## A 3.3-Ma Impact in Argentina and Possible Consequences

P. H. Schultz,\* M. Zarate, W. Hames, C. Camilión, J. King

Enigmatic glassy materials (escorias) and red bricklike materials (tierras cocidas) occur at a restricted stratigraphic level (the top of the Chapadmalal Formation). Materials from one locality near Mar del Plata are attributed to a mid-Pliocene impact event with a radiometric and magnetostratigraphic age of 3.3 million years ago (Ma). An extinction of endemic fauna (including the glyptodonts and flightless cariamid birds) correlates with the unit containing the impact glasses. Moreover, the age of the glasses is coincident within dating uncertainties with a pulselike change in the oxygen isotope marine record in the Atlantic and Pacific Oceans just before the late Pliocene deterioration of the climate.

The Argentine Pampas represents one of the largest Late Cenozoic sedimentary loess and loessoid sequences (the Pampean Formation) of the Southern Hemisphere. Particulates in the loess are derived from reworked pyroclastic deposits (tuffs), primary tephra units, and other volcanoclastic sediments originally deposited in the Andes (1). The sequences in southern Buenos Aires Province (BAP) reflect a multiple-stage process: fluvial transport and deposition by major rivers to the south that originate in the Andes followed by eolian erosion and redeposition (2). The resulting depositional loessoid sequence provides a stratigraphic reference for assessing South American mammal evolution.

Within a restricted stratigraphic level in the Pampean Formation, numerous glassy and vesicular slabs (locally known as "escorias") are found in association with red bricklike fragments ("tierras cocidas"). The glassy materials were first described in 1865 by Heusser and Claraz (3). Since then, several interpretations have been proposed, including origin by fire, volcanism, or diagenesis (4). Nevertheless, the origin of the escorias remained enigmatic for several reasons. First, the escorias near Mar del Plata occur in Pliocene eolian sediments, yet this region is a passive continental margin that has not been volcanically active since the late Jurassic. Second, escorias occur in loess on a locally elevated piedmont, inconsistent with down-

\*To whom correspondence should be addressed. Email: Peter\_Schultz@brown.edu. slope fluvial transport from the distant Andean volcanics without evidence (such as sorting or abrasion) for this transport. And third, the large sizes of the escorias (50 cm to 2 m in diameter) preclude eolian transport. Because the composition of the escorias more closely matched the locally reworked loessoid deposits, the escorias were attributed to some unspecified type of high-temperature process fusing the constituent loess rather than to volcanic or diagenetic processes (5).

A new interpretation of the BAP escorias emerges with the discovery that similar but much younger glasses farther to the west near Rio Cuarto contained evidence of an impact event (6). The type locality for the BAP escorias occurs along the Chapadmalal sea cliffs (Fig. 1) where the lateral continuity of exposures and abundant fossils provide stratigraphic context (5). The largest in-place fragment (2 m across) was surrounded by lower temperature baked zones of loess: black inner and red outer oxidized zones, which matched the isolated tierra cocida fragments found elsewhere in loess deposits of similar age. The escorias exhibit a distinctive folded and twisted texture with deformed vesicles indicating a dynamic process of formation and emplacement similar to glasses from other known impact sites (7). As in the Rio Cuarto impact glasses, mineral clasts from the loess form suspended xenocrysts within the glass matrix of the Chapadmalal escoria, and unmelted loess particulates are often trapped between folds. Typical escorias range from 0.2 cm to 25 cm, but their broken appearance and attached red-baked loess elicts indicate that many are fragments from larger objects.

The interstitial glass (Fig. 2) in the escoria contains schlieren with large variations in relief in thin section corresponding to differences in the hardness (index of refraction) of the glass, which is typical of rapidly quenched impact glass (8). Baddeleyite clusters were found within the glass matrix and are produced by the breakdown of zircon to monoclinic  $ZrO_2$  and  $SiO_2$  due to high (1720° to 1900°C) transient

temperatures (9). In these escorias, such clusters provide a good criterion for an impact origin, because other high-temperature processes such as lightning strikes and volcanism can be eliminated (9). Other petrographic indicators of shock in sedimentary and particulate settings, however, are problematic because of poor shock coupling across grains, which induces heating rather than transient high pressures that could produce planar deformation features (6, 10).

