U-PB ZIRCON AGE DETERMINATIONS ON VOLCANIC ASH BEDS IN THE PUCARA FORMATION (UTCUBAMBA VALLEY): A PRECISE AGE FOR THE TRIASSIC-JURASSIC AND THE HETTANGIAN-SINEMURIAN BOUNDARIES

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ABSTRACT

Volcanic ash beds are interbedded with fossiliferous Lower Jurassic sedimentary rocks in Utcubamba valley, northern Peru. Precise U-Pb dating of volcanic zircon from these ash beds allows for calibration of the ammonoid timescale with isotopic ages. The analyses point to an age of 201.58 ± 0.17/0.28 Ma (uncertainty without/with decay constant uncertainties) for the Rhaetian/Hettangian (Triassic/Jurassic), and to 199.53 ± 0.19/0.29 Ma for the Hettangian/Sinemurian boundary, respectively. The data suggest that the basalt extrusions of the Central Atlantic Magmatic Province may be responsible for the mass extinction at the Triassic-Jurassic boundary. Direct correlation to U-Pb zircon dated basalt flows from the Newark basin are hampered by the presumed inaccuracy of Ar-Ar ages due to the use of an inaccurate ^{40}K decay constant.

INTRODUCTION

The Pucara Formation in the Utcubamba valley hosts one of the best sedimentary records straddling the Triassic-Jurassic boundary. This boundary stands for one of the most important biotic crises on Earth: the end-Triassic mass extinction involved the disappearance of some 80% of all known species on land and in the sea. Widespread magmatic activity of the Central Atlantic Magmatic Province (CAMP) has been invoked as a cause for this catastrophic biotic event. A detailed model taking into account all of the environmental perturbations known to have occurred during this time was proposed by Guex et al (2004), suggesting that the main stresses on the environment may have been generated by repeated release of SO_2 gas, heavy metals emissions, darkening and subsequent cooling causing an important regressive event. This phase was followed by a major long term CO_2 accumulation during the Early Hettangian. The Hettangian is considered as the period of the post-extinction recovery of the ammonoids. The relationship between the extinction and its probable volcanic cause can only be established by demonstrating the synchrony of the two events. This requires accurate and precise ages for both the TJB strata in a perfectly calibrated marine section and of volcanic rocks of the CAMP.

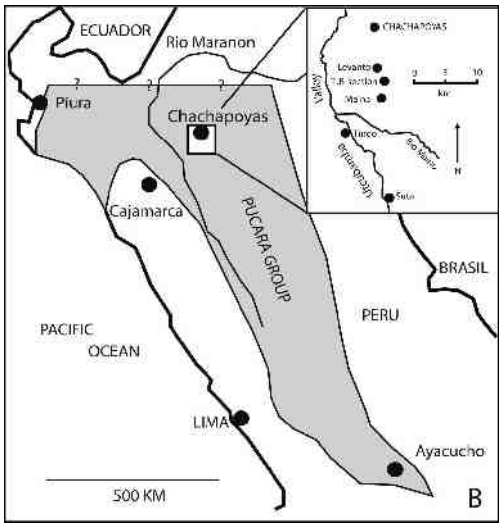

Fig. 1 Geological sketch map of the Pucara Formation in north-central Peru. Inset: Area of Chachapoyas, showing the location of the studied section in the Utcubamba Valley

We carried out detailed biostratigraphic research during the last years in the Utcubamba Valley, along long a new and fresh road section from Levanto to Maino (Fig. 1). This section preserves a complete deep marine sedimentary sequence from upper

Rhaetian to Early Sinemurian. The position of the Triassic-Jurassic boundary (TJB) in that section has been precisely located by ammonites. Ash beds containing zircon have been found interspersed throughout the section, allowing temporal calibration of the biostratigraphy with precise and accurate U-Pb zircon ages. The first results of the section have been published in Schaltegger et al. (2008). The section we are working on is displayed in Fig. 2, containing the results from U-Pb dating of zircon from ash beds. In this abstract we present new U-Pb age determinations, completing those of Schaltegger et al. (2008) and allowing most precise asessments of the ages of the Triassic-Jurassic boundary (TJB) and the Hettangian-Sinemurian boundary (HSB). These ages therefore directly bracket the duration of the Early Jurassic biotic recovery and also test the possible causal relationship between the TJB extinction and the eruption of the Central Atlantic Magmatic Province (CAMP).

