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U-Pb & FISSION TRACK GEOCHRONOLOGY OF BATHONIAN-CALLOVIAN "TUFFS" FROM ARGENTINA

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1. Introduction

Numerical calibration of the Stages of the Jurassic System is still poor. There are few areas in the world from where favourable material can be collected. Volcano-sedimentary layers **(VSL)** or volcanic lava flows interlayered with marine sedimentary deposits are the best potential material because several minerals can usually be separated from them; this material is able to be radiometrically dated using diverse dating methods. The search for such geochronometers may be focussed in areas where volcanic (i.e. tectonic) activity occurred during Jurassic time, but which were not deeply altered during the following history of the depositional basins. One of the most promising areas is the East Pacific margins. Within this area, the South of the South American Andean Cordillera seems to be the best suited place because of the presence of the nearby sedimentary basins with good ammonite faunas in the proximity of the volcanic activity (G.E.G. Westermann, pers. comm., 1989). Following our request, a comprehensive collection of fresh samples supposed to be VSL was undertaken in Argentina (Neuquén Province) in years 1987-1988, by S. Balent, S. Dambarenea, M. Manceñido and one of us (A.C.R.). The test samples were submitted to study in Paris for recognition of their actual nature, and for separation and qualification of geochronometers.

The preliminary study in 1988-1989, showed that samples of Bathonian to Callovian age were promising; however, the small quantities of datable minerals separated were not workeable; moreover, there was difficulty to visit the field and obtain the necessary information able to give precise thermodynamic conditions concerning the history of the sediments.

During the following years, additional knowledge and datable minerals were gathered; in addition, the progress in technology allowed dating of small samples; finally, better knowledge of the geochronometers allowed to choose more probably reliable minerals.

The aim of this paper is to report i- on some results of the preliminary research (in Paris) concerning the presence, nature, and quality of the geochronometers, ii- on the results of the fission track study (in London) undertaken in the aim at knowing the actual hydrothermal environment of the sediments; and iii- on the results of the U-Pb geochronologic study of the mid Jurassic VSL of Argentina.

2. Geological setting

To the East of the Andean Cordillera and Chile-Argentina boundary, there is a sedimentary basin, the Neuquén Basin, about 450 km N-S and 75 to 200 km E-W (see location map Figure 1). The NW-SE transgression allowed deposition of a marine Jurassic sedimentary sequence above Triassic volcanics. The basin is fed with terrigenous material coming from the south (Patagonia) as wells as from the West being the Piemont basin of the growing Andes (see eg.: Chotin, 1975). Connected to this western tectonically active area, volcanic material is brought to the basin since long.

The borders of the basin, mostly to the south, comprise detrital facies (congomerates, sands) which pass towards pelitic sediments and then to more limy facies.

The best outcrop for the mid Jurassic sediments is located near and to the South of the East-West road Chos Malal-Andacollo (the later site locally known for gold deposits) which follows the Arroyo Chacay Melehué. The name of this river is that of the section which is well known from geologists since 1910 and classical for Argentine-Chile Andes (Dellapé et al, 1979; Riccardi et al., 1988).

According to the field observation done during initial sample collection for fossils and VSL, the series does not appear tectonically nor hydrothermaly disturbed (A.C.R.). However, the geological map of the area (Zöllner and Amos, 1973) indicates that the Jurassic (and Cretaceous) sedimentary sequence is locally intruded by Oligocene volcanic rocks. Oligocene lava flows up to 2300 meters thick are mapped to the West of the map. Large Miocene to Quaternary volcanic bodies are also present to the East.

The mid Jurassic sediments show a band which is located about 15 km to the East of the presently preserved thick Oligocene volcanic sequence; in addition, a series of intrusive similar volcanic rocks outcrop 10 to 15 km more to the east. In this situation, the sequence was most probably submitted to repeated thermal constraints.