Major element chemistry of the interstitial glass within the Chapadmalal escorias (Table 1) indicates a source region distinct from a possible mafic volcanic source at depth (11) or from the petrographically similar Rio Cuarto impact glasses (6) but consistent with the local loessoid deposits. Volatile and refractory components within the Chapadmalal glasses, however, differ from the Rio Cuarto glasses because of anomalously high levels of  $K_2O$  (2 to 8 weight %) and Na<sub>2</sub>O (4 to 10 weight %) in the Chapadmalal glasses. Despite the evidence for high transient temperatures, more volatile components were not driven off completely in most of our samples. The unusually high concentrations of K and Na suggest that the Chapadmalalan escorias were derived not only from the nearly 200-m-thick loessoid deposits but possibly from marine clays known to occur at depth nearby (11).

The escorias and tierras cocidas are found within a relatively narrow stratigraphic level over a distance of 30 km, unless locally reworked by fluvial processes or burrowing animals (12). The escorias typically are



Fig. 1. General location of the Chapadmalal escorias, which are found within a well-defined stratigraphic layer unless subjected to fluvial reworking or bioturbation. The escorias show evidence for an impact origin, perhaps from a region hidden near shore.

P. H. Schultz, Geological Sciences, Brown University, Providence, RI 02912–1846, USA. M. Zarate, Consejo Nacional de Investigaciones Científicas y Técnicas, Instituto Argentino de Nivologia y Glaciología, Centro Regional de Investigaciones Científicas y Técnicas, cc 330, 5500 Mendoza, Argentina. W. Hames, Department of Geology, 210 Petrie Hall, Auburn University, Auburn, AL 36849, USA. C. Camilión, Consejo Nacional de Investigaciones Científicas y Técnicas, Universidad Nacional de la Plata, 3#584, 1900 La Plata, Argentina. J. King, Graduate School of Oceanography, Narragansett, RI 02882–1197, USA.

concentrated near the top of a distinctive reddish silty paleosol ranging in thickness from 50 to 80 cm and below an equally distinct but poorly developed paleosol-like layer (Fig. 3). In some regions, a diamicton layer occurs above the reddish layer where some of the largest escorias are found. The most important mid-Pliocene turnover of endemic mammal assemblages occurs in the Marplatan stage (13) immediately above the escoria-bearing layer located in the uppermost part of the Chapadmalalan stage. This unique and sudden turnover affected the glyptodonts, ground sloths, two ungulate orders, and the flightless cariamid birds. The precise timing of this turnover has not been well constrained.

The radiometric age of a Chapadmalalan escoria was determined from K/Ar and laser fusion <sup>40</sup>Ar/<sup>39</sup>Ar dating techniques. The bulk sample gave a K/Ar age of  $4.8 \pm 0.2$ Ma, whereas a nonmagnetic fraction of glass shards (250 to 450 µm in length) from a crushed sample yielded a younger age of  $3.8 \pm 0.2$  Ma for a sample size of about 5 g (Geochron Laboratories, Cambridge, Massachusetts). This difference in age is interpreted to reflect variable abundance of older, unmelted material in each of the K/Ar sample fractions. Four additional escoria samples were subsequently analyzed by laser fusion of individual aliquots of handpicked glass shards (14). Analyses of the same crushed glass fraction used for K/Ar dating gave an age of  $3.8 \pm 0.2$  Ma. The other three samples used clast-free shards (determined by microscopic examination) and gave consistent ages of  $3.3 \pm 0.2$  Ma (95% confidence level), the most precise of which yielded  $3.27 \pm 0.08$  Ma [10 datapoints; mean standard weighted deviation (MSWD) = 1.2] and  $3.33 \pm 0.10$  Ma (8) datapoints; MSWD = 1.9)

The radiometric age is consistent with bracketed age estimates for the stratigraphic layer based on magnetostratigraphy and correlations with land mammal fossil occurrences (15). A new magnetostratigraphic profile in-



**Fig. 2.** In thin section, the escorias contain strongly developed schlieren with mineral inclusions. The glass content (isotropic in crossed polars) ranges from 20 to 90%, with some examples undergoing localized devitrification.

cluding the Chapadmalal succession (Fig. 3) shows that the escoria-bearing layer occurs just before the onset of the Mammoth subchron (16), a timing consistent with our radiometric dates. This age coincides with a distinct maximum in the benthic  $\delta^{18}$ O values at about 3.3 Ma (new time scale) derived from deep-sea cores that was interpreted as a 2°C cooling of the Atlantic bottom waters combined with mi-

nor glaciation. The cause of this maximum is unknown (17). Oxygen isotopic analysis of drilled cores (18) from Atlantic and Pacific sites resolve this event into two distinct isotopic shifts (MG2 onset at 3.35 Ma and M2 onset at 3.3 Ma) (Fig. 3). The earlier steplike shift of MG2 begins just below the Mammoth subchron at both sites, a time that correlates with the paleomagnetic age of our escoria layer. The



