35. Lead Isotope Studies of Spanish, Spanish-Colonial and Mexican Majolica

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ABSTRACT: *Lead isotope data demonstrate new world procurement of raw materials for majolica glaze production by Spanish colonists in the sixteenth century.*

INTRODUCTION

Throughout the Spanish Colonial period majolica ceramics were used as basins, bowls, pitchers and other types of containers and serving pieces. They represent a sophisticated ceramic technology. The body of the ceramics is made of a calcareous clay or a mixture of calcareous and non-calcareous clays to produce a porous fabric. The glaze applied to the body is a tin opacified lead glaze to which a variety of pigments may be added. Procurement of the raw materials for the body and the glaze is also complex. Evidence for sixteenth century majolica production in the New World comes from both the historical record and studies of the chemical and mineralogical composition of the ceramic paste (1,2). Although the historical records do not document in detail when this production began, artifacts from the excavations of the Metropolitan Cathedral in Mexico City which predate 1573 have been analyzed by neutron activation analysis and petrography (3,4). When the composition of the majolica sherds from these excavations was recalculated for dilution by calcium carbonate, the paste composition of some of the majolica ceramics was found to match closely the composition of Aztec ceramics. Although it was assumed earlier that the source of the calcium carbonate was a secondary calcareous deposit during burial in the wet soil of Mexico City, it is now known that its source was the calcareous clays which were used in majolica production. In addition to the chemical data, the petrographic evidence is that the volcanic ash temper present in the sherds attributed to Mexican production is characteristic of local clay sources. Other majolica ceramics present in the excavated material from the Metropolitan Cathedral have a chemical and mineralogical compostion characteristic of Spanish production (3,4).

The evidence for sixteenth century majolica manufacture in the New World by the Spanish, documents a transfer of the technology of production but not the local procurement of glazing materials. The manufacture of the glazing compounds could have been more conservative, with production remaining in Spain, or the transfer could have been total, with lead and other materials for the glaze procured from Mexican sources at an early date. Although there is some historical evidence for the early use of New World lead sources by the Spanish, the documentation is not extensive (5). Lead isotope analyses of the glazes from majolica ceramics having chemical and mineralogical paste compositions characteristic of Mexico, would provide evidence for the source of lead. The comparison of our results with lead isotope data on Mexican ore sources would provide additional evidence for a local source.

Recently, Olin and Blackman have refined the classification of Mexican majolica using neutron activation analysis (6). Sherds from excavations at the Metropolitan Cathedral in Mexico City and from excavations on St. Catherines Island, Georgia extended the analyses of majolica ceramics to include seventeenth century types. The chemical classification of sixteenth-seventeenth century Mexican majolica produced two very distinct groups based on the differences in the measured concentrations for chromium, iron and scandium. One of the groups closely matched the composition of modern Puebla ceramics and was assigned as being of Puebla manufacture. The other compositional group was assigned to Mexico City. This was based on the fact that there is historical evidence for majolica production in Mexico City during the sixteenth century. The types which were chemically classified in this group have been assigned to Mexico City based on archaeological evidence. They include a plain white ware similar to the widely distributed Spanish white ware which is called Mexico City White. In our investigation of the lead composition in the glazes, samples of both Puebla and Mexico City production were included in order to determine whether separate sources of the lead used could be identified.

In addition to samples of Mexican production, sherds manufactured in Spain were included in this study. This data is important for confirming that lead from Spanish sources was not used in majolica production in the New World. Further work with the lead isotope data from these glazes is planned for the future in conjunction with work we are carrying out on recently excavated majolica from Spanish sources. Earlier published lead isotope data for other Spanish colonial artifacts will then serve as an important reference (7).

The seventy-four sherds analyzed for their lead isotopic compositions were excavated from fifteenth and sixteenth century Spanish sites in the Caribbean, Venezuela, Mexico and Spain. Descriptions and excavation sites are listed in Table 2. Additional sherds obtained from the Pureza street kiln-site in Seville, Spain (8), and Le Calle Juan Baron and Parque Colon in the Dominican Republic were also sampled. The major majolica types represented are Colombia Plain, Yayal Blue on White, Mexico City White and San Juan Polychrome.

