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## Study of worker's Exposure to Tantalum-bearing particles in a Mining and Metallurgical Plant

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<b>Abstract:</b>	<p>The objective of this study was to assess worker exposure to mineral dust particles and a metabolic model, based on the model adopted by ICRP, was applied to assess human exposure to Ta, and predicted values of Ta concentrations in excreta. The occupational exposure to Th, U, Nb, and Ta bearing particles during routine tasks to obtain Fe-Nb alloys was estimated using air samplers and excreta samples. Ta concentrations in food samples and in drinking water were also determined. The results support that workers were occupationally exposed to Ta bearing particles, and also indicate that a source of Ta exposure for both workers and the control group was the ingestion of drinking water containing soluble compounds of Ta. Therefore, some Ta compounds should be considered soluble compounds in gastrointestinal tract. Consequently the metabolic model based on ICRP metabolic model and/or the transfer factor f1 for Ta should be reviewed and the solubility of Ta compounds in gastrointestinal should be determined.</p>	
<b>Response to Reviewers:</b>	Dear Sir,	

We would to thank you for the suggestions. All suggestions were accepted.

The references were reviewed.

All questions were answered and the answers included in the manuscript.

The uncertainties were included in table 3.

Please find enclosed the revised manuscript.

Yours sincerely,

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## Study of Worker's Exposure to Tantalum-bearing Particles in a Mining and Metallurgical Plant

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### ABSTRACT

The objective of this study was to assess worker exposure to mineral dust particles and a metabolic model, based on the model adopted by ICRP, was applied to assess human exposure to Ta, and predicted values of Ta concentrations in excreta. The occupational exposure to Th, U, Nb, and Ta bearing particles during routine tasks to obtain Fe-Nb alloys was estimated using air samplers and excreta samples. Ta concentrations in food samples and in drinking water were also determined. The results support that workers were occupationally exposed to Ta bearing particles, and also indicate that a source of Ta exposure for both workers and the control group was the ingestion of drinking water containing soluble compounds of Ta. Therefore, some Ta compounds should be considered soluble compounds in gastrointestinal tract. Consequently the metabolic model based on ICRP metabolic model and/or the transfer factor  $f_i$  for Ta should be reviewed and the solubility of Ta compounds in gastrointestinal should be determined.

**Key words: uranium, thorium, tantalum, solubility parameters, and occupational exposure**

## INTRODUCTION

Tantalum (Ta) and niobium (Nb) are extremely scarce, but the modern world is dependent on these scarce metals. Nb and Ta are versatile refractory metals, and also show high resistance to corrosion. Due to their mechanical, thermal, and chemical characteristics the main applications of Nb and Ta include their use in superconducting materials, electronics, optics, numismatics and jewelry. Nb and Ta are also the basis for various super alloys and chemical compound used as dielectric coatings in telecommunications and small advanced electronics, such as cell phones, pagers and laptop computers, ballistics, and medical applications (Cardonne et al. 1995; Chaneliere et al. 1998; Cunningham 2001; Yen-Huei et al. 2003).

Geoscience Australia combined and averaged out critical metal ratings and found that tantalum was one of most critical metal (after rare earths, gallium, indium, tungsten, platinum group metals, and cobalt). Approximately 60% of annual world consumption of tantalum is used in the electronics industry, with more than half of this currently used in the manufacture of mobile phones. Additionally, there has been an average yearly growth rate of 8% to 12% in tantalum demand since about 1995, which has caused a significant increase in exploration for this element (Australian government, 2014).

Ta and Nb are chemically similar and occur in the same minerals in nature. The main Ta and Nb deposits in world are located in Australia, Canada, Brazil, and Central Africa, but the major Nb producers are Brazil and Australia. The primary Nb mineral is pyrochlore  $\text{Na}_2\text{Ca}_2\text{Nb}_2\text{O}_6(\text{OH},\text{F})$ , which also contains Ta, Th (thorium), and U (uranium) associated in the crystal lattice.

A mine and a metallurgical plant that process pyrochlore to produce Fe-Nb alloys, both located in the southwest of Goias state, Brazil, are the subject of the current study. The ore is extracted from an open-pit mine, which generates high dust concentrations, and airborne particles are also generated by the metallurgical process.

