PNAS
Proceedings of the National Academy of Sciences of the United States of America www.pnas.org

The strange case of the earliest silver extraction by European colonists in the New World

A. M. Thibodeau, D. J. Killick, J. Ruiz, J. T. Chesley, K. Deagan, J. M. Cruxent, and W. Lyman

PNAS published online Feb 21, 2007;
doi:10.1073/pnas.0607297104

The strange case of the earliest silver extraction by European colonists in the New World

A. M. Thibodeau*†, D. J. Killick‡, J. Ruiz*, J. T. Chesley*, K. Deagan§, J. M. Cruxent¶‖, and W. Lyman**

Departments of *Geosciences, ‡Anthropology, and **Materials Science and Engineering, University of Arizona, Tucson, AZ 85721; §Florida Museum of Natural History, University of Florida, Gainesville, FL 32611; and ¶Universidad Nacional y Experimental Francisco de Miranda, 4101 Coro, Venezuela

Edited by David H. Thomas, American Museum of Natural History, New York, NY, and approved December 21, 2006 (received for review August 22, 2006)

La Isabela, the first European town in the New World, was established in 1494 by the second expedition of Christopher Columbus but was abandoned by 1498. The main motive for settlement was to find and exploit deposits of precious metals. Archaeological evidence of silver extraction at La Isabela seemed to indicate that the expedition had located and tested deposits of silver-bearing lead ore in the Caribbean. Lead isotope analysis refutes this hypothesis but provides new evidence of the desperation of the inhabitants of La Isabela just before its abandonment.

archaeological science | historical metallurgy | La Isabela | lead isotopes

The first expedition of Cristóbal Colón (Christopher Columbus) to the Caribbean, from 1492 to 1493, returned to Spain with some gold taken from the Taíno inhabitants of the island of Hispaniola (now divided between Haiti and the Dominican Republic). Columbus's tales of the abundance of gold in the New World induced King Ferdinand and Queen Isabela of Spain to fund a second and much larger expedition (1). In early 1494, Columbus and ≈1,500 followers established the town of La Isabela on the northern coast of the present Dominican Republic (Fig. 1). His followers were eager to make their fortunes but were rapidly disillusioned by their failure to find any ores of precious metals (1, 2). La Isabela was beset by hunger, disease, hurricanes, mutiny, and conflicts with the Taíno. In 1496 Columbus was recalled to Spain to account for his misadministration of the expedition. The few hundred remaining inhabitants of La Isabela struggled until early 1498, when they abandoned the town and marched across the island to found new settlements on the south coast.

The archaeological site of La Isabela was intensively excavated in the late 1980s and early 1990s (1, 2). Among the finds were 58 triangular graphite-tempered assaying crucibles†† and 1 kg of liquid mercury, which was brought for the extraction of gold from powdered ore by amalgamation. The mercury was excavated from the ruins of the *alhóndiga*, a fortified structure erected for storage and protection of royal property (2). Within and immediately north of the *alhóndiga*, archaeologists also recovered ≈90 kg of galena (PbS), in blocks weighing up to 2 kg, and ≈200 kg of material classified in the field as metallurgical slag. Much of the ore and supposed slag was associated with a fired pit that appears to be the remnant of a small furnace that was located just north of the *alhóndiga* (2).

Results and Discussion

We examined polished sections of the galena and slag by using optical petrography and metallography, SEM, and electron microprobe analysis. Electron microprobe analysis of galena reveals highly variable silver content, ranging from ≈210 ppm to below the detection limit (≈29 ppm) [see supporting information (SI) Table 2 and *SI Methods*]. The materials that are classified as slag can be divided into two groups. The first type, of which ≈15 kg was recovered, is crystalline and strongly magnetic. Optical and SEM analyses reveal abundant grains of metallic iron and crystals of a calcium–iron silicate in a calcium–iron–silica glass. This material is the result of a failed attempt to smelt iron with