EXPERIMENTAL PROCEDURES

Lead isotope ratios were determined using a National Bureau of Standards' thermal ionization mass spectrometer designed for high precision measurements. The isotopic ratios for the glaze samples were calibrated and corrected for the effects of fractionation using NBS Standard Reference Material 981 for lead and are generally accurate to within 0.1% (95% limit of error) (9). The type of precision that can be obtained is shown in Table 1. The seven analyses of SRM 981 were run over a period of three days and show a relative standard deviation of 0.015% for the 208/206 ratios and 0.007% for the 207/206 ratios. The chemical separation of microgram quantities of lead by acid dissolution and electrodeposition techniques is well documented (10). The method's efficiency for lead recovery is 95% and is applicable to a wide variety of matrices. The analytical blank for this method, determined by isotope dilution mass spectrometry, is generally at the 2-3 nanogram/gram level.

The amount of lead extracted from the tin oxide glaze samples was 800 to 1000 μg in size. Approximately 0.5 μg of the extracted lead was loaded into the mass spectrometer and run at a temperature of 1200 C using the silica gel-phosphoric acid technique (10). Two of the samples, SC 37 and SC 38, were run in duplicate to test for sample homogeneity and reproducibility of the method (Table 2). The average standard deviation was less than 0.1% for multiple measurements of lead isotope ratios on a given sample.

RESULTS AND DISCUSSION

The results of these analyses are listed in Table 2. As shown in Figure 1, three groups were readily defined using the corrected 208/206 versus 207/206 ratios. The two groups in the upper right hand corner of the graph consist entirely of samples from Spain and early Spanish colonial sites (open and closed triangles). The closed squares are samples excavated from the Metropolitan Cathedral with few exceptions and based on previous elemental analyses, assigned to a Mexican production.

The upper Spanish majolica group (closed triangles) consists of sherds attributed to a Spanish production and excavated from sites in the Caribbean, Venezuela, the Metropolitan Cathedral in Mexico City and from Jerez and the Pureza street kiln-site in Seville, Spain. The lower Spanish group, (open triangles), consists of majolica samples excavated from Spanish settlements in the Dominican Republic, with one exception, a Colombia Plain sherd from Cuzco, Peru. Although this group does not include any majolica from Spain, the samples can be assigned to a Spanish origin based on typology and the chemical composition of the paste. All samples in the Mexican group (Figure 1) can be assigned to Mexican production based on chemical composition (6). The lead isotope ratios for this Mexican group are very homogeneous. Based on the assumption of multivariate normality, the lead values fall within the 95% probability limits of belonging to the same group with the exception of two samples. The major types of majolica represented in the group consist of Mexico City White and San Juan Polychrome. The two exceptions are a Puebla Polychrome from the Dominican Republic and an unidentified type from Cubagua, Venezuela.

The results of our analyses were compared to a lead isotope study on thirty-four mineral deposits from northern Mexico by Cumming et al. (11). These deposits were divided into categories of massive sulfide deposits, sedimentary deposits, vein deposits and limestone replacement deposits. The deposits from this area contain almost all of the important lead mineralization in the country and exhibit a systematic distribution throughout northern Mexico. The massive sulfide deposits are confined to the west coast; the vein deposits extend from the west coast to central Mexico; and the limestone replacement deposits extend from central to eastern Mexico.

The analytical procedure used by Cumming et al. for lead isotope determination was similar to that of our study. Using NBS Standard Reference Material 981, the reproducibility of the mass discrimination measurement was 0.03%. To analyze for internal reproducibility, nine duplicate sets of samples were run. The standard deviation for these nine sets was 0.07%, well within the acceptable limits for 0.1% accuracy, and is comparable to the type of precision obtained by our laboratory. The geological ore samples were compared to the Mexican majolica glaze group for the purpose of determining possible lead sources. Using Mahalanobis distance and Hotelling's T2 statistics, samples from seven of the thirty-four deposits fell within the 95% confidence interval for the Mexican glazes and are potential ore sources (Table 2). Three of the deposits were from the same area. Figure 2 is a graph of the lead isotopic ratios for both the Mexican group and the ore data to illustrate the distribution of the ore data in relation to the Mexican glaze samples. A map of the geological region associated with the ore data and majolica production sites is shown in Figure 3.

