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


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

This information is current as of February 2007.

Supplementary Material
Supplementary material can be found at:
www.pnas.org/cgi/content/full/0607297104/DC1

This article has been cited by other articles:
www.pnas.org#otherarticles

E-mail Alerts
Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here.

Rights & Permissions
To reproduce this article in part (figures, tables) or in entirety, see:
www.pnas.org/misc/rightperm.shtml

Reprints
To order reprints, see:
www.pnas.org/misc/reprints.shtml

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


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.

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 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.
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 found and assayed galena from Caribbean ore deposits. Although 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 km² through the provinces of Ciudad Real, Badajoz, Córdoba, and Jaén and have been mined for thousands of years (12). Galena has been mined for variable but significant amounts of silver and copper (12). 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 207Pb/206Pb 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 km² 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

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

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

G, galena; S, lead silicate slag; R, repeat measurement.
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 Pedrachines 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 Pedrachines 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 cupellation 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 furnaces, 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 melting 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 cupellation 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 heath. 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 >8 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 a 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 shipped 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 HNO3 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 HNO3 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:TI 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% HNO3, 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 Pb samples were processed alongside the Pb samples to measure the total process blank. Analyses were normalized to the NBS-981 standard. All results were Hg-corrected and empirically normalized to Tl by using the external 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 (206Pb/204Pb = 16.9405, 207Pb/204Pb = 15.4963, and 208Pb/204Pb = 36.7219). Internal error reflects the reproducibility of the measurements on
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: $^{206}\text{Pb}/^{204}\text{Pb} = 0.028\%$, $^{207}\text{Pb}/^{204}\text{Pb} = 0.028\%$, and $^{208}\text{Pb}/^{204}\text{Pb} = 0.031\%$.

Mark Baker provided a great deal of assistance with sample preparation and analysis. Marcos Martín-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.