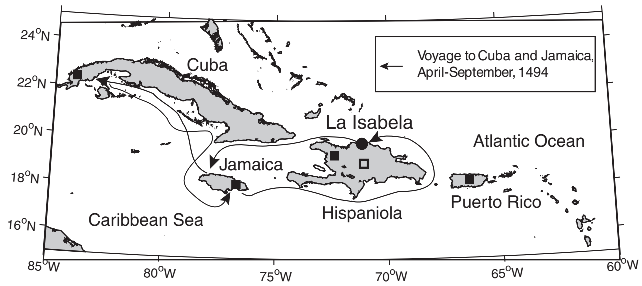

Fig. 1. Location of La Isabela. Filled squares are approximate locations of Pb deposits in the Greater Antilles (5). Open square is approximate location of the Pueblo Viejo Au–Ag oxide deposit in the Dominican Republic (7). Arrows represent the principal exploration route traveled by the second expedition after La Isabela was established.

a calcareous flux (coral): the temperatures achieved were not sufficient to allow the slag to flow freely, and thus it could not separate from the metal. The second and more abundant material (≈185 kg) is a dense black glass. Optical and SEM analysis of multiple specimens shows that this glass is a lead silicate that contains tiny spheres of lead metal and chemically eroded remnants of quartz crystals that were shattered by thermal stress (see SI Fig. 4). Sulfur was not detected. Some samples of slag contain minute, complex inclusions of metallic lead, litharge (PbO), and metallic silver (Fig. 2).

From these observations, we infer that some inhabitants of La Isabela were attempting to recover silver from galena by cupellation. The galena was reduced to metallic lead, a process that requires only that crushed ore be sprinkled on a bonfire of stacked wood (3). Sulfur is removed as sulfur dioxide fume, while any silver content dissolves into the metallic lead. Cupellation is the second stage of the process, whereby metallic lead is melted under a cover of a charcoal fire and subjected to an oxidizing blast produced by bellows. This process oxidizes the molten lead to molten litharge but does not oxidize any noble metals present. To concentrate silver, the molten litharge must be removed as it forms by absorption into or reaction with the lining of the furnace base.

Author contributions: D.J.K. and J.R. designed research; A.M.T., D.J.K., J.T.C., K.D., J.M.C., and W.L.; performed research; J.R. contributed new reagents/analytic tools; A.M.T. analyzed data; A.M.T. and D.J.K. wrote the paper; and K.D. and J.M.C. excavated site and provided samples.

The authors declare no conflict of interest.

This article is a PNAS direct submission.

†To whom correspondence should be addressed at: Department of Geosciences, University of Arizona, Gould–Simpson Building no. 77, 1040 East 4th Street, Tucson, AZ 85721. E-mail: amthibod@email.arizona.edu.

‖Deceased February 23, 2005.

††Martinón-Torres, M., Rehren. T., 34th International Symposium for Archaeometry, May 3–7, 2004, Zarogoza, Spain.

This article contains supporting information online at www.pnas.org/cgi/content/full/0607297104/DC1.

Table 1. Pb isotope ratios measured on samples of galena and lead silicate slag from La Isabela

Sample	$^{206}Pb/^{204}Pb$ ratio	$^{207}Pb/^{204}Pb$ ratio	$^{208}Pb/^{204}Pb$ ratio
3a-G	18.224	15.614	38.369
3a-G (R)	18.221	15.610	38.354
6a-G	18.210	15.606	38.345
10a-G	18.211	15.608	38.349
13a-G	18.216	15.608	38.350
17a-G	18.214	15.608	38.349
17a-G (R)	18.212	15.607	38.346
23a-G	18.206	15.603	38.338
3b-G	18.196	15.602	38.328
6b-G	18.207	15.605	38.341
10b-G	18.210	15.606	38.345
13b-G	18.213	15.609	38.352
13b-G (R)	18.211	15.606	38.344
17b-G	18.218	15.609	38.347
23b-G	18.224	15.610	38.356
22-S	18.240	15.631	38.400
4-S	18.237	15.625	38.386

G, galena; S, lead silicate slag; R, repeat measurement.

