PIXE and Ionoluminescence for Mesoamerican Jadeite Characterization

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Abstract. Greenstones were highly appreciated in pre-Hispanic Mesoamerica. Most of the finest green artefacts were worked in jadeite and other minerals such as serpentine and nephrite. Jadeite is perhaps the most precious stone of the jade family in ancient Mesoamerica, and it was widely used and traded since the Preclassic Horizon (1500 B.C.). The main beds are located in the Maya region, in the Motagua area of Guatemala. In this work, three pieces of a necklace of greenstones from an offering discovered in an extensive excavation carried out in the palatial structure of Xalla, at Teotihuacan site, in the central highlands of Mexico, were studied using external beam PIXE. The aim of this study is to determine the elemental composition of the greenstones and to establish the sourcing, trade and relationship between these regions. The offering corresponds to the early Miccaotli period (around 155 A.D.). The necklace is composed by eleven round pieces of green colors ranging from light to dark green. The analysis of three pieces was compared with several samples from Manzanal sources of Motagua. Green luminescence of high intensity was observed in the archaeological pieces but only in one case the luminescence was blue-violet. When comparing with the mineral samples of other green minerals, only the jadeite presented the green and violet luminescence. The corresponding spectra were obtained by proton induced luminescence in vacuum on the mineral samples. The comparison of the elemental composition of the archaeological items and the known mineral samples indicates that only one archaeological piece is related to the Manzanal source. The luminiscence spectra, corresponding mainly to Mn^{2+}, Ce^{3+} and Al^{3+} emissions, are discussed. No correlation was observed among light emission color and jadeite sources.

Keywords: Jade, Jadeite, Teotihuacan, Mesoamerica, PIXE, Ionoluminescence, Motagua

INTRODUCTION

Greenstones were highly appreciated in pre-Hispanic Mesoamerica. Most of the finest green objects were worked in jadeite and other green minerals. Jade term refers to two types of metamorphic rocks formed from serpentine: Jadeite and nephrite. Nephrite ($Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$) is the amphibole jade rich in Ca and Mg. In contrast, Jadeite is the Na rich pyroxene jade: $Na(Al,Fe^{3+})Si_2O_6$. Common impurities in this mineral include Ti, Mn, Mg, Ca, K and Cr. Jadeite usually occurs as a grayish green rock, but it can be found as white, blue gray and mauve varieties. Green jade is the most popularly recognized color althought it is the less common. PIXE combined with other techniques has shown good results for jadeite and nephrite characterization [1-2].

Green jadeite is perhaps the most precious stone of the jade family in ancient Mesoamerica, and it was widely worked and traded since the Preclassic Horizon (1500 B.C.) [3]. In fact, there is only one known region source of jadeite in the Mesoamerican area. The main beds are located in the Maya region, spread in the Motagua area of Guatemala and Honduras [4].

In this work, some pieces of a necklace of greenstones from an offering discovered in an extensive excavation carried out in the palatial structure of Xalla (in the project »Teotihuacan: elite and government«, directed by L. Manzanilla) [5] at the ancient metropolis of Teotihuacan, capital of the most important civilization in the central highlands of Mexico during the Classic period, were studied using our external beam PIXE. The 11 huge beads (with diameters from 2.1 to 4.8 cms.) were carefully set in a very early small pit between two substructures,

together with *Spondylus princeps* shells and a marine gasteropod [6]. The offering corresponds to the early Miccaotli period (around 155 A.D.) The necklace is composed by eleven round pieces of green colors ranging from light to dark green. The elemental analyses of three beads were compared with several samples from Motagua sources of Guatemala and other green minerals samples commonly used in Mesoamerica. The aim of this study is to determine the elemental composition of the greenstones and to establish the sourcing, trade and relationship between these regions.

Ionoluminescence (IOL) was observed in both jadeite mineral samples and archaeological objects. IOL spectra were obtained in vacuum by proton irradiation only for jadeite source samples. Since luminescence of minerals is related to specific trace elements this approach may complete the PIXE measurements for mineral studies [7].

ANALYTICAL APPROACH

Three archaeological samples and three samples from two sources of the Motagua River area were analyzed by PIXE using the external beam setup of the Pelletron Acelerator. Two detectors are used for X-ray detection. The first one, optimized for light elements detection, is a Si-Pin Amptek detector of 150 eV resolution for Mn-K$_a$ line with a 1 mm dia. Ta collimator. A He jet improves the detection of low energy X-rays. For heavier elements detection, a LEGe detector with a 155 µm al filter was used. The energy of the 1.5 mm dia. proton beam was 3 MeV.

Before PIXE measurements, a fragment of a mineral sample of jadeite from Motagua River area was powdered and measured by X-ray diffraction and X-ray Fluorescence in order to determine the mineralogical and elemental composition. This jadeite sample was used as reference material for PIXE measurements. NIST SRM 2704 and SRM 2711 of sediments were irradiated as well under similar conditions for calibration of the system and measurement of X-ray detection efficiency. To measure the elemental concentrations, AXIL code and the PIXEINT program were used.