In view of the geographical distribution of the ores and their possible use in majolica glazes, we are inclined to limit the list of sources even further. It is interesting to note that high probabilities given for the two massive sulfide deposits, Cuale and Campo Morado, are widely separated geographically. Cumming et al. state that the Cuale and Campo Morado are part of a group of similar deposits found within the Mesozoic submarine volcanic complex of western Mexico and that similar rocks, possibly moved eastward by tectonic activity, have been recognized in isolated outcrops between Camp Morado and El Pavo. Therefore, the most probable source or sources of lead used in Mexican majolica is thought to be similar to that found in the sulfide deposits of central Mexico.

CONCLUSIONS

Spanish and Mexican majolica can be distinguished on the basis of their lead isotopes. Furthermore, the lead isotope data provide evidence which documents an indigenous Mexican procurement and production system for majolica before 1573. Based on a previously published study by Cumming et al. on lead depositions in Mexico, we have been able to identify five sources of lead which are isotopically similar to the lead used in the glaze of Mexican ceramics.

The lead used in Spanish majolica would appear to have come from two sources. Additional analyses on newly excavated ceramics from Spain will provide more information on the number of lead sources available.

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TYPICAL PRECISION FOR LEAD ISOTOPIC STANDARD[a]

Run No.	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$
1.	2.16300	0.91376
2.	2.16276	0.91388
3.	2.16288	0.91383
4.	2.16342	0.91374
5.	2.16362	0.91370
6.	2.16335	0.91383
7.	2.16344	0.91377
Average	**2.16321**	**0.91379**
SD	**0.00033 (0.015%)**	**0.00006 (0.007%)**

[a] SRM 981, National Bureau of Standards

Table 1. Type of precision obtained in thermal ionization mass spectrometry.

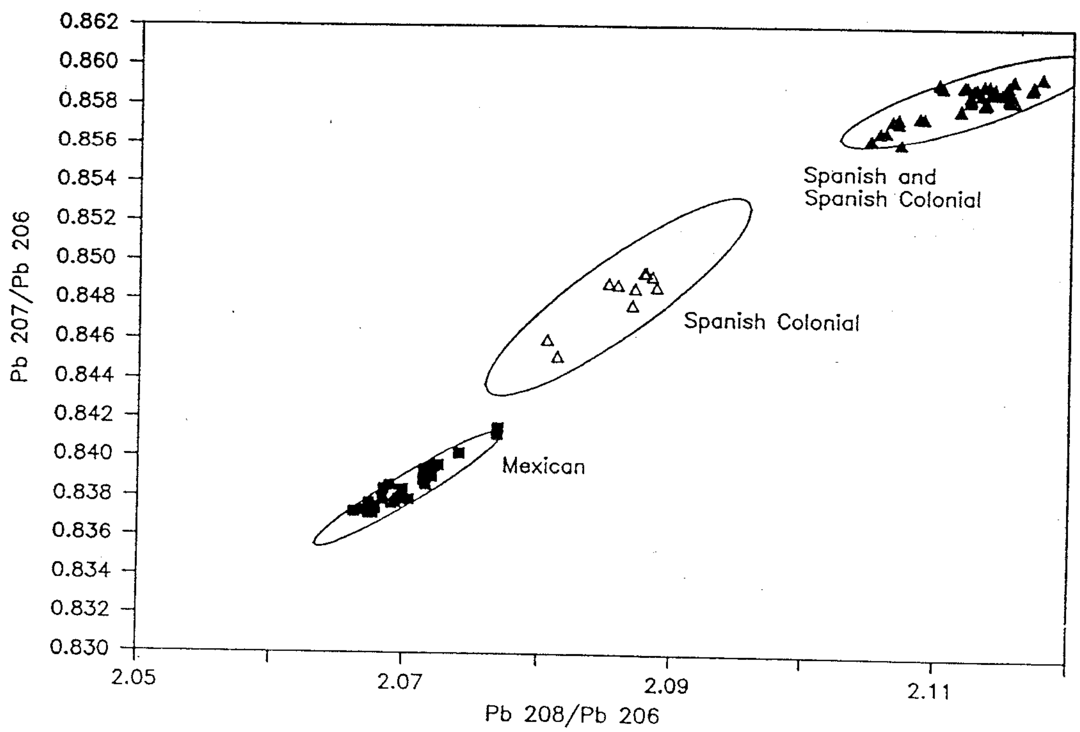

Figure 1. Plot of 208/206 versus 207/206 for all Majolica samples. Ellipses represent 95% confidence intervals.