In medieval Europe, bone ash was commonly used for lining cupellation hearths (3), because it absorbs litharge but does not react with it. Using bone ash in the cupellation process makes it possible both to extract silver and to recover desilvered lead by crushing and resmelting the used hearth linings. At La Isabela, the cupellation hearth was evidently lined with quartz-rich sand, which reacted with the molten litharge. This process formed a lead silicate glass from which the lead could not be recovered. Additionally, the formation of the glass would have made the oxidation of lead less efficient and caused higher losses of metallic lead, and potentially silver, to the slag during the cupellation process (Fig. 2).

The spatial association of cupellation with the royal storehouse supported the hypothesis that the second expedition might have found and assayed galena from Caribbean ore deposits. Although lead mineralization is scarce in the Greater Antilles, galena is present in small volcanogenic massive sulfide deposits in Cuba, Haiti, and Jamaica and in vein deposits in Puerto Rico (4, 5). All of these islands were visited during Columbus's second voyage (Fig. 1).

To determine the provenance of the galena, we measured the lead isotope ratios of 12 samples of galena and 2 samples of lead silicate glass. The results cluster tightly, and the majority of values overlap within the 2σ analytical error (Table 1). The similarity of the isotopic ratios supports our interpretation that all of the galena found at La Isabela derives from the same source. The slight displacement of lead isotope ratios evident in the samples of lead silicate glass suggests some admixture with lead from sand. Beach sands in this region are rich in quartz and coral, and locally derived lead can substitute for calcium in the latter.

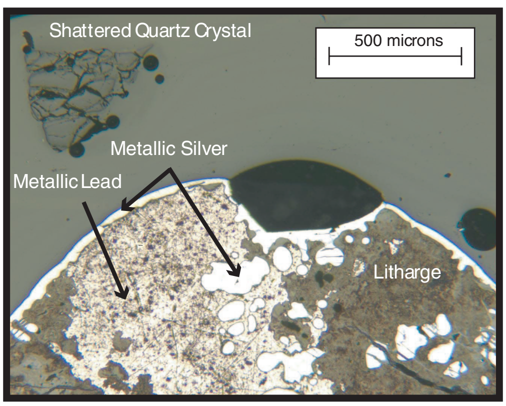

Fig. 2. Reflected light image of a lead silicate glass slag from La Isabela.

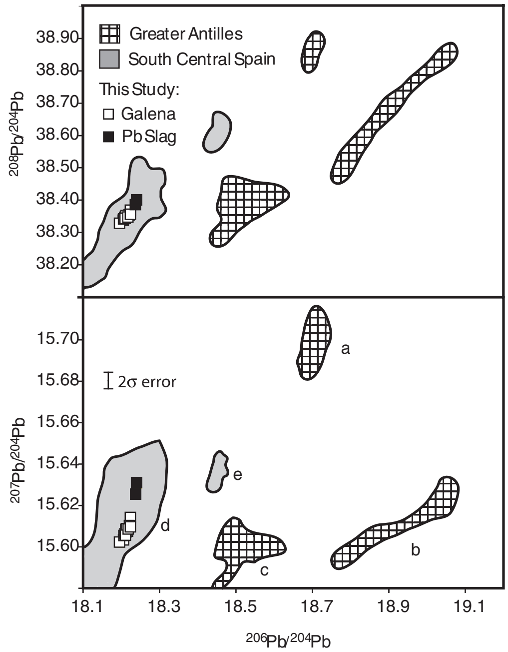

Fig. 3. Comparison of lead ore and lead silicate slag from La Isabela with galena and sulfide mineralization in the Greater Antilles (5, 7) and galena from the Alcudia Valley–Los Pedroches, and Linares–La Carolina mining districts in Spain (11). Individual groupings represent a, Cuba (n = 2); b, Haiti, Puerto Rico, and Jamaica (n = 4); c, Pueblo Viejo Au–Ag oxide deposit (n = 9); d, the Alcudia Valley, Los Pedroches, and Linares–La Carolina areas (n = 83); and e, Los Pedroches (n = 4). Error limits for $^{207}Pb/^{204}Pb$ measurements are shown; all other errors are smaller than symbols. Data from ref. 11 that are not shown lie outside range of the plot. For each area, n = the number of analyses represented by each shaded ore field.