REGIONAL GEOLOGY AND STRATIGRAPHY

The detailed paleogeography of the Pucara basin in northern Peru is not well established. However, there is a major stratigraphic trend in the Utcubamba Valley such that marine strata from the uppermost Triassic and Lower Jurassic represent much shallower water depths in the south near Chilingote, 20 km south of Suta (see Fig. 1) where we find limy sequences rich in ammonites. The stratigraphic sequence near Suta is intermediate and the thickest sequence is located at Levanto where we collected our tuff beds. These findings indicate a S-N deepening trend of the basin around the TJB. The original paleogeographic scheme of Rosas et al. (2007) indicates a Toarcian volcanic arc to the west of the Pucara basin, which is bordered by Gondwanan Paleozoic rocks at the margin of the Amazonian craton to the east. Our new data may allow the speculation that the Pucara basin may have been situated behind a volcanic arc, which was active during the Upper Triassic (latest Norian) to Lower Jurassic further to the west (see also Miskovic and Schaltegger, this volume). Hafnium isotope determinations on the dated zircons yielded εHf values between -4 and -9, and depleted mantle model ages (t_{DM} of 1.4 to 1.6 Ga). Such values can be interpreted as mixing of an old Mesoproterozoic basement with younger, more juvenile sources during late Triassic/Early Jurassic magmatism (Miskovic and Schaltegger, this volume).
The section is a thick monotonous sequence of siltstones alternating with slightly more calcareous silty beds. More than 20 fossiliferous beds have been excavated, allowing a very precise correlation with the standard ammonoid zonations used in the Upper Rhaetian and Lower Jurassic. The Rhaetian/Hettangian (Triassic/Jurassic) boundary is defined above the last occurrence of *Choristoceras crickmayi* and below the first occurrence of *Psiloceras spelae*, bracketing an uncertainty interval of some 6 meters for the boundary, the Hettangian/Sinemurian boundary is bracketed by *Badouxia canadensis* and *Coroniceras*, leaving a c. 15 meter thick uncertainty interval for this boundary.

U-Pb AGE DETERMINATIONS

ANALYTICAL TECHNIQUES

Zircons were extracted from ash beds using conventional techniques: samples were crushed using a jaw-crusher and a disk-mill; heavy minerals were separated from a fraction <350 microns using a Wilfley table, a Frantz magnetic separator and methylene iodide heavy liquid (D=3.3). Final selection was done under a binocular. The zircons were dated using highest precision methods: analysis of single grains by Isotope dilution – thermal ionization mass spectrometry (ID-TIMS). U-Pb in zircon is the most reliable chronometer, because zircon has the lowest diffusion coefficients for Pb (Cherniak and Watson 2001), and is resistant to post-crystallization disturbance. Nevertheless, an important complication is the post-crystallization loss of radiogenic lead due to elevated temperatures or during fluid percolation, which is enhanced according to the degree of radioactive decay enduced damage of the crystalline structure. This effect is at least partly compensated for by treating the zircon with annealing-leaching (« chemical abrasion ») techniques prior to analysis, in order to remove lattice domains that are severely disturbed by decay damage (Mattinson 2005). This treatment involves annealing at 900°C during 48 hours and leaching in HF at 180°C during 120 hours. Isotopic analysis was partly performed at ETH Zürich on a MAT262 mass spectrometer, partly at University of Geneva on a TRITON mass spectrometer, both equipped with electron multipliers backed by a digital ion

counting system. The multipliers must be constantly calibrated using U500, Sr SRM987, and Pb NBS982 and SRM983 standard solutions. Both lead and uranium were loaded with 1µl of silica gel-phosphoric acid mixture on outgassed single Re-filaments, and Pb as well as U (as UO_2) isotopes measured sequentially on the electron multiplier. Total procedural Pb blank was estimated at 0.5 ± 0.2 pg. The analyses in Schaltegger et al. (2008) were done using a ^{205}Pb-^{235}U tracer solution, the data shown in Fig. 2 are measured using the EARTHTIME ^{202}Pb-^{205}Pb-^{233}U-^{235}U tracer solution (see www.earth-time.org).

