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A R T I C L E I N F O

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ABSTRACT

In Mesoamerica, dead bodies were often smeared with red pigment, either hematite or cinnabar. Most archaeological remains include bones whose surface may be red colored. Being cinnabar a mercury compound whose chemical formula is HgS, it is not clear if Hg ions diffuse into the hydroxyapatite lattice. In this work we found that cinnabar is not easily dissociated and, therefore, ions from cinnabar spread after death, if any, do not diffuse into hydroxyapatite.

However, in bones from the archaeological site of Ranas, close to Querétaro, Mexico, we found Hg ions in interstitial positions of the bone hydroxyapatite lattice. Ranas was a cinnabar mining zone. Hence, the presence of Hg ions in bone hydroxyapatite lattice cannot be due to *post mortem* rituals and it has to be attributed to breathing or swallowing of mercury vapors or solutions during life. It is, then, a case of poisoning with mercury, probably due to exposition to vapors originated in the mine exploitation or to contaminated food.

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1. Introduction

Pigments are often constituted by toxic compounds, among them cinnabar, a compound of sulfur and mercury (Batta et al., 2013; Martín-Gil et al., 1995). Their manipulation and exploitation, as well as their use, is at the origin of environmental pollution and people poisoning. Indeed, body painting, breathing in pigment mines, toxic food (polluted by colored dishes or kitchen tools), among other habits were and are frequent in indigenous people and ancient cultures (Díez, 2009; Lombardi et al., 2012).

In Mesoamerica, it is common to find skeletons covered or stained by red pigments independently of location or period; red color was related, among many other meanings, to underworld (Scherer, 2012). For instance, in Palenque, the Red Queen (Maya culture, 600–900 AC) was covered by a thick layer of red pigment (Gonzalez Cruz, 2011). In Oaxaca, at Monte Albán, Atzompa (Zapotec culture 500 BC–700 AC), a burial covered by a red pigment was reported. In Teotihuacán, in the Xolalpan phase (*ca.* A.D. 400–650) the body of an adult was partially exposed to fire and red pigment was applied to the body (Burial 114 Tet 9) (Sempowski, 1999).

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Although red dyes as Cochinilla or as Palo de Campeche were produced and used in Mesoamerica, they were not at the basis of funerary red pigments which were, mainly, hematite (Fe₂O₃), or cinnabar (HgS), or both, as in Jaina (Batta et al., 2013). The most precious was cinnabar, generally found in a massive, granular, or earthy form; the color is bright scarlet to brick-red. Cinnabar was distinctive of high social hierarchies as in the tomb of the king of Calakmul, Campeche, Yuknom Yich'ak K'ak also known as Jaguar Paw. There, cinnabar covered everything, the ruler shroud as well as grave goods or tomb mural paintings. Note that cinnabar has been sought since the Neolithic Age (Martín-Gil et al., 1995). In Mesoamerica it was mined in the Sierra Gorda de Querétaro (Lazcano Sahagún, 1986) from 200 to 300 AD. Cinnabar is a very stable compound which is not easily dissociated; it is an extremely insoluble solid with a solubility product of $10^{-36.8}$ for the reaction (Ravichandran et al., 1998):

 $HgS \leftrightarrow Hg^+ + S^-$

Only at high temperature or in contact with acids, $\mathrm{Hg^{+}}$ and $\mathrm{S^{-}}$ ions are produced.

Cinnabar colored bones are red and even after washing they maintain some pigmentation. The interaction of cinnabar with human body has been discussed in previous works (Batta et al., 2013). It remains undissociated on corpse surface and then on bone surface.