The isotopic composition of lead in the ore and slag samples from La Isabela, however, does not fall within the known range of values obtained for galena-bearing deposits in the Caribbean. These samples include galena from the Greater Antilles and sulfide minerals from the Pueblo Viejo Au–Ag oxide deposit in the Dominican Republic (Fig. 3). Although the data are scarce, they are consistent with models of crustal evolution for the Caribbean region and with other lead isotope measurements of rock and ore from the Greater Antilles, the Lesser Antilles, and Central America (4–10). We therefore conclude that the galena at La Isabela was not collected from a Caribbean source.

Because historic documents do not indicate that anyone from Columbus's fleet reached the American mainland during the second expedition, we assume that the only other option is that the expedition brought galena from Europe. To evaluate this possibility, we looked to ore deposits near Cádiz, the port from which Columbus's second fleet sailed. The largest area of lead mineralization in Spain lies in the Los Pedroches–Alcudia Valley and the adjacent Linares–La Carolina ore fields (11). Collectively, these mining districts extend over an area of 10,000 km^2 through the provinces of Ciudad Real, Badajoz, Córdoba, and Jaén and have been mined for thousands of years (11). Deposits from the Alcudia Valley are dominantly Pb–Zn polymetallic veins that contain variable but significant amounts of silver and copper (12). Galena is the dominant mineral within the Linares–La Carolina area (13).

Santos Zalduegui and others (11) report lead isotope data for 125 samples of galena from the Alcudia Valley, Linares–La Carolina ore field, and the Los Pedroches batholith area. A comparison of these data with our measurements reveals that the galenas from La Isabela fall well within the range of values reported for the Linares–La Carolina fields and the Alcudia–Los Pedroches areas (Fig. 3). Other major sources of lead in Spain include the Betic Cordillera in the southeast (14), the western Pyrenees and Basque–Cantabrian basin in the north (15), the Rubiales ore deposit in the northwest (16), and the Catalonian Coastal Ranges in the northeast (17). However, the lead isotope ratios of these deposits (14–17) do not match those of the La Isabela galenas. The lead isotope data alone cannot rule out the possibility that the galena came from some more distant part of Europe, the Mediterranean or North Africa. However, we believe that the combination of the specific historical circumstances, the geographical proximity of lead ore deposits to the port of departure of Columbus's second fleet, the mineralogy of the deposits, and lead isotope data strongly support our conclusion that the galena recovered at La Isabela derives from the Alcudia Valley–Los Pedroches or Linares–La Carolina ore fields.

Why would the second expedition have brought galena from Spain? The archaeological evidence from La Isabela (2) shows that metallic lead was used for shot and lead sheathing to protect the wooden hulls of ships. However, it is unlikely that the galena was brought for solely this purpose, because (*i*) galena would need to be smelted before use, and raw ore would have been an extremely inefficient use of the precious cargo space on the first transatlantic ships; and (*ii*) lead metal is among the supplies requested by Columbus as necessary for the colony after their arrival in 1493 (2). That almost all of the galena found at La Isabela was located in or near the *alhóndiga* supports the inference that it was royal property. Because the *alhóndiga* was used to store metallurgically important materials (such as mercury), we believe it is most probable that the galena was brought to La Isabela as a reagent for assaying ores for precious metals. In late medieval Europe, galena was used as a reagent in fire assays by smelting precise amounts of galena with other powdered ores together in a crucible so that the resulting lead would collect any noble metals present (M. Martinón-Torres, personal communication). After cupellation of the lead metal, the gold and silver content of the assayed ore could be determined by subtracting the quantities assumed or known to be present in the reagent galena (M. Martinón-Torres, personal communication). The low average silver content of the galena supports the interpretation that it was brought as an assaying reagent.

The archaeological distributions of galena, slag, and cupelling residues were heavily concentrated just inside and outside of the north end of the *alhóndiga.* Piles of slag and galena were mapped on either side of two stone pillars that the excavators interpret as foundations for an arched portal through the north wall of the structure, which gave access to the furnace area, the beach and the shipyard (2). The scatter of slag and ore through the entranceway and into the structure suggests that the cupellation of the galena and the smelting of iron were among the last activities to have taken place at the *alhóndiga*, when there was no longer any concern about maintaining access to the beach or about dumping industrial waste within the royal storehouse.