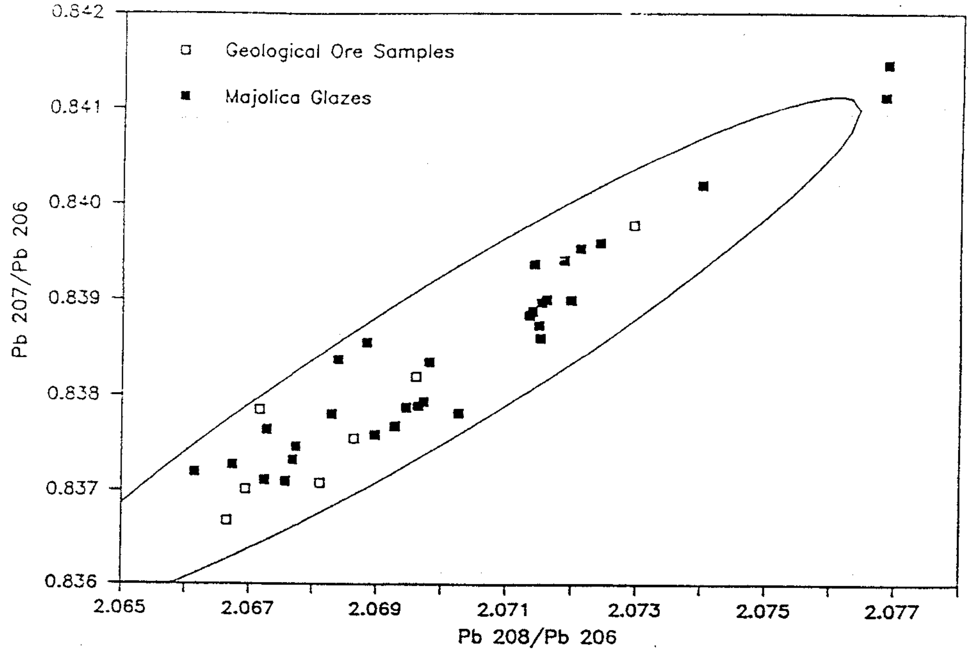

Figure 2. Plot of 208/206 versus 207/206 isotope ratios for Mexican glaze group and geological ore samples. 95% confidence ellipse based on glaze samples only.