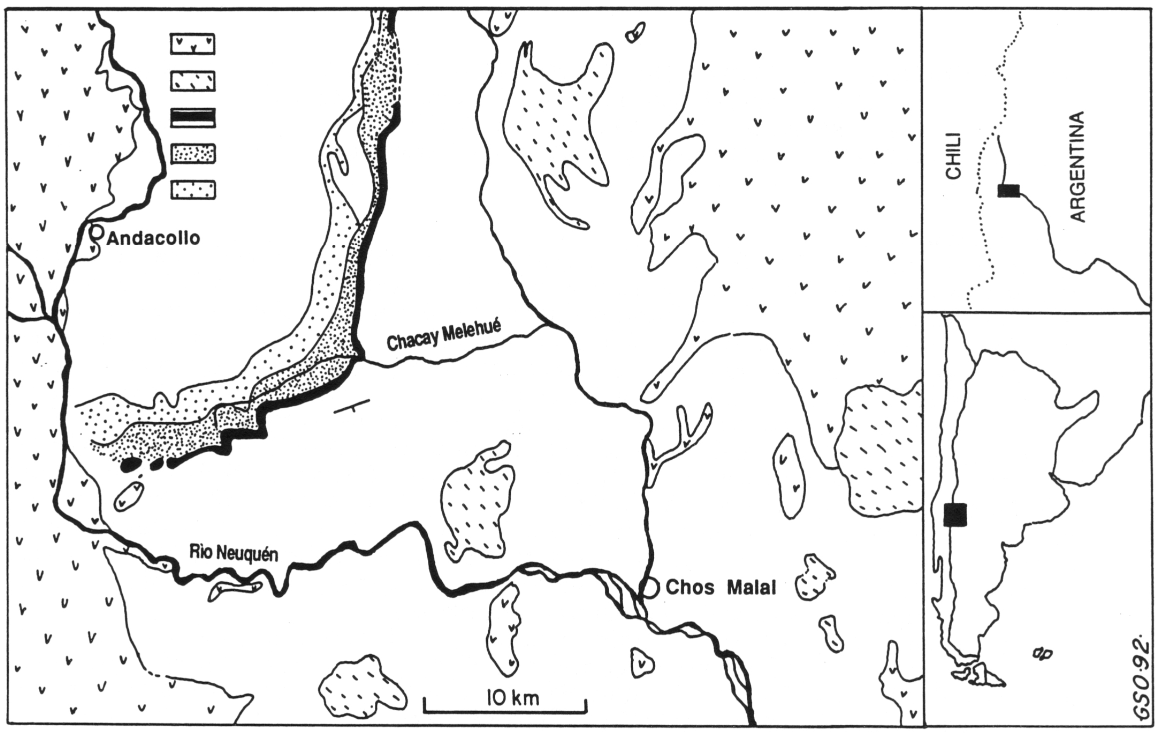

Figure 1. Location of the Chacay Melehué section.

Scale bar is 10 km; some Jurassic sediments are shown schematically as well as a few other geological features; symbols in the 5 boxes indicate Liassic deposits, Dogger deposits, gypsum, intrusive Cenozoic rocks, Cenozoic lava flows from bottom to top. Triasic rocks crop out to the NW, Late Jurassic to Cretaceous sediments crop out to the SE.

3. Stratigraphy of the dated levels

The marine Jurassic sediments of the Chacay Melehué section (1200 m in tickness) comprise large fossils such as Bivalves (Leanza et al., 1987) or Ammonites (Riccardi, 1984). The later are mostly endemic but, after diverse interpretations, the sediments are now acceptedly correlated with Pliensbachian to Oxfordian Stages.

The four levels, light in colour, from where samples were collected and selected for this study (82-84-85 and 89 from base to top) are interlayered in marine black pelites. They may be located in the field with regard to the evaporitic formation "Yeso Principal" (main gypsum) white marker bed (the Tàbanos Fm) at the top of the mid Jurassic marine sequence.