**Fig. 3.** Comparison of the marine  $\delta^{18}$ O record with the magnetostratigraphy, lithostratigraphy, land-mammal stratigraphy, and radiometric age of the escoria from the Playa Los Lobos section in Argentina. The age model of the marine record from the Atlantic [Ocean Drilling Program (ODP) Site 659] and Pacific (ODP Site 846) (**A**) is constrained by both magnetostratigraphy and orbital tuning (**B**), after (*18*). The inclination values from Playa Los Lobos versus stratigraphic depth after A.F. demagnetization of 20.0 mT are shown in (**D**). The magnetostratigraphic interpretation (**C**) indicates that the termination (t) of Mammoth (3.22 Ma) is at ~12 m, the onset (o) of the Mammoth (3.33 Ma) is at ~13.8 m, and the termination (t) of the Gilbert (3.58 Ma) is at ~15.7 m. The Ar/Ar date of 3.3 ± 0.1 Ma for the escoria at 15.0 m (**E**) is consistent with magnetostratigraphic units labeled P6 and P7 (*12*) (E). The South American stages (**F**) represent chronostratigraphic units based on land-mammal assemblages (*20*). The observed changes occur above the Early Pliocene–Late Pliocene boundary (**G**). The loss above the P7 lithostratigraphic unit.

**Table 1.** Comparison of Holocene Rio Cuarto (5), mid-Pliocene Chapadmalal glasses, and bulk loess composition from this study. Average of five (A), four (B), and eight (C) separate electron microprobe analyses of interstitial glass on different samples of the Chapadmalal glasses with the standard deviation shown in parentheses. For the bulk loess, average of nine separate analyses of fused bulk sample derived from the layer containing the escoria. The sample was fused at 1350°C for 2 hours following gradual heating over 1 hour. The low total may be due to the presence of ferric rather than ferrous iron and the presence of carbon (S, Cl, and P in trace amounts). All analyses were performed at the NSF/Keck Electron Microprobe Facility at Brown University.

	Rio Cuarto impact glass		Chapadmalal glasses			Loess
	Light brown	Clear	A	В	с	
SiO <sub>2</sub>	58.3	58.4	58.8 (1.4)	62.2 (0.2)	58.6 (0.4)	60.7 (0.8)
TiO <sub>2</sub>	2.0	0.0	0.82 (0.12)	0.61 (0.04)	0.82 (0.07)	1.0 (0.14)
Al <sub>2</sub> O3	15.8	25.1	16.6 (0.6)	10.4 (0.9)	15.2 (0.7)	17.9 (0.3)
FeO	10.3	1.4	4.8 (0.6)	3.1 (0.5)	3.7 (0.4)	6.7 (0.3)
MnO	0.27	0.04	0.09 (0.05)	0.10 (0.01)	0.10 (.02)	0.11 (0.05)
MgO	1.7	0.34	2.9 (0.7)	2.9 (0.2)	2.2 (0.2)	2.9 (0.1)
CaO	4.2	6.5	6.2 (1.1)	5.8 (0.5)	4.8 (0.4)	2.2 (0.1)
Na <sub>2</sub> O	4.3	5.4	7.2 (0.4)	6.8 (0.3)	7.7 (0.2)	1.6 (0.1)
K <sub>2</sub> O	2.8	3.2	2.2 (0.2)	7.6 (0.3)	6.5 (0.2)	2.1 (0.1)
Totals	99.7	100.4	99.6	99.5	99.6	95.2

derived age of 3.35 Ma of this event is within the radiometric age uncertainty for our escorias and the astronomically tuned calibrations for the paleomagnetic record.

Consequently, the escorias and tierras cocidas are proposed to be products of a mid-Pliocene impact. The source crater for the Chapadmalal escoria has not been located. Nevertheless, the size of the largest glass bomb (2 m in length) identified thus far is comparable to the largest glasses recovered at other major impact structures (19), which suggests an impact in Argentina of similar magnitude. Because the shoreline has eroded inland several kilometers since the Pleistocene, surface expression of any nearshore or offshore structure would have been easily erased.

The distinctive glasses provide a critical isochron for the Pampean Formation, placing better time constraints on faunal evolution in general (20). It is intriguing that there is a significant faunal turnover just above the escoria layer, marked by the disappearance of many endemic genera (13). Within uncertainties, the radiometric age of the impact glass and paleomagnetic age of the deposits coincide with a pulselike change in the deep-sea stable isotopic record, reflecting a sudden change in climate and ocean circulation. These coincidences suggest that the impact may have directly induced regional faunal extinctions or triggered broader environmental changes leading to ecosystem collapse in Argentina.

