordant and equivalent, with a weighted mean 206Pb–238U date of 127.42 ± 0.03 (0.07)[0.15] Ma (MSWD = 1.23) (Fig. 3b), which is interpreted as dating the eruption and deposition of this tuff.

4. Correlation of tuff horizons with the Tethyan ‘standard’

Ammonite evidence places both tuff horizons firmly within the Neuquén Basin ammonite zonation: the lower tuff lies just above the base of the Spitidiscus riccardii Zone and the upper is high in the Paraspiticeras groeberi Zone. Correlation of the Neuquén ammonite zonation with the West Mediterranean zonal scheme of the Tethyan Realm, which is taken as the ‘standard’, was discussed by Aguirre-Urreta & Rawson in Reboulet et al. (2014) and their Late Hauterivian to earliest Barremian correlation is summarized in Figure 4. The base of the Spitidiscus riccardii Zone is correlated with the base of the Subsaynella sayni Zone, which marks the base of the Upper Hauterivian. The Paraspiticeras groeberi Zone is correlated with part of the highest Hauterivian Pseudothurmannia ohmi Zone.

Calcareous nannofossil records support this correlation. Combining the calcareous nannofossil records from the Mina San Eduardo, Caepe Malal and Agrio del Medio sections, seven bioevents have been identified through the Agua de la Mula Member. Most of these correspond to bioevents that have been used to construct the Mediterranean zonation of the Tethyan Realm (Sissingh, 1977; Applegate & Bergen, 1988). However, the FO and LO of Clepsilithus maculosus, considered Boreal bioevents (Rutledge & Bown, 1996) are also recognized here and elsewhere in the Neuquén Basin (Fig. 4) (see selected nannofossil species in Fig. S3 in the online Supplementary Material available at http://journals.cambridge.org/geo).

From the seven bioevents recognized, three of them are discussed here, the FO and LO of Lithraphidites bollii and the LO of Cruciiellipsis caullihiri. Lithraphidites bollii, a consistent marker, has been found in several Mediterranean sections and oceanic boreholes, allowing valuable correlations (e.g. Cecca et al. 1994; Sprovieri et al. 2006; Aguado et al. 2014). Applegate & Bergen (1988) used the FO of L. bollii as a marker for the base of CC4-A. The CC4-A and CC4-B boundary has been considered Early Hauterivian in the Tethyan Realm, and has been correlated with the Crucieraites loryi ammonite zone (Bergen, 1994) and with Polarity Chron CM5 (Ogg & Hinnov, 2012b). However, in several sections of the Neuquén Basin, the FO of L. bollii occurs at a higher level, near the base of the Upper Hauterivian (Aguirre-Urreta et al. 2005). The LO of L. bollii has been used as a reliable marker within the CC5 Zone. In the Tethyan region, it occurs within the Pseudothurmannia ohmi ammonite zone (Bergen, 1994), at the top of the Hauterivian (Aguado et al. 2014; Reboulet et al. 2014) and within the Polarity Chron CM5 (Ogg & Hinnov, 2012b). In the Neuquén Basin, this bioevent is recorded high in the Agua de la Mula Member, in beds included in the Paraspiticeras groeberi ammonite zone, which in turn is correlated with part of the Pseudothurmannia ohmi Zone (Fig. 4).

The LO of Cruciiellipsis caullihiri has been used as a global marker for the Early–Late Hauterivian boundary (Bralower et al. 1995; Mutterlose et al. 1996; Ogg, Agterberg & Gradstein, 2004). In the Tethyan Realm, this bioevent is associated...
with the LO of *E. striatus* (Ogg, Ogg & Gradstein, 2008) in the middle part of the *Subsaxayella sayni* ammonite zone (Bergen, 1994) close to the base of CM8r in Italy (Channell et al. 1995; Channell, Cecca & Erba, 1995). As the *S. sayni* Zone has not been recognized in the Boreal Realm, the LO of *C. cuvillieri* has proved to be an important link between both realms. However, in the Boreal Realm both bioevents (LO of *C. cuvillieri* and LO de *E. striatus*) occur in the Upper Hauterivian (Bown et al. 1998). In the Neuquén Basin, the LO of *Crucellispis cuvillieri* is at the base of the *Crioceratites schlagintweitii* Zone (Aguirre-Urrreta et al. 2005) of early Late Hauterivian age.