It has been proposed that cinnabar "preserves" bone, and a longterm antibacterial activity of HgS has been suggested (Cervini-Silva et al., 2013). In post mortem contact between cinnabar and human bodies no strong interaction between hydroxyapatite and HgS has been observed. Indeed, cinnabar, to interact strongly should be dissociated into mercury and sulfur ions. Those ions, if any, would be trapped in hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ which is the mineral component of bone. Hydroxyapatite is prone to retain heavy metals, among them Hg, through substitution of calcium, forming for instance Hg₃(PO₄)₂ (Lee et al., 2005; Oliva et al., 2011). Hence, if mercury is found in buried bones and teeth it cannot come from the cinnabar covering; it must be due to poisoning from mercury vapors or toxic food (polluted by colored dishes, kitchen tools or environment). If Hg⁺ is swallowed or inhaled, it should be mainly trapped by enamel which is constituted by ca. 96% of hydroxyapatite; collagen in enamel is considerably lower as compared to that in dentin (Acil et al., 2005). If Hg⁺ ions are on the body, they may be absorbed through skin and access bones.

In this work we characterize red teeth and bones, first to identify the pigment and then to study the interaction of that pigment (most probably cinnabar) with archaeological hydroxyapatite. The purpose is to differentiate individuals who, *post mortem*, were exposed to pigment from those whose activity was related to pigment exploitation and, thus, were exposed during their life to Hg⁺ ions, either as vapors or as ions incorporated into toxic food. The difference must be given by the trapping of metal ions by hydroxyapatite. For this study, bones and teeth from well-defined origin were chosen.

On the one hand, bones from Tlatelolco, Jaina and Monte Albán were selected as they were in *post mortem* contact with red pigment, independently of epoch and culture, and, on the other, red bones from Ranas which must have been exposed *in vita* to mercury and its compounds as it has been reported that in Ranas, a site close to Querétaro (Sierra Gorda), cinnabar was intensively exploited (Langenscheidt, 2006; Mejía Pérez Campos and Herrera Muñoz, 2006).

2. Archaeological context

2.1. Mining

The archaeological interest of the present investigation is to determine if there were human groups exposed and poisoned by mercury. If so, were they miners? In ancient Mexico, opencast mines are the most frequent, for instance in La Joya (Jalisco) there are 1264 *fosas* (mines) of this type; in the Sierra de las Navajas (obsidian exploitation) they are named *cráteres*; a large number of extraction *fosas* has been reported in Zinapécuaro and Zinapécuaro-El Prieto (Suyuc Ley et al., 1998). There was also underground mining with tunnel, galleries and wells as those located in the Pico de Orizaba (Veracruz), Otumba (Mexico City valley) and the Cerro de las Navajas (Pachuca) (Pastrana, 1986; Tenorio et al., 1998).

Mining, in the Sierra Gorda, had the purpose to extract cinnabar, using stone tools as hammers with handles, grooved hammers and grinding stones among others (Craddock et al., 2002). From 200-300 to 1300 AD, cinnabar was exploited in the Sierra Gorda. Seven mines nearby Toluquilla have been excavated and 190 buried bodies were found. In the Ranas zone more or less twenty were found (Conaculta Bulletin, 2009; Mejía Pérez Campos and Herrera Muñoz, 2013).

2.2. Origin of the samples

The chosen teeth and red bones are from the archaeological sites presented in Fig. 1. Ranas, in the Sierra Gorda, is an area where

cinnabar mining was practiced; but, in Jaina, Monte Albán or Tlatelolco it was not. All samples present a red color on surface and there are no macroscopic features which differentiate them. Still, they belong to cultures very diverse in time and geographic site.

Most samples are from Ranas (*Serrana* culture) where the main activity was the exploitation of cinnabar. The location of Ranas site (200–300 to 1300 A.D.) was strategic. The *Serrana* Culture, which occupied the South portion of the Sierra Gorda, exploited the mineral resources, cinnabar and red ochre, and controlled the natural accesses to enter or exit from the Sierra Gorda. The mine economy, which consisted mainly on cinnabar commerce, is a rather exceptional case in Mesoamerica. As already mentioned, buried bodies have been found from which some red pigmented bones were selected.