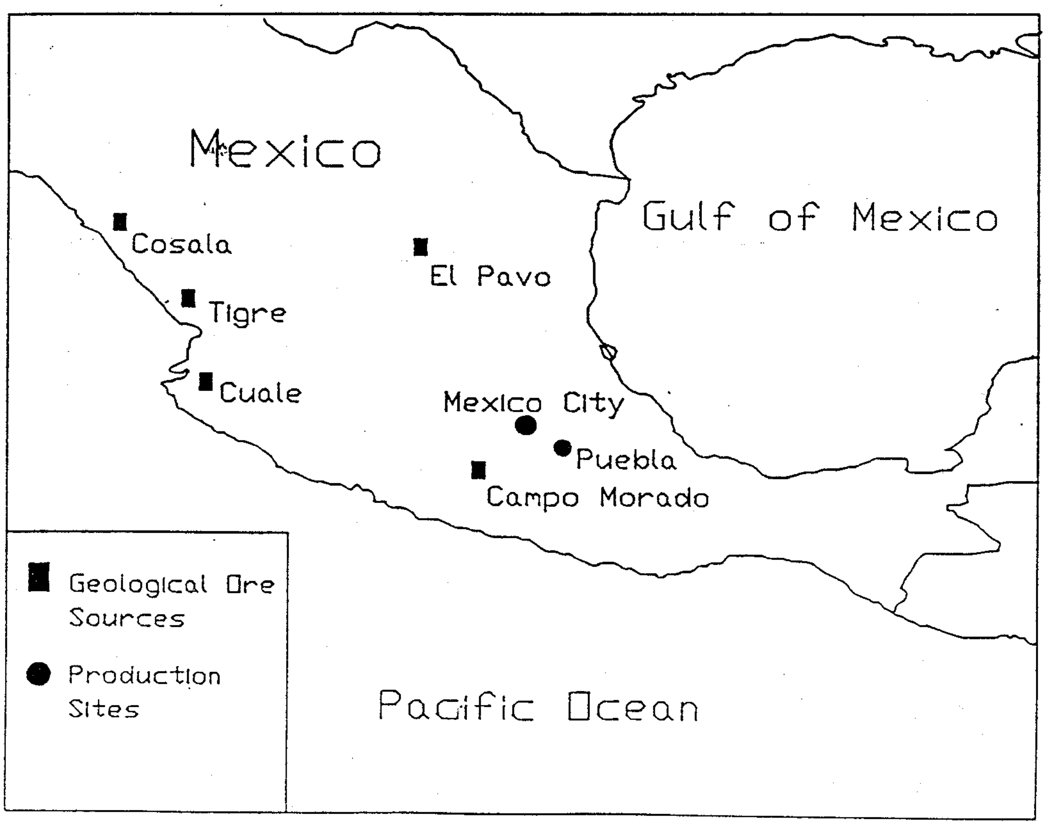

Figure 3. Map of some of the geological ore sources in Mexico.

Table 2. Lead isotope ratios of Majolica pottery.

SPANISH AND SPANISH COLONIAL

CAL#	NBS#	208/206	207/206	204/206
COLUMBIA PLAIN, CONVENTO DE SAN FRANCISCO, DOMINICAN REPUBLIC				
SA 11	1750	2.112336	0.858419	0.054957
SB 86	1837	2.113174	0.858735	0.055050
SB 87	1838	2.115698	0.858451	0.055087
SB 88	1839	2.107130	0.856170	0.054798
SB 89	1840	2.115070	0.859023	0.055094
SB 90	1841	2.114698	0.858790	0.055141
SB 93	1842	2.106919	0.857294	0.054781
YAYAL BLUE ON WHITE, CONVENTO DE SAN FRANCISCO, DOMINICAN REPUBLIC				
SB 70	1830	2.113347	0.859190	0.055053
SB 73	1831	2.112311	0.858659	0.055022
SB 78	1832	2.111841	0.859143	0.054909
SB 79	1833	2.117080	0.859174	0.055098
SB 80	1834	2.109962	0.859276	0.054963
SB 81	1835	2.108861	0.857539	0.054918
SB 82	1836	2.112046	0.859137	0.054928
COLUMBIA PLAIN, LA VEGA VIEJA, DOMINICAN REPUBLIC				
SD 55	1855	2.113743	0.859202	0.055048
"ALAFIAS ARABES", LA VEGA VIEJA, DOMINICAN REPUBLIC				
SD 58	1851	2.113314	0.858269	0.054930
SD 59	1852	2.113552	0.858324	0.054989
COLUMBIA PLAIN, NUEVA CADIZ, VENEZUELA				
SA 18	1751	2.117006	0.859025	0.055105
SB 60	1826	2.114176	0.859044	0.055088
SB 61	1827	2.115363	0.858432	0.055074
SB 62	1828	2.113838	0.858803	0.055081
SB 66	1829	2.112382	0.858435	0.054983
YAYAL BLUE ON WHITE, NUEVA CADIZ, VENEZUELA				
SB 52	1823	2.111618	0.857951	0.054917
SB 55	1824	2.115111	0.859160	0.055021
SB 56	1825	2.108525	0.857585	0.054885
YAYAL BLUE ON WHITE, CUBAGUA, VENEZUELA				
SB 29	1755	2.112542	0.858973	0.055062
SEVILLA WHITE, METROPOLITAN CATHEDRAL, MEXICO CITY				
SC 26	1762	2.112789	0.859003	0.055014
SC 27	1763	2.110239	0.859099	0.055007
YAYAL BLUE ON WHITE, SURFACE FINDS, JEREZ, SPAIN				
SD 08	1769	2.104848	0.856368	0.054795
SD 11	1770	2.105975	0.856831	0.054820
SD 17	1771	2.105507	0.856760	0.054820

COLUMBIA PLAIN, PUREZA KILN SITE, SEVILLE, SPAIN

PU1712	1987	2.115606	0.859472	0.055009
PU1825	1988	2.106449	0.857397	0.054806
PU1869	1989	2.106919	0.857514	0.054783
PU1874	1990	2.117771	0.859583	0.055121
PU2049	1991	2.115260	0.858534	0.055057