## **References and Notes**

- 1. M. E. Teruggi, J. Sed. Petrol. 27, 322 (1957).
- M. A. Zárate and A. Blasi, Quat. Internat. 17, 115 (1993).
- J. C. Heusser and G. Claraz, Neue Denk. (Nov. Mems.) der Allgemeine Schweiz. Gessell. XXI 27, Zurich (1865).
- 4. Other interpretations for the origin of the escorias include vitrified high-silica sediments produced by early inhabitants or the burning of silica-rich grasses [F. Ameghino, Anales del Museo Nacional de Buenos Aires XIII (ser. 3a), 39 (1910], precipitation of chalcedony or opal from silica-rich solutions [C. R. Cortelezzi, Revista del Museo de La Plata (nueva serie), sección Geología, VII, 233 (1971)], and loess fused by natural fires fluxed with organics [A. Bloom, Geol. Soc. Am. Abstr. Prog. 24, A136 (1992)]. Detailed studies carried out early in this century, however, demonstrated that the escorias could not have been derived from the burning of grasses and sediments due to the necessity for high temperatures (1300°C and 1350°C) and the absence of vegetative remains [F. Outes, E. Herrero Ducloux, H. Bücking, Rev. Museo de la Plata XV, 1, 138, (1908)]. Because their chemical analyses indicated that the composition of the escorias was identical to volcanic ashes, they classified the scoriaceous escorias and tierras cocidas as andesitic lavas and tuffs.
- M. A. Zárate and J. L. Fasano, Palaeogeogr. Palaeoclimatol. Palaeoecol. 72, 27 (1989).
- P. H. Schultz, C. Koeberl, T. Bunch, J. Grant, W. Collins, Geology 22, 889 (1994); P. H. Schultz and R. Lianza, Nature 355, 234 (1992).
- J. Pohl, D. Stöffler, H. Gall, K. Ernston, in *Impact and Explosion Cratering*, D. J. Roddy, R. O. Pepin, R. B. Merrill, Eds. (Pergamon, New York, 1977), pp. 343–404.
- 8. D. Stöffler, Fortschritte Mineral. 49, 50 (1972).
- 9. A. El Goresy, J. Geophys. Res. **70**, 3453 (1965). Because baddeleyite rarely occurs in volcanic materials,

its use as a good criterion for impact also depends on its occurrence, for example, in a glass matrix entraining other xenocrysts derived from local lithologies and exhibiting distinctive impact glass textures, particularly when out of geologic context for a plausible alternative process (such as a volcanic source or a fulgurite).

- S. W. Kieffer, J. Geophys. Res. **76**, 5449 (1971);
  R. A. F. Grieve and A. M. Therriault, *Lunar Planet. Sci.* XXVI, 515 (1995).
- M. Yrigoyen, Relatorio de Geología de la Provincia de Buenos Aires, VI Congreso GeológicoArgentino (1975), pp. 139–168. Thick (up to 800 m) Miocene clays with interbedded evaporites underly the loess about 50 km north of the study area.
- M. A. Zárate, thesis (Museo de la Plata, La Plata, Argentina, 1989).
- 13. L. Kraglievich, Rev. Mus. Cienc. Nat. Trad. Mar del Plata 1 (1), 8 (1952). E. Tonni, M. T. Alberdi, J. L. Prado, M. S. Bargo, and A. Cione [Paleogeogr. Paleoclimatol. Paleoecol. 95, 179 (1992)] recognized that the most important turnover recorded in the Chapadmalal Formation occurred between the stratigraphic unit containing the escorias (where 36 genera became extinct and 3 new genera appeared) and the overlying unit. This turnover mostly affected endemic families and genera. Among others, the xenarthrans (for example, Glyptodontidae: Plohophorous, Trachycalyptus, Plohophoroides; Mylodontidae: Proscelidodon: Dasipodidae: Doellotatus). Marsupialia (Thylacosmilus atrox), and the native ungulates (Brachitherium, a litoptern; Xotodon, a toxodontid) disappeared. Also, the last record of the flightless cariamid birds is registered during the Chapadmalalan.
- 14. These analyses were performed at the Laboratory for Argon Isotopic Research at MIT following procedures described by K. V. Hodges *et al.* [*Contrib. Min. Petrol.* **117**, 151 (1994)]. Fish Canyon sanidine was used to monitor neutron fluence, with an assigned age of 27.95 Ma [P. R. Renne *et al.*, *Geology* **22**, 783 (1994); A. K. Baksi, D. A. Archibald, E. Farrar, *Chem. Geol.* **129**, 307 (1996)], and the J-value for the samples is 0.001439  $\pm$  0.000008 (2 $\sigma$ ). Regressions of data were based on the method of D. York [*Earth Planet. Sci. Lett.* **5**, 320 (1969)].