Samples 82, 84, and 85 come from about 300 m below the gypsum marker bed. Samples 84 and

85 are not different in age by more than 0.1 to 0.2 Ma and the former one is only slightly older. This estimate results from several hypotheses including a mean rate of sedimentation, with compaction, calculated at 135 (±50) m/Ma; this rate is based in turn, on the following lines: 250-300 m of sediments represent half the Bathonian Stage; that Stage is probably 4 ±1 Ma long (Odin, et al.; this volume, p. 24); in this interval, VSL are about 15 m far from each other.

The fossiliferous sediments allowed zonal definition, within this interval, of the limit between the *Lilloettia steinmanni* (below, gehrti Horizon) and the *Eurycephalites vergarensis* (above) ammonite zones of Argentina. According to Riccardi et al. (1988), this boundary is equated, in turn, to the *Macrocephalites macrocephalus* / *Clydoniceras discus* ammonite zone limit of Southern Europe (Cope et al., 1980); the later limit corresponds to the Late Bathonian-Early Callovian substage boundary.

Sample 89 comes from about 85 m below the gypsum marker bed. Ammonites allow to propose near that sample the limit between the *Neuqueniceras bodenbederi* / *Hectoriceras proximum* zones from Argentina. This limit is, in turn, equated to a moment located near the middle of the *Macrocephalites gracilis* ammonite zone of southern Europe (Cope et al., 1980), or the equivalent *Sigaloceras calloviense* zone of northern Europe. This means in the middle of the youngest of the two zones of the Early Callovian Stage.

4. Presence and qualification of geochronometers

The volcanic nature of the sampled levels was presumed due to their light colour contrasting with the black colour of the bracketing shales. Their thickness, from 5 cm to several dm and exceptionally up to 2 m and more, is laterally very continuous; this suggests an aeolian provenance for volcanic material. Some of the layers are soft, others are hard.

The samples were studied in thin sections; after disaggregation they were sedimented, washed, ultrasonically cleaned, sieved and the mineral fractions separated by magnetic separation, heavy liquids, hand picking, and appropriate acid treatments when needed. X-ray diffraction analysis, optical, microscopic, and cathodoluminescence (CTL) observations were used to identify the minerals and their quality. The presence / abundance of pyroclastic minerals in the 4 samples discussed in this report are summarized in Table 1.

Table 1: Pyroclastic minerals from the Bathonian-Callovian VSL from the Neuquén Basin

sample	Stratigraphy (Ammonites)	Mica	Quartz	Felspar	Zircon	Apat
		(thin sections)			(ppm)	
T89	late Early Callovian	+++	+++	ghosts	90	+
T85	basal Callovian	+++	+++	ghosts	>30	30
B84	topmost Bathonian		(soft sample)		+	+
B82	Latest Bathonian		(soft sample)		+++	+

+++ common; + present

VSL (Volcano-Sedimentary Layers) T 89 and T 85 are hard whitish tuffs. VSL B 84 and B 82 are soft and more like bentonites.

The Early Callovian sample T 89 contains abundant quartz (with volcanic features), biotite flakes (oriented), and ghost of felspars as seen in thin sections, together with well shaped U-bearing heavy minerals as seen using CTL. There are very abundant idiomorphic zircon crystals, brilliant, generally 30 to 80 mm in size, sometimes larger. Apatite crystals are comparatively rare, larger in size (up to 300 mm) and appear less brilliant than zircon ones suggesting possible weathering. The complete spectrum of pyroclastic minerals testifies for the volcanic origin of the layer; the absence of sorting of heavy minerals suggests aerial transport and primary deposition of volcanic ashes.

Sample B 85 contains the same spectrum of pyroclastic minerals. Zircon and apatite crystals are equally abundant. Zircon crystals (from big to very small in size) appear less well preserved than in sample T 89; apatite crystals (small) are well shaped, usually transparent, partly altered.

The latest Bathonian sample B 84 allowed separation of a very small proportion of zircon crystals (idiomorphic and transparent) and apatite crystals (slightly altered).

The Late Bathonian sample B 82 contain common zircon and less common apatite crystals; all are idiomorphic and well preserved.