In early 1496, the Spaniards had located gold deposits in southern Hispaniola and subsequently established the port of Santo Domingo on the southern coast of the island. Throughout the latter half of 1496, Spanish settlement was gradually transferred to Santo Domingo, which significantly reduced the population of La Isabela (1). Despite the relocation, La Isabela remained occupied through 1497, although food rationing, hunger, and sickness heavily plagued the shrinking settlement (1). In May of 1497, La Isabela was sacked, and the *alhóndiga* was looted by a band of discontented rebels led by Francisco Roldán (1). Although a few settlers likely remained until late 1497, the site was effectively abandoned by 1498 (1).

Given the archaeological context of the ore and slag, the cupelling of these ores likely postdates the breakdown of royal authority that led to the looting of the *alhóndiga*. We suggest that toward the end of the site's occupation, some desperate survivors sought to salvage what they could from La Isabela before abandoning it. With the help of at least one person with basic knowledge of assaying procedures, they set out to cupel the galena stored in the *alhóndiga*. In so doing, they modified the standard medieval cupelling process by substituting beach sand for the usual bone ash hearth. Whether this unusual process reflects a shortage of bone ash or a lack of metallurgical knowledge we cannot say. However, the failed attempt to smelt iron, which appears to be contemporary with the processing of galena, supports the latter inference.

Thus, we believe that the processing of lead and iron ore at La Isabela was not the work of skilled assayers working for the Crown, but instead the result of the imperfect knowledge held by those at La Isabela who remained during the final stages of its occupation after the relocation of mining activities to other parts of Hispaniola. That >88 kg of galena was left unprocessed suggests that those cupelling the ore were disappointed with the return and abandoned their efforts. In conclusion, what seemed at first to be evidence of the earliest European mining and processing of precious metals in the New World appears, on further inspection, to be poignant testimony to the disillusionment and desperation of settlers who had embarked on the second expedition in the hope of making their fortunes.

Methods

Twelve samples of galena and two samples of lead silicate glass were analyzed for this study. All samples were chipped off larger pieces of material and accurately weighed. Six of the galena samples were taken from pieces that had previously been thin-sectioned and examined by using SEM. Each sample was stored in a clean dry Falcon tube (BD Biosciences, San Jose, CA). Samples were then transferred into clean 24-ml Teflon containers. Ten milliliters of 8 M HNO_3 was added to each galena sample, and 2 ml of HF was added to each sample of lead silicate glass. All samples were capped and heated on a hot plate at 125°C. To ensure total dissolution, samples were periodically placed in an ultrasonic bath. An additional sample that was composed solely of 10 ml of 8 M HNO_3 was processed alongside the Pb samples to measure the total process blank.

After complete dissolution, all solutions were diluted to a Pb concentration of ≈200 ppb based on sample weight. Sr and Pb were separated on the same Sr–Spec resin (Eichrom, Darien, IL) columns by using protocol developed at the University of Arizona. Data for a mixed National Bureau of Standards (NBS)-981:Tl yields data with reproducibility similar to that described in ref. 18. Runs of United States Geological Survey basalt standard (BCR-2) are in excellent agreement with BCR-2 values measured by Woodhead and Hergt (19), using double-spiking thermal ionization mass spectrometry methods.

Lead isotope analysis was conducted on a GV Instruments (Hudson, NH) multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Arizona. Samples were introduced into the instrument by free aspiration with a low-flow concentric nebulizer into a water-cooled chamber. A blank, consisting of 2% HNO_3, was run before each sample. Before analysis, all samples were spiked with a Tl solution to achieve a Pb/Tl ratio of ≈10. Throughout the experiment, the standard National Bureau of Standards (NBS)-981 was run to monitor the stability of the instrument.