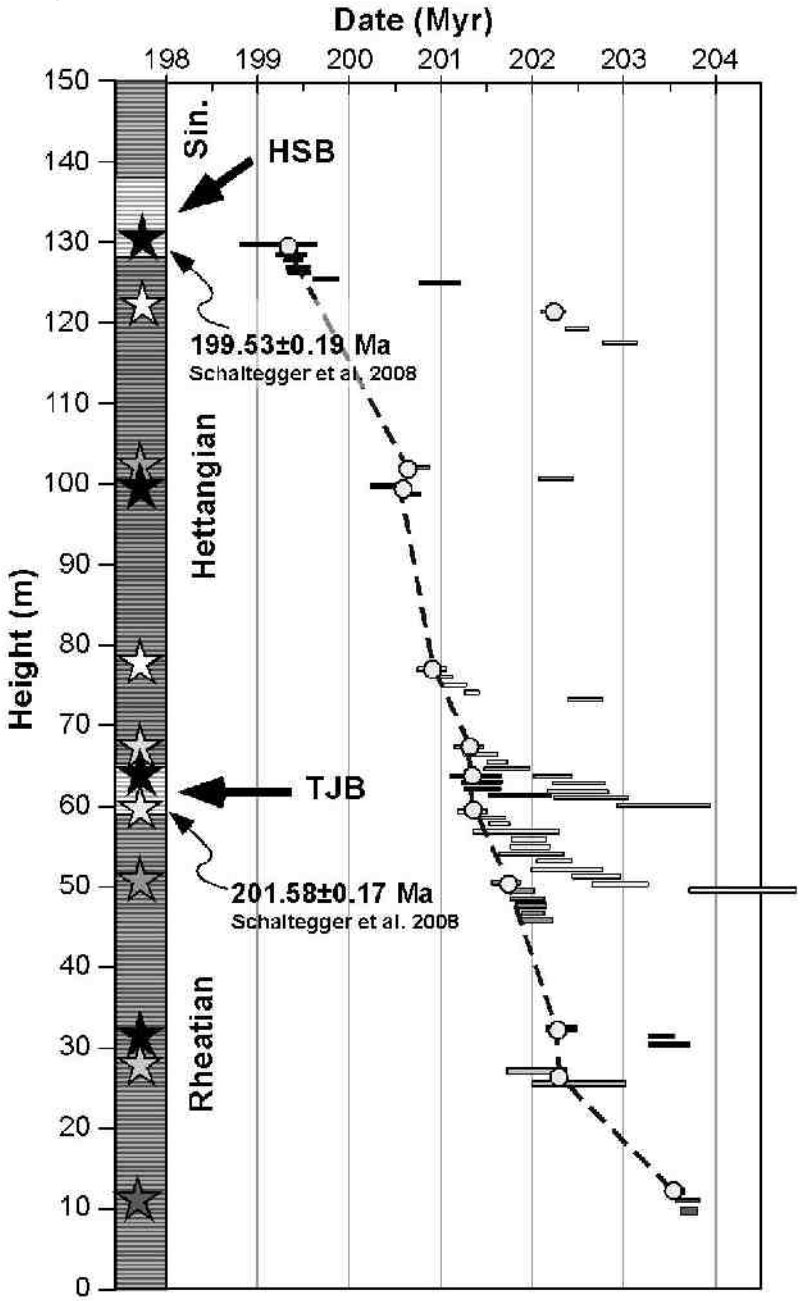

Fig. 2: Detailed schematic stratigraphic section with ages of sampled and studied ash beds. TJB = Triassic Jurassic Boundary = Rhaetian-Hettangian boundary. HSB = Hettangian-Sinemurian Boundary. The two ages of Schaltegger et al. (2008) are indicated; new analyses are shown as individual age values with error bars (Schoene et al., in prep.)