Biotite mica flakes are pink in colour in all sample and "expansed" as seen in thin section. Suspected felspars are identified as ghost, replaced by calcite in thin section; CTL confirm complete alteration and replacement of previously common felspars. Traces of Karlsbad twinning suggest that they were initially sanidine. The quartz component of the thin sections observed in microscope (pegmatitic habit) or using CTL ("volcanic" colour) show features of pyroclastic nature. Zircon and apatite are very brilliant under CTL observation; this was used to estimate abundance of these components before separation. Zircon crystals from hard tuffs commonly show a small dark center assumed to be due to a different U content in the core.

In summary, well preserved zircon and apatite crystals are common in the 4 VSL selected from the Chacay Melehué section. No one K-bearing mineral is qualified for radiometric dating. The alteration of K-bearing minerals suggests that the sequence has been submitted to strong alteration, possibly at the time of deposition, most probably later: during weathering or hydrothermal leaching.

In order to know more about the thermal history of the section, the clay size fraction (able to record heating processes) was studied. In a marine basin, the clay formed from glass shard alteration is commonly smectite. That mineral easily recrystallizes under the hydrothermal environment. The results of the diffractometric study of the clay fraction separated from the VSL is shown in Table 2.

Table 2: X-ray diffraction of the clay size fraction of some VSL from the Chacay Melehué section. The dominant component is an illite-smectite mixed-layer

Sample	XRD normal			XRD EG	XRD heating treatment		
	Mixed layer	14 Å & 7 Å		Mixed layer	Mixed layer	14 & 7 Å	
B 82	11.2 Å	?	m	12.3 = 9.1	10Å	14Å < 7Å	w
B 84	11.5 Å	?	w	12. 1= 9.2	10 Å	14Å < 7 Å	w
others	10.9-11.5*	0->w	vw->st	11.6 to 12.3	10 Å	14Å ≤ 7Å	vw->w

Notes:

0= absent; ? = not clear; vw= very weak; w= weak; m= mean; st= strong.

* lower in the section (Liassic samples) the mixed layer peak reached 10.1 to 10.4 Å; after glycolation there is no or little swelling;

The main component is an illite-rich illite-smectite mixed layer; a very small proportion of chlorite is also present. Precise interpretation of the data would need comparison with the black shales but it was not possible to obtain samples. The clay mineral association may tentatively be interpreted as resulting from hydrothermal evolution of the original smectitic clay; the small proportion of chlorite would come from alteration of the biotite. The hydrothermal influence seems to be confirmed by 2 observations: i- the slightly more evolved (more illitic) nature of the older layers about 1 000 meters below the dated VSL (suggesting a higher hydrothermal influence in older levels) and ii- lower in the section, two samples show practically no pyroclastic minerals (they are probably not VSL) and contain only illite or a mixture with a high proportion of chlorite; this suggests that the black pelites are illitic and/or illitic-chloritic; kaolinite may be present in some levels too.

5- Geochronological studies

The fission track study was initiated in order to identify the possible hydrothermal alteration. If absent, this would have given interesting preliminary dating results for time scale calibration; if present and intense, this would make the analytical results unable to give the actual age of deposition. This was an important information because it was planned to undertake a modern statigraphical study in the Neuquén basin where only biostratigraphic approach was applied. In particular, the chemostratigraphic and magnetostratigraphic approaches would have been very interesting; it was necessary to know, before sampling, whether or not the original records were preserved.

5.1. Fission track study (A.J.H.)

Zircon and apatite crystals selected from 3 VSL: 82, 84, and 85 were proposed for fission track study in London. Both zircon and apatite from the same samples were used for analyses.

Zircons results show a scatter of individual crystal apparent ages from ≈ 70 to 150 Ma within each sample. The mean ages are shown in Table 3; they are not consistent with the stratigraphic age (≈160 Ma, Odin & Odin, 1990). Apatite indicates even younger ages as is expected for partially reset ages. Although near each other in terms of thickness (± 15-20 m) and stratigraphic ages (±0.5 Ma), the dated VSL give significantly different mean apparent ages: from 150 to 115 Ma for zircons and from 75 to 100 Ma for apatite. The most rejuvenated apatite (in the slightly youngest layers) are found together with the least rejuvenated zircon.