After the PIXE analysis, luminescence induced by a 3 MeV proton beam (IOL) was performed in vacuum using an optic fiber coupled UV-VIS spectrometer as it is described in ref. [8]. IOL is a natural complementary tool for PIXE analysis. The objective of this study was to characterize the light emitted during the proton irradiation of the archaeological pieces and mineral samples Figure 1 shows the high intensity of the green light emission during the external beam irradiation. The objective of this experiment was to determine if there is a correlation among the light emission and the presence of specific elements correlated to the provenance and sources.

SAMPLES

Three round pieces of different colors from the Xalla necklace were selected for PIXE analysis. Their colors ranged from light to dull green. Since jade minerals usually are heterogeneous, each piece was irradiated in three different regions in order to obtain more representative results.

On the other hand, one sample of jadeite from Manzanal source (Ma) in the Motagua River area and one jadeite samples from the same region (VM) but from a different source were irradiated under the same conditions in three regions as well. Only mineral samples were used for IOL studies.
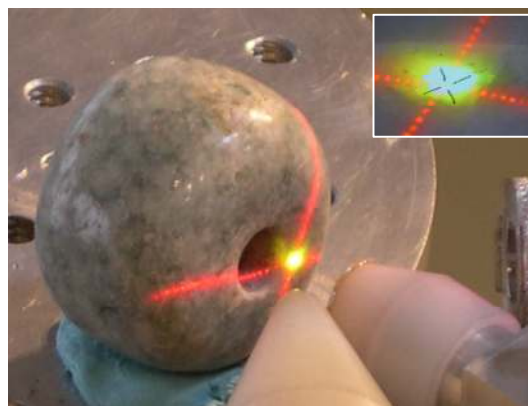

FIGURE 1. Ionoluminescence observed in the jadeite items.

RESULTS

PIXE analyses

In the archaeological pieces and mineral samples, 17 elements were detected: Mg, Al, Si, Cl, K, Ca Ti, Mn, Fe, Cr, Ni, Zn, Ga, Rb, Sr and Zr, but Hg traces were observed only in the archaeological pieces. Since the pieces are from an offering, the Hg origin may be related to cinnabar remains. Due to the low efficiency of the system Na was not detected. The use of the powdered jadeite sample and its elemental composition from XRF measurements was then relevant to estimate that Na contents of the samples may reach 10%. Low Mg contents fit the expected general composition for jadeite and indicate that the pieces are not nephrites or serpentines.

Table 1 shows the results of the analyses. With exception of K, the Manzanal results agree with previous reports of elemental concentrations (Mg 0.72%, Al, 12.5% Si 27.2%, Ca 1.28%, K 0.15%, Ti 0.024%, Mn 0.031%, Fe 1.05%, Na 9.5%) [9].

We can observe that Manzanal and archaeological samples do have Cl contents but Ti, Cr Rb and Zr are not randomly present. For this reason, factor analysis

of the logarithm of the data was applied in order to show the clustering among archaeological pieces and mineral samples. Figure 2 shows the corresponding statistical results. Piece C clusters clearly with the Manzanal sources while pieces A and B do not. Nevertheless, these pieces have a similar composition mainly differentiated by Cr and Ti trace contents. Since the composition of major elements and minor elements of the archaeological pieces are very similar, we may expect that their probable provenance may be related to other mineralogical sources from the same area, but further analyses on jadeite mineral samples from other sources of this region are required [10].
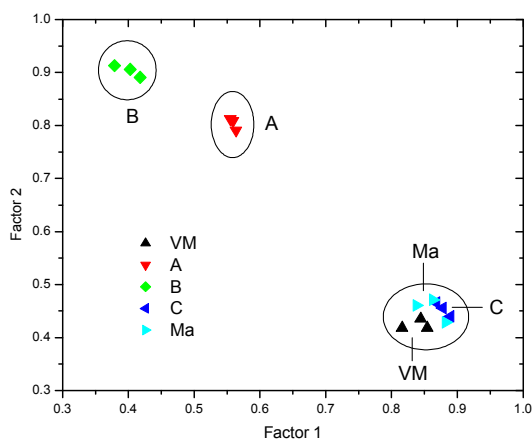

FIGURE 2. Clustering from PIXE data after factor analysis.

Ionoluminescence of Jadeite

Green and violet luminescence was observed in mineral samples and archaeological items. Only the archaeological piece A showed a medium intensity blue-violet luminescence while a very bright green light emission was observed in pieces B and C. The mineral samples showed violet and green luminescence in specific areas of the beam spot. Zoning evidences various sequences of crystallization and fluid sources during the rock formation [11]. The jadeite samples were set on regions of higher luminescence in order to collect specific color emissions.

The IOL spectra are showed in figure 3. Since luminescence emission is independent on the excitation method, recent reported data on Cathodo-luminescence were used to interpret the spectra [11]. In the case of jadeite regions of light green color, the IOL spectra shows a high intensity peak centered in 580 nm (green) and a very low emission in the 330 nm region. The 580 nm emission can be related to Mn^{2+} as activator. In the medium green color regions of the sample there is dominant emission between 320 and 450 nm that correspond to the blue-violet light color.