All results were Hg-corrected and empirically normalized to Tl by using the exponential law correction according to ref. 18. To correct for machine and interlaboratory bias, all results were normalized to values reported by Galer and Abouchami (20) for the National Bureau of Standards (NBS)-981 standard ($^{206}Pb/^{204}Pb$ = 16.9405, $^{207}Pb/^{204}Pb$ = 15.4963, and $^{208}Pb/^{204}Pb$ = 36.7219). Internal error reflects the reproducibility of the measurements on

ANTHROPOLOGY

individual samples, whereas external errors are derived from long-term reproducibility of NBS-981 Pb standard and result in part from the mass bias effects within the instrument. In all cases, external error exceeds the internal errors and is reported here. External errors associated with each Pb isotopic ratio are as follows: $^{206}Pb/^{204}Pb = 0.028\%$, $^{207}Pb/^{204}Pb = 0.028\%$, and $^{208}Pb/^{204}Pb = 0.031\%$.

Mark Baker provided a great deal of assistance with sample preparation and analysis. Marcos Martinón-Torres provided valuable information on assaying practices in medieval Europe. This work was supported by a graduate fellowship from the National Science Foundation Integrative Graduate Education and Research Traineeship program in the Archaeological Sciences (to A.M.T.). The Dirección Nacional de Parques de la República Dominicana provided funds for excavation of La Isabela and permitted scientific analysis of the samples described here. Excavations were also supported by National Endowment for the Humanities Grant RK20135-94 and the National Geographic Society. The development of analytical methodology and isotopic analyses were supported by the Keck Foundation and National Science Foundation Grants EAR-9976676, EAR-0125773, and EAR-0409417.

1. Deagan K, Cruxent JM (2002) *Columbus's Outpost Among the Tainos: Spain and America at La Isabela, 1493–1498* (Yale Univ Press, New Haven, CT).
2. Deagan K, Cruxent JM (2002) *Archaeology at La Isabela, America's First European Town* (Yale Univ Press, New Haven, CT).
3. Craddock P (1995) *Early Metal Mining and Production* (Smithsonian Inst, New York).
4. Cumming GL, Kesler SE (1976) *Earth Planet Sci Lett* 31:262–268.
5. Cumming GL, Kesler SE, Krstic D (1981) *Earth Planet Sci Lett* 56:199–209.
6. Cumming GL, Kesler SE (1987) *Chem Geol* 65:15–23.
7. Cumming GL, Kesler SE, Krstic D (1982) *Econ Geol* 77:1939–1942.
8. Lebrón MC, Pefit MR (1994) *Tectonophysics* 229:69–100.
9. O'Blein S, Guillot S, Lapierre H, Mercier de Lépinay B, Lardeaux JM, Millan Trujillo G, Campos M, Garcia A (2003) *J Geol* 111:89–101.
10. Davidson JP (1987) *Geochim Cosmochim Acta* 51:2185–2198.
11. Santos Zalduegui JF, Garcia de Madinabeitia S, Ibarguchi JI, Palero F (2004) *Archaeometry* 46:625–634.
12. Palero FJ, Both RA, Arribas A, Boyce AJ, Mangas J, Martin-Izard A (2003) *Econ Geol* 98:577–605.
13. Lunar R, Moreno T, Lombardero M, Regueiro M, López-Vera F, Martínez del Olmo W, Mallo García JM, Saenz de Santa Maria JA, García-Palomero F, Higueras P, *et al.* (2002) in *The Geology of Spain*, eds Gibbons W, Moreno T (Geological Society, London), pp 473–510.
14. Arribas A, Tosdal RM (1994) *Econ Geol* 89:1074–1093.
15. Velasco F, Pesquera A, Herrero JM (1996) *Miner Deposita* 31:84–92.
16. Tornos F, Arias D (1993) *Eur J Mineral* 5:763–773.
17. Canals A, Cardellach E (1997) *Miner Deposita* 32:243–249.
18. Rehkämper M, Mezger K (2000) *J Anal At Spectrom* 15:1451–1460.
19. Woodhead JD, Hergt M (2000) *Geostand Newsl* 24:33–38.
20. Galer SJG, Abouchami W (1998) *Mineral Mag* 62A:491–492.