Therefore, the resetting phenomenon results from complex history; it did not occur at a temperature high enough to completely reset both zircon and apatite clocks; it was not simple and general enough to equally reset either zircon or apatites located in layers 20 meters apart. The global results simply show that the dated rocks have been hydrothermally seriously affected.

Table 3: Fission track data for Bathonian-Callovian samples of Argentina (measured in London)

Sample and Locality	Mineral and No. Crystals	Spontaneous ρ_s (N_s)	Induced ρ_i (N_i)	$P\chi^2$	Mean ρ_s/ρ_i $\pm 1\sigma$	Dosimeter ρ_d (N_d)	Fission Track Age Ma ($\pm 1\sigma$)	Apatite Mean Track Length (µm)	Length Standard Deviation (µm)
T-85	apatite	0.2162	0.5840	40%		1.153	74.1±6.5	12.68±0.43	1.91
	20	(184)	(497)			(7191)		(n=21)	
	zircon	14.31	2.123	~1%	7.035	0.3779	148±9		
	20	(5333)	(791)		±0.399	(5376)			
B-84	apatite	0.1877	0.4796	>90%		1.153	78.3±13.8	-	
	9	(45)	(115)			(7191)			
	zircon	12.21	2.068	40%		0.3771	125±17		
	(2)	(372)	(63)			(5374)			
B-82	apatite	0.2525	0.4956	90%		1.150	101±7	12.49±0.39	1.63
	20	(322)	(632)			(7969)		(n=18)	
	zircon	7.777	1.391	~2%	5.477	0.3763	115±8		
	(14)	(3059)	(547)		±0.375	(5374)			

Notes: (i). track densities (r) are as measured and are (x10 ^{6} tr cm^{-2}) ; numbers of track counted (N) shown in brackets;
(ii). analyses by external detector method using 0,5 for the 4π/2π geometry correction factor;
(iii). ages calculated using zircon SCN1 = 113 ±3; apatite SCN5 = 349±5;
(iv). PX^2 is probability of obtaining X^2 value for v degrees of freedom, where v = n° crystals -1; where Px^2<5% then age is calculated using mean rs/ri value

5.2. U-Pb zircon geochronology (H.B.)

Two zircon separates were measured on a newly designed highly sensitive and clean equipment able to measure single zircon U-Pb ages.

Before measurements, zircon crystals were carefully selected. For example, zircon crystals from T 89 were observed to be most of gem quality; but larger have rough coating, cracks, and cloudy metamictisation and were removed in the final sampling. The picked crystals were all abraded, non magnetic at highest current and lowest tilt, and non metamict. The nature of the 7 dated fractions (1 to 3 for T 85 and 5 to 8 for sample T89) is summarized in Table 4 and the analytical U-Pb data are quoted in Table 5. The analytical results are reported in Figure 2.

Table 4: Selected fractions of zircon samples from Chacay Melehué (Jurassic from Argentina)

sample n°	size (mm)	quality	weight analysed (mg)
T 85-1	> 75	best	1.1060
T 85-2	> 75	good	0.1380
T 85-3	< 75	very good	1.1641
T 89-5	44-58	-	0.6525
T 89-6	> 75	fair	1.8521
T 89-7	> 75	best	0.3550
T 89-8	> 150	-	0.4113

Table 5: U-Pb analytical results. The laboratory blanks for these analyses were 19±5 pg total Pb and 1±2 pg U. Constants used were $(^{238}U)l = 1.55125 .10^{-10}.g^{-1}$; $(^{235}U)l = 9.8485 .10^{-10}.g^{-1}$; common lead in the zircon was taken to be 160 Ma old Stacey-Kramers second stage lead.