SPANISH COLONIAL

COLUMBIA PLAIN, CONVENTO DE SAN FRANCISCO, DOMINICAN REPUBLIC

SA 01	1750	2.087931	0.848492	0.054285
SA 03	1820	2.088737	0.848724	0.054327

COLUMBIA PLAIN, LA VEGA VIEJA, DOMINICAN REPUBLIC

SA 51	1752	2.087697	0.849124	0.054220
SA 58	1822	2.087812	0.849476	0.054290
SD 54	1847	2.088379	0.849297	0.054252

COLUMBIA PLAIN, CUZCO, PERU

SB 43	1759	2.081293	0.845212	0.054092

UNIDENTIFIED TYPE, LA CALLE JUAN BARON, DOMINICAN REPUBLIC

SD 51	1844	2.086951	0.847822	0.054208

BLUE OVER WHITE, PLAZA OF THE PRIESTS, DOMINICAN REPUBLIC

SD 52	1845	2.087128	0.848658	0.054274

BLUE ON BLUE, PARQUE COLON, DOMINICAN REPUBLIC

SD 56	1849	2.085122	0.848907	0.054365

BLUE ON BLUE, LA CALLE JUAN BARON, DOMINICAN REPUBLIC

SD 57	1850	2.080506	0.846043	0.054157

MEXICAN

UNIDENTIFIED TYPE, METRO EXCAVATIONS, MEXICO CITY

SB 27	1754	2.069443	0.837875	0.053448

UNIDENTIFIED TYPE, CUBAGUA, VENEZUELA

SB 36	1756	2.076822	0.841122	0.053785

MEXICO CITY WHITE, METROPOLITAN CATHEDRAL, MEXICO CITY

SC 12	1765	2.069270	0.837677	0.053466
SC 13	1966	2.067559	0.837094	0.053495
SC 16	1760	2.069708	0.837934	0.053431
SC 17	1967	2.066139	0.837192	0.053549
SC 20	1968	2.071414	0.839357	0.053635
SC 21	1969	2.068963	0.837586	0.053554
SC 22	1970	2.069632	0.837890	0.053451
SC 24	1971	2.074012	0.840180	0.053574
SC 25	1761	2.067230	0.837109	0.053505
SC 28	1764	2.067727	0.837460	0.053476

SC 29	1972	2.067677	0.837321	0.053488
SC 30	1973	2.069795	0.838348	0.053538
SC 57	1974	2.072108	0.839518	0.053628
SAN JUAN POLYCHROME, METROPOLITAN CATHEDRAL, MEXICO CITY				
SC 37	1765	2.071384	0.838875	0.053514
SC 37	1975	2.071342	0.838835	0.053482
SC 38	1766	2.071865	0.839395	0.053585
SC 38	1976	2.072414	0.839580	0.053595
SC 40	1977	2.071592	0.838993	0.053493
SC 42	1978	2.071969	0.838986	0.053496
SC 43	1979	2.068824	0.838551	0.053583
SC 46	1981	2.066729	0.837268	0.053557
SC 47	1982	2.067261	0.837639	0.053556
SC 48	1983	2.071479	0.838731	0.053500
SC 50	1984	2.071503	0.838598	0.053436
SC 52	1986	2.070254	0.837813	0.053461
VALLE WARE, METROPOLITAN CATHEDRAL, MEXICO CITY				
SC 62	1768	2.067753	0.837340	0.053501
SAN LUIS POLYCHROME, PARQUE COLON, DOMINICAN REPUBLIC				
SD 50	1843	2.068385	0.838376	0.053555
PUEBLA POLYCHROME, PARQUE COLON, DOMINICAN REPUBLIC				
SD 53	1846	2.076862	0.841461	0.053749

MEXICAN ORE DEPOSITS, (CUMMING ET AL.)

CAL#	OTHER #	208/206	207/206	204/206
		CUALE		
CUM005	CL-CS	2.069605	0.838213	0.053625
		CAMPO MORADO		
CUM007	CM	2.072959	0.839779	0.053568
		TIGRE		
CUM012	TIG	2.066663	0.836689	0.053545
		COSALA		
CUM020	CSL-LA	2.066949	0.837036	0.053645
CUM021	"	2.068132	0.837095	0.053605
CUM022	"	2.068656	0.837565	0.053680
		EL PAVO		
CUM057	M-EP-LY	2.067160	0.837862	0.053599