5. **Discussion: significance of the new dates**

In a seminal paper published 40 years ago, Baldwin, Coney & Dickinson (1974) discussed the dilemma of the Cretaceous time scale and sea-floor spreading rates. Their main conclusion was that Cretaceous spreading rates could not be finally established until the Cretaceous time scale was more precisely calibrated to numerical time. Several attempts in recent years to calibrate the magnetic time scale for the Late Jurassic–Early Cretaceous have failed, either for lack of precise ages from altered oceanic floor basalts, or for poor biostatigraphic control of these oceanic sequences (Mahoney et al. 2005).

We present here two robust ages tied with precise calcareous nannofossil bioevents and ammonites of Late Hauterivian age in the Neuquén Basin. The first one, of 129.09 ± 0.04(0.08)[0.16] Ma, is from a tuff level only 7 m above the base of the Upper Hauterivian sequence, so we can place with some confidence the Early–Late Hauterivian boundary at 129.5 Ma. This age is very close to that proposed by Channell et al. (1995) and Channell, Cecca & Erba (1995) based on direct correlation of ammonite biozones and land section magnetostratigraphy, together with radiometric ages. It is much older than the data published by Fiet et al. (2006) who bracketed the Hauterivian between 123.6 ± 1.7 Ma and 118.3 ± 1.7 Ma based on K–Ar dating of glauconite combined with orbital chronology. It also differs markedly from Ogg & Hinnov’s (2012a) placement of this boundary at 133 Ma. It should be noted here that in their figure 27.6 these authors misplaced the Early–Late Hauterivian boundary in the middle of the *Balearites balearics* Zone instead of the base of the *Subsaxayella sayni* Zone as internationally accepted (Rebullot et al. 2011, 2014).

Our second age, of 127.42 ± 0.03(0.07)[0.15] Ma, is from a tuff level that correlates with the upper part of the *Pseudothurmannia ohmi* Zone and is therefore close to the top of the Hauterivian. So we suggest the Hauterivian/Berriasian boundary is around 127 Ma. Again our datum is much older than that of Fiet et al. (2006) who placed that boundary at 118.3 ± 1.7 Ma, but younger than the ages of Ogg & Hinnov (2012a) and Cohen et al. (2013) who placed the top Hauterivian at 130.8 Ma and ~ 129.4 Ma, respectively.

The new data presented here imply moving the base of the Barremian by 3 to 4 Ma in comparison with Gradstein et al.’s (2012) and the International Commission on Stratigraphy’s (ICS) time scale. However, this displacement is comparable with Vennari et al.’s (2014) placement of the base of the Cretaceous at 140 Ma, 5 million years younger than on the present ICS 2013 time scale. Their work is also based on a U–Pb CA-ID-TIMS numerical age combined with nannofossil and ammonite biostratigraphy of the Neuquén Basin.

Our new ages also support the proposal of He et al. (2008) who dated the M0r, which is presently taken as marking the base of the Aptian, to 121.2 ± 0.5 Ma by 40Ar–39Ar dating. This is very important because the age of the M0r has been used as a key point to construct the Early Cretaceous magnetic polarity time scale and to estimate the Pacific Ocean spreading rates. These results are also relevant for the stratigraphy of the Agua de la Member of the Agrio Formation. The two age dates indicate a sedimentation rate ranging from 170 m/Ma to 190 m/Ma in the eastern part of the basin (Agrio del Medio and Mina San Eduardo localities, respectively) and 110 m/Ma in the northwest (Cape Malal section). These sedimentation rates are consistent with a mixed siliciclastic-carbonate ramp setting and higher than those of pure siliciclastic shelves (Einsle, 2000).

In conclusion, our two new radiometric ages—129.5 Ma for the base of the Late Hauterivian and 127 Ma for the base of the Barremian—support the proposal of Channell et al. (1995), Channell, Cecca & Erba (1995) and He et al. (2008) to move the base of the Aptian around 121 Ma and that of Vennari et al. (2014) to move up the base of the Berriasian to 140 Ma. Investigations in progress will hopefully provide more robust data in order to improve the numerical dating of the Berriasian and Valanginian in the marine succession of the Argentine Andes.

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Supplementary materials

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