n°	206/204 Pb (a)	238U ppm	206 rPb ppm (b)	Pb com. ppm (c)	206Pb/238U (e) (e)	207Pb/235U (e) coeff (f)	207/206 Pb	correl.
1	1908 ±29	251.0	5.522	0.049	0.025440 ±0.058	0.17640 ±0.332	0.050290 ±0.306	0.518
2	606 ± 4	443.0	9.732	0.263	0.025403 ±0.058	0.17520 ±0.433	0.050021 ±0.389	0.787
3	1175 ±16	318.4	7.045	0.107	0.025584 ±0.125	0.18076 ±0.513	0.051241 ±0.441	0.657
5	4032 ±260	242.4	5.257	0.015	0.025530 ±0.064	0.18278 ±0.382	0.051928 ±0.359	0.432
6	4608 ±244	226.4	5.120	0.017	0.026126 ±0.157	0.20630 ±0.409	0.057269 ±0.363	0.766
7	3623 ±340	255.9	5.864	0.012	0.026478 ±0.125	0.21663 ±0.807	0.059340 ±0.711	0.800
8	2062 ± 82	240.6	5.248	0.032	0.025200 ±0.098	0.17097 ±0.749	0.049201 ±0.667	0.856

(a) measured uncorrected ratio; (b) radiogenic, corrected for spike, fractionation, blank, and common Pb; (c) common lead in zircon; (e) uncertainties ±1s in %; (f) between 207/235 and 206/238

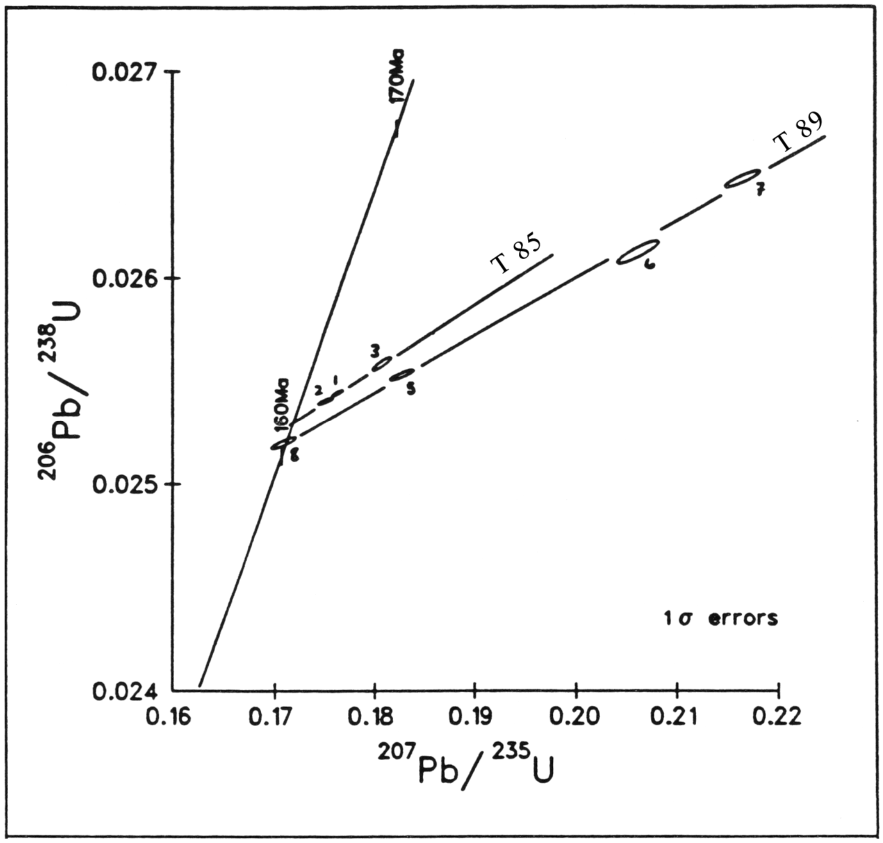

Figure 2: Concordia plot of the U-Pb isotopic results

Figure 2 shows that the zircon isotopic composition from the 2 samples follow two distinct linear arrays interpreted as discordia lines from which 2 apparent ages can be calculated at the intercept with the concordia curve. The given uncertainty in calculated ages is numerical error propagation from measured analytical errors (which corresponds to instantaneous analytical precision) and does not include indeterminate (geological) errors nor the errors from the spike or decay constants.