RESULTS

Schaltegger et al. (2008) reported precise ages for two samples critical for the TJB and the HSB: An ash bed at the very top of the Rhaetian is situated just above the last local occurrence of *Choristoceras crickmayi* and 5 meters below the first occurrence of *Psiloceras spelae*, approximating the TJB (Fig. 2). The sample yielded a mean $^{206}Pb/^{238}U$ age of 201.58 ± 0.17/0.28 Ma (uncertainty without/with decay constant uncertainties) for zircon crystallization and deposition of this ash tuff. A second dated ash bed is located between the last local occurrence of *Badouxia canadensis* and the first occurrence of *Coroniceras sp.* and lies therefore very close to the Hettangian-Sinemurian boundary (Fig. 2), yielding a mean $^{206}Pb/^{238}U$ age of 199.53 ± 0.19/0.29 Ma, which is considered to be representative of zircon crystallization and ash bed deposition. Additional age determinations have been added to these two ages, which are summarized in Fig. 2: Over the total stratigraphic record of 150 meters 12 samples have been dated so far, of which 8 yielded significant age results (Schoene et al., in prep.).
The samples mostly follow the stratigraphic sequence, indicating that there is only a minor portion of zircon containing inheritance of old lead (cores). Some of the data yield well-defined analytical clusters, which will result in precise ages with small uncertainties. Other samples, however, show a large dispersion of analytical points, which is largely beyond analyrical scatter. The reason for such age dispersion is a protracted growth of zircon in a given liquid of the same magmatic system. Zircon tends to saturated in the liquid during the ascent of the magma through the crust and to crystallize over timescales of a few 100 ky, a duration we now can resolve with precise dating techniques. We anticipate that the youngest grains approximate the emplacement of the ash bed in each case, assuming complete removal of partial lead loss domain by the chemical abrasion pre-treatment.

DISCUSSION

AGE OF THE TRIASSIC-JURASSIC BOUNDARY

The previously accepted age estimate of the TJB (199.6 ± 0.3 Ma) is based on a weighted mean $^{206}Pb/^{238}U$ zircon age from a marine section in the Queen Charlotte Island of Canada (Palfy et al. 2000). This age was calculated from three concordant multigrain analyses; the entire dataset, however contains analyses that show excess scatter in their $^{206}Pb/^{238}U$ values, probably reflecting combined effects of lead loss and inheritance. The new age determination in Schaltegger et al. (2008) shows an age for the TJB that is some 2 my older.

IS THE MAGMATISM OF CAMP POSSIBLY CAUSING THE MASS EXTINCTION?

The magmatism of the CAMP was of short duration. Courtillot and Renne (2003) supported an estimated duration of some 500 ± 100 ky for the entire CAMP magmatism based of magneto- and cyclostratigraphic arguments. A major problem of correlating age determinations from CAMP basalts wish ash beds in sedimentary successions concerns the systematic offset of the K-Ar and U-Pb decay schemes: Numerous previous studies have noticed that ^{40}Ar-^{39}Ar dates are systematically 0.3 to 1.0% younger than U-Pb ages of the same rocks (Renne et al. 1998; Min et al. 2000) which cannot entirely be related to sequential closure of the two isotopic systems during cooling. There is a broad agreement that much of the bias can be accounted for by an inaccurate ^{40}K decay constant or physical constants (Min et al. 2003). If there is a direct correlation between the end-Triassic extinction and CAMP volcanism, a U-Pb age for the TJB would therefore be significantly older than the ^{40}Ar-^{39}Ar age of the coeval CAMP rocks. A more accurate correlation is only possible using U-Pb age determinations of CAMP volcanics. Such data are available from volcanic units within the continental Newark Supergroup, such as the Palisades and Gettysburg sills (200.9 ± 1 and 201.3 ± 1 Ma) as well as the basal flow of the North Mountain Basalt (NMB, 201.7 +1.4/-1.1 Ma (Dunning and Hodych 1900; Hodych and Dunning 1992); 201.27 ± 0.06 Ma (Schoene et al. 2006).
To be the cause of the mass extinction, some of the CAMP basalts have to be older that the stratigraphic level containing the extinction event. The NMB is often regarded as being the oldest CAMP basalt flow in North America; we have therefore to explain the fact that our age for the TJB (201.58 ± 0.17 Ma) is younger that the 201.27 ± 0.06 Ma age of NMB. The age discrepance may be explained by the following arguments: (1) There is an uncertainty interval of about 6 meters between the last Triassic genus *Choristoceras* and the first oldest Jurassic *Psiloceras* (P.spelae), which bracket