- M. J. Orgeira, *Phys. Earth Planet. Lett.* **64**, 121 (1990);
  J. L. Flynn and C. C. Swisher III [*Geochronol. Time Scales Global Strat. Corr., SEPM Spec. Pub.* **54**, 317 (1995)] estimated that the Chapadmalense spanned a time from 4 to 3.4 Ma, based on correlations between an incomplete section and undifferentiated lithostratigraphic units in Bolivia.
- The magnetostratigraphic time scale follows F. J. Hilgen [*Earth Planet. Sci. Lett.* **104**, 226 (1991); *ibid.* **107**, 349 (1991)]. The absence of the Kaena subchron within the Gauss reflects locally increased sedimentation rates of loess after the paleosoils developed before the Mammoth subchron.
- W. Prell, *Science* **226**, 692 (1984); D. Hodell, D. Williams, J. P. Kennett, *Bull. Geol. Soc. Am.* **96**, 495 (1985); D. A. Hodell and J. P. Kennett, *Paleoceanography* **1**, 285 (1986).
- R. Tiedemann, M. Sarnthein, N. J. Shackleton, *ibid.* 9, 619 (1994).
- Suevitic bombs as large as 0.5 m from the 24-kmdiameter Ries Crater have been recovered (10). Impact glasses as large as 1 m have been recovered from the 14-km-diameter Zhamanshin crater [V. I. Feldman, et al., in Impactites, A. A. Marakushev, Ed. (Moscow University, Moscow, 1980), pp. 70–92], and impact glasses as large as 2 m have been recovered from the 18-km-diameter El'gygytgyn crater [V. I. Bouska, P. Povondra, P.V. Florenskij, Z. Rand, Meteoritics 16, 171 (1981)].
- 20. For example, our new dates for the escoria layer suggest that the chronological boundaries between South American Pliocene stages established by A. Cione and E. Tonni [J. Soc. Am. Earth Sci. 9, 221 (1996)] may have to be revised.
- 21. We sincerely thank W. Collins and R. Lianza for their unfailing cooperation and support, Fernanda Vicetto for first sharing her small green glasses that led us to the region, and J. Clarke for help in exploring their occurrences. We also thank K. Hodges for access to the MIT <sup>40</sup>Ar/<sup>39</sup>Ar geochronology facility and J. Devine for assistance in using the Keck/NSF electron microprobe at Brown University. This research was supported in part by NASA grant NAG5-3877.

28 July 1998; accepted 29 October 1998

## The Dusty Atmosphere of the Brown Dwarf Gliese 229B

Caitlin A. Griffith, Roger V. Yelle, Mark S. Marley

The brown dwarf Gliese 229B has an observable atmosphere too warm to contain ice clouds like those on Jupiter and too cool to contain silicate clouds like those on low-mass stars. These unique conditions permit visibility to higher pressures than possible in cool stars or planets. Gliese 229B's 0.85- to 1.0-micrometer spectrum indicates particulates deep in the atmosphere (10 to 50 bars) having optical properties of neither ice nor silicates. Their reddish color suggests an organic composition characteristic of aerosols in planetary stratospheres. The particles' mass fraction  $(10^{-7})$  agrees with a photochemical origin caused by incident radiation from the primary star and suggests the occurrence of processes native to planetary stratospheres.

The past 6 years have provided the first detections of planets and the slightly larger brown dwarfs outside our solar system (1, 2).

Among these substellar mass objects, Gliese 229B (Gl229B) is unique: With an effective temperature of 900 K, it is the coolest for which spectroscopic measurements are possible (1, 3, 4). Gl229B's temperature forces a reduced chemistry (a  $NH_3$ ,  $CH_4$ ,  $H_2O$ , and  $H_2$  composition), similar to the upper atmospheres of the jovian planets (5). Consequently, Gl229B's near-infrared (IR) spectrum (6, 7) is dominated by methane and water fea-

C. A. Griffith, Department of Physics and Astronomy, Northern Arizona University, Flagstaff, AZ 86011– 6010, USA. R. V. Yelle, Center for Space Physics, Boston University, 725 Commonwealth Avenue, Boston, MA 02215, USA. M. S. Marley, Department of Astronomy, New Mexico State University, Las Cruces, NM 88003–0001, USA.