Apparent ages at 160.5 Ma (±0.2 Ma 2s, MSWD = 2.24) and 161.0 Ma (±0.3 Ma 2s, MSWD= 0) were calculated for samples T 89 and T 85 respectively. A single fraction is analytically concordant: T 89-8. The other have contaminant type 2 discordance i.e. they are interpreted as mixtures in diverse proportions of 2 components: 1 representative of the time of explosion, and the other of an older time.

6. Conclusions

Samples suspected to be VSL were collected from a section at Chacay Melehué (Neuquén Basin, South America) which is known for long, but not yet fully studied. The biostratigraphy has been established from mostly endemic faunas; they were recently correlated to European zonations (Riccardi et al., 1988). The samples discussed here are correlated with the Bathonian-Callovian Stage boundary (B 82, B 84, T 85) and the late Early Callovian (T 89).

The new sedimentological study of the material proves that the four samples selected are true VSL with abundant and diversified pyroclastic minerals: some are tuffs (initially not transformed and later hardened), other are bentonites (soft, with original volcanic glass transformed to clay). The samples appear, therefore, of high potential for geochronological study and measurement of the time of deposition of the sediments and related fossils.

However, the petrographical and mineralogical studies indicate that the K-bearing minerals are deeply altered; this alteration most probably results from hydrothermal activity as documented by the kind of alteration, the nature of the clay size fraction, and the geology of the area.

The fission track study further support the proposal that the section was actually submitted to hydrothermal alteration. This unfortunate situation makes the fission track data unable to give precise information on the time of deposition. But fission track data, are more powerful in showing that the section has poor potential for chemo- or magneto-stratigraphical studies. In this situation, the Chacay Melehué section cannot be investigated in terms of modern stratigraphical tools and cannot become a global reference section from those points of views as it was initially hoped.

In spite of this, the section is of interest for geochronological approach. The selected zircons are well preserved and look reliable material. CTL observation allowed us to distinguish frequent cores with different CTL behaviour (dark centers); these cores might be interpreted as inherited material in the light of the U-Pb data; this is our first use of the technique in this domain and further experience has to be obtained to confirm our interpretation.

U-Pb results indicate an age of 161.0 Ma for a sample considered to be very near (practically at) the Bathonian-Callovian boundary (T85) but with no one of the 3 analytical points on the concordia curve. This age of 161 Ma is fully consistent with our previous (uncertain) estimate (Odin & Odin, 1990) at about 160 Ma. From the four points analysed for sample T 89, one is on the Concordia curve and the three other rather far from it. This may be interpreted as indicating more or less important contribution of inherited lead (probably magmatic zircon cores) to the isotopic ratios. The resulting age of 160.5 ±0.2 Ma is from a sample correlated with late Early Callovian. The 2 dates are consistently in sequence; the stratigraphic age difference between the two dated levels (if we accept i- a duration for the Callovian Stage of about 6 Ma; ii- an equal duration for the three subdivisions of the Callovian or for the Ammonite biozones) might be estimated of the order of 1.5 ±0.5 Ma and is slightly larger than shown by the difference in U-Pb dating results.

The present set of results is the first contribution able to suggest a precise age for the Bathonian-Callovian boundary using the up to date "single" crystal U-Pb isotope dilution technique in Edmonton. It is also the first contribution to a precise radiometric dating in S America able to calibrate the Jurassic time scale.

In order to find meaningful geochronological data, the study has shown the necessity for an integrated approach of the field and samples which means good knowledge of a number of parameters able to document the history of the sediments. In this context, it is clear that availability of diversified samples and visit in the field with a geochemical point of view is a prequisite to obtain reliable results.

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