For comparison purposes samples from different periods and societies were chosen, i.e. Jaina, Monte Albán and Tlatelolco. Jaina, a Mayan necropolis (classic Maya, 300–900 A.D.), is an island close to Campeche; it is very well known due to the exquisite clay figurines found there. After excavation, a large number of human bones from Jaina were deposited in the Museum of Anthropology of Mexico City. In a previous work (Batta et al., 2013) it was shown that red color, in Jaina bones, was due either to cinnabar or to hematite. Monte Albán (Preclassic Zapotec, 2000 B.C.-200 A.D.) is a complex urban site located on a low mountain rising above the plain, in the central section of the Valley of Oaxaca. It is one of the earliest cities of Mesoamerica and it was progressively abandoned ca. IX century A.D. Instead, Tlatelolco was founded as late as 13 years after Tenochtitlan, in 1337 A. D. Tlatelolco was the last bastion of Mexica power under Cuauhtémoc leadership, resisting more than 80 days without food or water. In August 13th, 1521, Tlatelolco fell under Spanish army, it was the end of Mexica history. Thus, bones come from periods which cover Preclassic to Postclassic and from Mayan culture (lowlands) to Serrana culture (mountains).

3. Experimental

3.1. Samples

Samples were selected from the most reddish areas of bones or teeth. The features and the origin of the various samples are summarized in Table 1. Five samples from Ranas were chosen as the most representative to be compared to other red colored samples from Mesoamerica. There are two molars, one from Jaina and the other from Tlatelolco, which may be compared to an incisive tooth from Ranas. A piece of skull from Monte Albán was chosen to determine the differences in Hg content between teeth and bones. It may be compared to four bone samples from Ranas. The samples were studied without any modification or treatment. Only, for some X-ray diffraction studies they had to be grinded to obtain the required powder.

3.2. Characterization techniques

Scanning electron microscopy reveals the morphology of the sample particles. If coupled to an energy dispersive spectrometer the local elemental analysis of the sample is obtained. Only elements with an atomic weight lower than carbon are not detected. It is then possible to analyze selectively the particles constituting the studied material. For Scanning Electron Microscopy/Energy Dispersive Spectrometry (SEM/EDS) studies, a JEOL JSM-7600F (Field Scanning Electron Microscope) coupled to an EDX Oxford INCAX-Act was used. The samples were studied at low (\times 1000) and high (\times 10,000) magnification. Note that the samples were not sputtered with any conductor material to avoid any further contribution to the EDS spectra.



Fig. 1. Location of the Ranas, Monte Albán, Tlatelolco and Jaina archaeological sites in Mexico.

The characterization by X-ray diffraction provides the identification of compounds. To observe a compound with this technique the sample content has to be higher than 3%, the compound has to be crystalline and the crystal size larger than 3 nm. X-ray diffraction patterns were recorded with a Brucker AXS Advance D-8 diffractometer coupled to a cobalt anode tube. The K α radiation was selected with a diffracted beam monochromator. The samples had to be powdered to mix them with an internal standard, corundum, to measure carefully the cell parameters of hydroxyapatite. As the samples were very small it was not possible to scratch the external zone of the bone, then they were totally powdered. The results therefore correspond to the full bone. Changes in the cell parameter values should point towards the presence of foreign atoms, in this case mercury, incorporated to the crystal lattice.

4. Results

4.1. Morphology

The micrographs obtained by scanning electron microscopy are compared in Figs. 2 and 3. They all present a rather smooth surface where very brilliant spots appear in samples J-molar, MA-skull and R-incisive. In samples from Tlatelolco, and from Ranas, R1, R2, and R4, those brilliant particles were not observed. In a micrograph, the particle contrast depends on the atomic weight of the elements constituting the compound. In this case the brilliant small particles, *ca*. 0.1–1 μ m, should contain a very heavy element. They do not have a defined shape but they clearly interact with the bone support.

4.2. Local elemental composition

The local elemental composition was determined by EDS, Fig. 4. In sample R2, the main identified elements were, as expected, calcium, phosphorus, mercury, sulfur and, of course, oxygen. However in R1, R3 and R4, the main elements were Ca, P, Al, Si and some Mg. Of course, Ca and P reveal hydroxyapatite presence, *i.e.* bone. Magnesium, iron, calcium and aluminum are due to soil aluminosilicates.