the location of the real TJB. From our age determinations we can estimate the rate of deposition to be c. 15 ky/m, which means that the "true" TJB may be by c. 75 ky or more younger. (2) We have to take into account that the two age determinations were carried out in two different laboratories, using two different isotope tracer solutions that were not intercalibrated. (3) The sample of the NMB dated by Schoene et al. (2006) does not necessarily represent the earliest basalts present in the area nor does the 190 m thick flow at the base of NMB necessarily represent one single event.
Therefore, there are not enough radiochronological data available at the moment to know the precise age of the truely oldest CAMP basalts. This needs to be further tested, most importantly by U-Pb dates of similarly high-precision to those reported in Schoene et al. (2006) , and measured with the same U-Pb tracer solutions.

DURATION OF THE HETTANGIAN AND OF POST-EXTINCTION BIOTIC RECOVERY

The HSB was dated at an age of 199.53 ± 0.19 Ma (Schaltegger et al. 2008). The additional data support this age and confirm that the Hettangian was lasting for about 2 m.y. This period is considered to by typical for the period of post-extinction biotic recovery, i.e. the time needed for the fauna to reach pre-extinction biodiversity. An important question raised by the presented data is whether 2 my is a typical recovery period? There are very few precise numerical dates allowing a comparison with other periods. The best ones are those established recently by Ovtcharova et al (2006) for the post-Permian extinction recovery of ammonoids in the Lower Triassic of Southern China. They found that the duration of the recovery interval (Griesbachian, Dienerian and Smithian substages) , was close to 2 my, very similar to the duration of the ammonoid recovery in the Hettangian found in this study. From these two studies we estimate that 1-2 my is a reasonable duration for both Lower Triassic and Lower Jurassic biotic recoveries.

CONCLUSIONS

The new outcrops in Utcubamba Valley form a complete mid-Rhaetian to Sinemurian marine sedimentary section. Biostratigraphic correlation was carried out by means of ammonites and age information was determined from zircon bearing volcanic tuffs, which yielded precise and accurate temporal framework for the Hettangian, including the Triassic-Jurassic boundary (TJB; $^{206}Pb/^{238}U$ age of 201.58 ± 0.17/0.28 Ma; without/with decay constant uncertainty), and for the Hettangian-Sinemurian boundary (199.53 ± 0.19/0.29 Ma). The age of the TJB is c. 0.8 to 1.0% older than precise $^{40}Ar/^{39}Ar$ ages reported for basalts of the Central Atlantic Magmatic Province (CAMP) in northern and southern Americas and northwestern Africa. The fact that $^{40}Ar/^{39}Ar$ ages are often approximately 1% too young when compared to U-Pb radioisotopic ages has been repeatedly recorded and is interpreted in terms of using an inaccurate ^{40}K decay constant in Ar-Ar dating.
Taking the systematic offset between U-Pb and Ar-Ar ages into account, our new data allow for the first time a firm confirmation for synchrony between the volcanism of the Central Atlantic Magmatic Province (CAMP) and an important marine faunal extinction at the Triassic-Jurassic boundary. They also provide an excellent basis to estimate the tempo of the biotic recovery after end-Triassic extinction.

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