The observed band can be linked to Ce^{3+} and Al^{3+} emissions at 330 and 420-450 nm, respectively. In the dull green regions of the mineral the green and violet light emissions are reduced. Since Fe is present in higher amounts in the darker regions, Fe^{3+} may be acting as inhibitor, although in the greener regions there is a very weak emission in the red region (700 nm) that can be related with Al^{3+}, Ti^{4+} and Ca^{2+}. In all the cases, Ce was not detected by PIXE but its emission was clearly observed by IOL. Detection limit of Ce for our system is 80 µg/g. From the IOL observations, there is not a direct correlation among the light color emission and the provenance of the jadeite. Moreover, further analysis of other green minerals, such as nephrite, and serpentine, lizardite, antigorite, did not show any luminescence, this probably due to the higher amounts of Fe in their compositions.
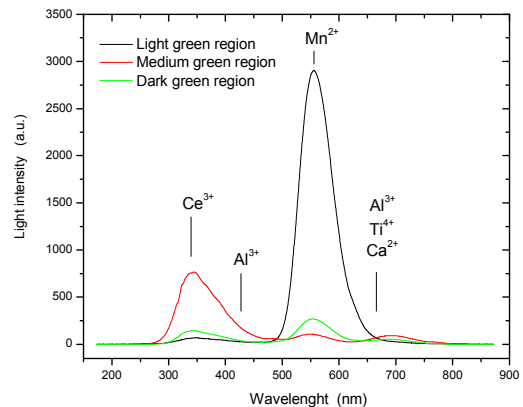

FIGURE 3. IOL spectra for various regions of jadeite.

CONCLUSIONS

PIXE analysis is a suitable method for non destructive study of jadeite for provenance purposes. Besides the heterogeneity of the archaeological and mineral items it was possible to determine that the archaeological piece C corresponds to the Manzanal source of the Motagua River area. Pieces A and B may have a Motagua River provenance but probably from other sources. Further analyses of other beds are required to establish the provenance of these pieces.

IOL green emissions in jadeite are related to Mn^{2+} while the violet one is due to Ce^{3+} and Al^{3+} emissions. Since pieces B and C showed only a high intensity green light emissions while a violet light was observed for piece A, the provenance may not be directly correlated to the color of the emitted light. However, only jadeite samples showed luminescence. Further measurements for other sources are necessary.

TABLE 1. PIXE results of the archaeological pieces and the jadeite sources samples. Average uncertainties for major and trace elements are 10 and 20%, respectively.

Sample	Mg	Al	Si	Cl	K	Ca	Ti	Mn	Fe
	%	%	%	µg/g	µg/g	%	%	µg/g	%
VM1	0.51	11.5	24.8	-	239	1.24	0.209	303	1.23
VM2	0.81	12.6	28.4	-	350	1.41	-	189	0.52
VM3	0.38	13.3	27.8	-	506	0.99	-	206	0.79
A1	0.88	12.6	26.6	24	417	1.45	0.154	151	0.77
A2	0.91	13.0	26.3	38	477	1.30	0.063	185	0.81
A3	0.56	11.5	24.4	57	917	1.59	0.134	224	0.96
B1	0.62	12.1	25.5	40	620	1.58	-	340	0.81
B2	0.99	10.3	22.9	52	612	2.14	-	415	1.01
B3	0.61	9.9	22.4	174	1088	2.21	-	392	0.9
C1	0.85	13.2	26.5	56	644	1.28	0.110	264	0.72
C2	0.28	14.0	28.4	69	723	0.94	0.059	159	0.51
C3	0.45	14.8	29.1	51	612	0.70	0.074	201	0.5
Ma1	0.23	13.3	26.9	44	502	0.91	0.152	240	0.87
Ma2	0.35	12.4	26.7	58	533	0.93	0.239	195	0.94
Ma3	0.10	14.3	28.7	63	467	0.67	0.067	155	0.66

Sample	Cr	Ni	Cu	Zn	Ga	Rb	Sr	Zr	Hg
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
VM1	-	18	5	27	14	-	37	64	-
VM2	-	26	8	17	15	-	179	-	-
VM3	-	22	5	43	20	-	18	84	-
A1	-	15	4	21	25	10	17	215	-
A2	-	18	7	14	35	12	15	742	22
A3	-	18	4	26	30	11	19	233	8
B1	155	31	5	46	22	5	20	105	36
B2	94	34	4	36	19	3	15	96	22
B3	145	27	5	51	16	7	26	111	28
C1	-	26	8	30	21	8	10	115	22
C2	-	22	11	52	21	-	13	170	174
C3	-	23	11	54	26	-	10	203	137
Ma1	-	20	14	106	20	-	34	176	-
Ma2	-	19	14	68	15	-	31	-	-
Ma3	-	23	19	131	20	-	31	173	-

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