In Fig. 5 corresponding to sample R2, Hg and S were mapped. The same small particles that contain Hg also contain S. Thus, they are cinnabar particles.

Actually, the interesting values in this analysis are the atomic ratios which could give a hint on the compound. In this sense the ratio Ca/P should be close to 1.66 which is the expected value in hydroxyapatite and Hg/S should be 1 as in cinnabar. Table 2 compares the Ca/P and Hg/S ratios. The Ca/P ratio depends very much on the analyzed zone, as an example two values are reported in J-molar: Ca/P ratio varied between 1.91 and 5.03, in T-molar the range was 2.31–12.8, although most measurements were rather similar (1.5–1.9), the differences may be attributed to local deficiencies of phosphor or calcium; again, remember that this type of analysis is local. Samples with Ca/P *ca*. 2 are samples with a local decomposition of hydroxyapatite or with calcium minerals, as calcium carbonates, covering the surface.

The Hg/S ratio in the samples where mercury and sulfur were identified is 1.1, showing that, within error range, the corresponding compound must be cinnabar. The value obtained for Hg/S in J-

Table 1

Labeling of the samples studied in this work, the origin as well as the culture are specified.

Sample	Origin	Culture	INAH file	Description
J-molar	Jaina (Yucatán)	Classic Mayan	Cam. 1973,burial 29	Molar tooth
T-molar	Tlatelolco (Mexico City valley)	Postclassic Mexica	Burial 14 isolated	Molar tooth
MA-skull	Monte Albán (Oaxaca)	Preclassic Zapotec	Temp. VII	Skull fragment
			Grave A	
R-incisive	Ranas (Querétaro)	Preclassic Serrana	Plat. Sup.; Multiple burial between fireplace and bed E	Incisive tooth
R-bone	Ranas (Querétaro)	Serrana	Ranas 3. 1985	Tibia fragment
Sample R1				
R-bone	Ranas (Querétaro)	Serrana	Ranas 1, 1976	Fibula fragment
Sample R2				
R-bone	Ranas (Querétaro)	Serrana	Ranas 1. 1976	Femur fragment
Sample R3				
R-bone	Ranas (Querétaro)	Serrana	Ranas 2, 1984	Humerus fragment
Sample R4				



Fig. 2. Differences in sample surface morphologies: a) [-molar, b) MA-skull, c) T-molar and d) R-incisive.

molar is too low, it has a large error; this sample also showed zones enriched in Fe attributable to Fe_2O_3 or simply to iron containing minerals present in the environment. These measurements show that only some samples are covered by cinnabar particles. To validate these results, they may be complemented with X-ray diffraction based techniques which always provide a statistically valid composition. Note that all samples from Ranas, excepting sample R2, do not present Hg or S, and, therefore, do not contain cinnabar on their surface.

4.3. Compounds

The X-ray diffraction patterns of samples J-molar, T-molar, MAskull, and R-incisive are compared in Fig. 6. The Tlatelolco sample, T-molar, is a highly crystalline hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ whose composition must be calcium enriched as shown by the EDS results, again, as already mentioned in the EDS analyses no Hg compounds appear. The Jaina sample, J-molar, is mainly constituted by crystalline hydroxyapatite, although defined and intense peaks of calcium carbonate were identified, showing that, in this molar, the amount of adhered calcium carbonate particles is very significant. No cinnabar is identified; therefore the small amount of Hg and S reported in EDS study is not significant. The sample from Monte Albán, MA-skull, not only shows the expected hydroxyapatite, a high amount of non-crystalline material appears revealed by the bump from 15 to 38° (2 θ) which can be attributed to organic material as well as to amorphous alumino-silicates present in earth. Still, the most interesting feature in this diffractogram is the intense peak at *ca*. 26.5° (2 θ) due to cinnabar, HgS, which must be present as large crystals; in the EDS analysis Hg and S were also observed. For the R-incisive, as the differences in color were notorious between root and crown, a diffractogram corresponds to the first zone and another one to the other. They both present only hydroxyapatite and a large amount of non-crystalline compounds.

X-ray diffraction patterns of bone samples (MA-skull, R1, R2, R3, and R4) present hydroxyapatite as the main compound. In some



Fig. 3. Morphology of the brilliant particles (higher magnification) present in samples a) J-molar and b) MA-skull.



Fig. 4. EDS spectrum (right) of the particle labeled with "spectrum 1" present in the image (left) of sample R2. Sulfur and mercury are clearly identified. Al and Si are attributed to the aluminosilicates which constitute environmental soil.



Fig. 5. EDS mapping of b) sulfur and c) mercury present in image a). Hence, particles containing Hg and S are present on the surface of this sample (R2).

cases a crystalline phosphate, Na₂Mg₅(PO₄)₄.7H₂O, attributable to a partial decomposition of bone in earth, is observed. Note that cinnabar was not detected in bones, only sample R2 shows a very small amount. The identification of compounds by X-ray diffraction for all samples is summarized in Table 3 and compared to the corresponding EDS results.

To determine if Hg or S were incorporated into the hydroxyapatite structure the cell parameters were measured. Indeed, the presence of another ion, such as Hg whose size is different, should expand or contract the network. The Pauling radii are 0.099 nm for calcium and 0.102 nm for mercury, therefore the cell should be expanded if mercury enters hydroxyapatite network and X-ray diffraction peaks should shift towards smaller angles. From those peaks, knowing that the hydroxyapatite lattice is hexagonal, the cell parameters may be determined. Figs. 7 and 8 compare the hydroxyapatite peak positions referred to the corundum peak at 35.15° (2 θ). As the sample from Tlatelolco does not contain cinnabar as already shown by EDS and X-ray diffraction it may be used as a reference. Peaks of sample R-incisive root are located in the same position as those of Tlatelolco sample. In the pattern of sample J-molar, peaks at 32.2 and 31.72° (2 θ) are not resolved, thus

Table 2

Elemental composition as determined by EDS. Ca/P of hydroxyapatite is ideally *ca*. 1.66 and Hg/S in cinnabar *ca*. 1.0.

Sample	Ca/P (Atomic ratio)	Hg/S (Atomic ratio)
J-molar	1.91 and 5.03	0.62
T-molar	2.31 and 12.8	No Hg, no S
MA-skull	2.32 and 1.93	1.02
R-incisive	1.78	No Hg, no S
R1-tibia	1.64	No Hg, no S
R2-fibula	1.81	1.13
R3-femur	1.53	No Hg, no S
R4-humerus	Only aluminosilicates	No Hg, no S

it was not possible to determine the cell parameters with the required precision. Instead, the pattern of sample R-incisive (crown) not only presents peaks located at the same angles as the sample from Tlatelolco, but peaks at smaller angles are also observed, hence two interplanar distances are present in the same structure, *i.e.* two sets of cell parameters should characterize this material.

Table 4 compares the cell parameters which were determined from the X-ray diffraction peaks 300 and 211 of Figs. 7 and 8 using as internal standard the 35.15° (2 θ) corundum reflection. Hydroxyapatite structure is hexagonal, therefore, only two parameters *a* and *c* describe it. The values reported in the X-ray diffraction JCPDS card (card number 01-084-1998) are a = 9.416 Å and c = 6.884 Å. The obtained values for T-molar sample are slightly lower; still, the difference is within error range, it is then a good reference which presents the unaltered hydroxyapatite values. Sample MA-skull presents larger parameters showing that the network of hydroxyapatite is enlarged. This effect is much more evident in the two samples R-incisive. It is interesting to note that R-incisive (crown) sample presents two degrees of deformation, revealed by the ratio a/c, and therefore two sets of cell parameters. Most probably the larger ones correspond to the external layers of the tooth and the other to internal layers. Furthermore, the values for internal layers are similar to those of R-incisive (root).

5. Discussion

Results show that samples from Ranas, in different degrees, present evident deformations in the hydroxyapatite unit cell. Instead the other samples show cinnabar particles on surface (samples T-molar, MA-skull and R2) but X-ray diffraction does not reveal any change in the cell parameters. However, there are samples, MA-skull and R2, which present both effects, *i.e.*, cinnabar on surface and change in the cell parameters.



Fig. 6. X-ray diffraction patterns of a) T-molar, b) J-molar, c) MA-skull, d) R-incisive (root), and e) R-incisive (crown).

If the cell parameters increase most probably some atoms of the crystalline network have been substituted by larger atoms. Hydroxyapatite is an ion exchanger and may incorporate ions as Hg into the hexagonal lattice evidenced by the cell parameters. No other metal than mercury was detected by EDS; thus, ions such as F^- have to be discarded. The ionic radii are 0.114, 0.110, 0.127 and 0.140 nm for Ca²⁺, Hg²⁺, Hg⁺ and OH⁻, respectively. If calcium is substituted by mercury, Hg²⁺ being slightly smaller, the cell parameters are expected to shorten; instead they increase. Hence, mercury ions, Hg²⁺ or Hg⁺, occupy interstitial positions. Such proposition could explain the differences in the deformation of unit cell, revealed by the values of a/c. Hg ions can reach the bones in two ways, either Hg ions were swallowed or breathed from some solution or gas containing them, or they diffused into bones after death. The last proposition has to be discarded as Hg ions cannot come from the cinnabar particles covering the skeleton as cinnabar is a very stable compound. In the first mechanism, bone has to be in contact with a solution or gas already containing mercury ions. It is worth mentioning that miners remained in the mine with little opportunity to wash. After returning to their huts, they transferred the dust to their living quarters and contaminated their families by chronic exposure and mercury absorption through the skin and food (Lombardi et al., 2012). Although chronic mercury poisoning very rarely seems to

Table 3

Comparison of X-ray diffraction and EDS results in bones and teeth.

Material	Sample	HgS		Other crystalline compounds	Non-crystalline compounds
		X-ray diffraction	EDS		
Teeth	T-molar	None	0%	Hydroxyapatite	None
	J-molar	None	Very small %	Hydroxyapatite and CaCO ₃ .	Very small %
	R-incisive (root)	None	0%	Hydroxyapatite	High %
	R-incisive (crown)	None	0%	Hydroxyapatite	High %
Bones	MA-skull	High %	High %	Hydroxyapatite	High %
	R1-tibia	None	0%	Hydroxyapatite,	None
				Na2Mg5(PO4)4.7H2O	
	R2-fibula	Small	High %	Hydroxyapatite	None
	R3-femur	None	0%	Hydroxyapatite	0%
	R4-humerus	None	0%	Hydroxyapatite	Very small
				$Na_2Mg_5(PO_4)_4.7H_2O$	-

cause pathological lesions in bones, levels of this metal in human remains are believed to stay relatively constant after death, and should still be there in archaeological bones (Rasmussen et al., 2013a; Tucker, 2007).

In addition, in a mercury rich environment, such as Ranas, the mechanisms by which mercury reaches body tissues are probably the same which are well described in reviews dealing with this toxic element (Diez, 2009): organic mercury (for instance, that contained in fish living in polluted areas) is absorbed from the gastrointestinal tract, bound to erythrocytes, especially to the sulfur atom of thiol ligands, and then metabolized to inorganic mercury and eliminated via the fecal route (in a very small amount and with a very slow rate of conversion), or stored in liver and kidney, as divalent mercury ion. So, it is not surprising that some mercury reached the teeth or the bone tissue of almost all people living in Ranas, not necessarily miners. Such mechanism may also explain the case of Monte Alban skull (air pollution from distant mines, temporal stay in a cinnabar-rich environment or toxic food).

Therefore, our results show that Hg must have diffused during the life of the individual. The ratio between the two cell parameters a/c reveals the deformation of the unit cell. In pure hydroxyapatite it is 1.367. In our samples it varies from 1.366 to 1.401 showing that,

with the insertion of Hg, the elemental cell dimension is increased preferentially in the **a** direction. Hg may be present inside the bone, onto the lamellae of the trabecular bone tissue making the overall concentration much higher (Rasmussen et al., 2013b).

To summarize, bones, if covered with cinnabar in a ritual manner, do not retain Hg whereas all bones from Ranas contain Hg ions into the hydroxyapatite lattice. Ranas is a zone where cinnabar was exploited; therefore, environment (air, water and soil) and food have been polluted by decomposed cinnabar. Mine workers, smashing rocks, could have produced cinnabar dissociation, the resulting ions may have been swallowed as vapors or may have contaminated soil, food, etc. Then, as already explained the mercury ions were breathed or swallowed in toxic food and ended up in hydroxyapatite structure. Hydroxyapatite cell parameters, determined by X-ray diffraction, are a clear criterion to determine possible cases of poisoning by heavy metals. This method is complementary to scanning electron microscopy and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) (Cucina et al., 2011).

Still, samples MA-skull and J-molar remain to be explained. Sample MA-skull presents cinnabar particles and expanded hydroxyapatite cell parameters. It seems then that the body was



Fig. 7. X-ray diffraction pattern in the interval 31–36° (2θ) of samples a) T-molar, b) J-molar, c) R-incisive (crown), and d) R-incisive (root). The peak at 35.15° (2θ) corresponds to corundum (internal standard) shown with a red bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. X-ray diffraction pattern in the interval $31-36^{\circ}(2\theta)$ of samples R1, R2, R3 and R4 compared to the T-molar sample. The peak at $35.15^{\circ}(2\theta)$ corresponds to corundum (internal standard) shown with a red bar. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

 Table 4

 Cell parameters determined from the position of hydroxyapatite peaks.

Sample	a (Å)	<i>c</i> (Å)	a/c
T-molar	9.423	6.892	1.367
MA-skull	9.536	6.981	1.366
R-incisive (root)	9.689	7.012	1.381
R-incisive (crown)	9.699 and 9.880	7.123 and 7.136	1.361 and 1.384
R1-tibia	9.448	6.76	1.397
R2-fibula	9.448	6.74	1.401
R3-femur	9.448	6.76	1.397
R4-humerus	9.450	6.81	1.387
JCPDS value	9.416	6.884	1.367



Fig. 9. Schema representing, in left hand side, bone poisoned with mercury ions and, in right hand side, bone with a cinnabar particle on top.

covered with cinnabar and that, in some unique circumstances (probably unusual acidity), some mercury diffused *post mortem* into hydroxyapatite; there is no reason to assume some poisoning in a zone where no cinnabar mines were exploited but poisoning from polluted dishes with some Hg containing pigment or toxic food is most probable. Sample R2, as well, presents cinnabar particles on surface and modified hydroxyapatite cell parameters. In this case, the individual, being from Ranas, may have been poisoned by Hg ions (cell parameters values) and due to a mortuary rite it was covered with cinnabar after death. In Fig. 9 the proposed structures are schematized. Either cinnabar is spread on top of bone

and a very low proportion, if any, dissociates to diffuse into hydroxyapatite, or either mercury poisons the individual and, then, mercury is distributed into hydroxyapatite lattice.

6. Conclusion

The study of representative human bones from Ranas showed that hydroxyapatite lattice contained Hg ions. Although Hg seems to substitute some calcium ions in the hydroxyapatite network, they are found, mainly, in interstitial positions altering unit cell dimensions. Such result is interpreted as a poisoning due to the exploitation of cinnabar mines or to poisoning through polluted dishes or toxic food. This proposition is confirmed if the Ranas bones are compared to skeletons from other Mesoamerican cultures whose rituals included the covering of remains with cinnabar. Indeed cinnabar is a very stable compound which hardly interacts with hydroxyapatite, the diffusion of mercury atoms into the bone through taphonomical mechanisms was not observed.

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