Due to chemical and radiological toxicities of Th and U, these elements have been studied extensively in connection with human health (Linsalata et al. 1991, Dias da Cunha et al. 1998 (a), Scapolant et al. 1998, WHO – 2001, Ansoberlo et al. 2002, Kurttio et al. 2002; Straddling and Hodgson 2002, Metzger and Cole 2004, Patocka et al. 2004, Pietrzak-Flis et al. 2005, Li et al. 2007). However there are very few studies about the effects of Ta on human health and their conclusions are contradictory: some showed that Ta is inert inside the human body (Blanco et al. 1974, Matthay, et al.1977), while Smith et al. (1976) showed that exposure to Ta particles for long periods caused damage in the alveolar region in the lungs, and Machlin et al. (1952) showed that tantalum hydroxide caused

hypertrophy of liver. In addition, some studies showed that the Ta half-life in the human body is of the order of years (Machlin et al. 1952; Nadel et al. 1968; Sill et al. 1969) but other show the Ta half-life in lungs is on the order of days (Llamas et al. 1969; Edmunds et al. 1970; Friedman et al. 1972; Gamsu et al. 1973). However, it should be highlighted that there are no data on the effects of human exposure to mineral dust particles containing Ta, and the limits on air concentration recommended by *American Conference of Governmental Industrial Hygienists* (ACGIH 1966) were based on data obtained from a single experiment using only five rats exposed to a lethal dose (Coulston et al. 1975). Recently, Lima et al. (2007) used simulated lung fluids to show that Ta solubility depends on mineral crystal structure, implying the necessity to determine the solubility of Ta present in each mineral.

The risk to human health caused by the incorporation of a specific element depends on the route of intake – ingestion, inhalation, or through the skin. In most situations the most important routes of intake are inhalation and ingestion. Inhalation is usually the most important for workers, since ingestion can readily be controlled in the workplace. Ingestion is often important for public exposure when elements enter the food chain. However the risk for human health depends, also, on the bio-kinetic behavior of each element, its concentration, and the physiological characteristics of each individual exposed (ICRP-30 1979, ICRP-54 1989, ICRP-56 1989, ICRP-66 1994, ICRP-78 1999, ICRP 2002). The *International Commission on Radiological Protection* (ICRP) has adopted models that describe the behavior of different radioactive nuclides in the human body (ICRP-54 1989, ICRP-56 ICRP-66 1994, ICRP-78 1999).

A summary of the general metabolic model adopted by ICRP, including the main pathways of intake, internal transfers, and route of excretion, is shown in *ICRP Supporting Guidance 3: Guide for the Practical Application of the ICRP Human Respiratory Tract Model* (ICRP 2002). Absorption is a two-stage process, following ICRP definitions, involving *i*) dissolution, the dissociation of inhaled and/or ingested materials into chemical compounds that can be absorbed into the transfer compartment; and *ii*) uptake, the absorption of these compounds into the transfer compartment. Therefore, the inhaled particle size, element concentration, and the solubility are important factors for uptake and thus for risk assessment (ICRP-66 1994, ICRP, 2002, Baily et al. 2003).

To assess human intake due to inhalation of airborne particles containing radionuclides, Bertelli and Lipsztein (1987) proposed a model that merges the models adapted by ICRP-30 (1979) for the respiratory tract and gastrointestinal tract, with a set of compartments representing the main organs and/or tissues in which each specific radionuclide is deposited. If the exposure occurs via inhalation then the intake begins in the nose, but if the exposure

occurs via ingestion then the intake begins in the stomach and the respiratory tract is not considered. In this model, each organ and tissue of the human body is represented as a compartment and the human metabolism is modeled as a system of first order differential equations with constant coefficients. Several mathematical methods exist to solve this system of equations (Birchall and James 1989, Eckerman et al. 1992).

These specific parameters for each element represent: physical and biological half-life, clearance rate from each organ and tissue, and the deposition rate in each organ and tissue. These coefficients are based on experimental data and are available in the literature (ICRP-54 1989, ICRP-56 1988, ICRP-66 1994, ICRP-78 1999, Skrabale et al. 1980).

When the pathway for intake is inhalation, the deposition fraction for each compartment in the respiratory tract depends on particle size (*Activity/Mass Median Aerodynamic Diameter* AMAD/MMAD), and the transfer factor to transfer compartment depends on the solubility of each chemical compound in lung fluid (ICRP 2002, ICRP-66 1994). If ingestion is the pathway, then the specific parameters represent the biological clearance and deposition rates in each compartment of the gastrointestinal tract (GI tract) and depend on the chemical solubility of each element in gastrointestinal fluids. In this GI model, the portion of the element transferred from the gastrointestinal tract to the transfer compartment is represented by a transfer factor,  $f_i$ , that depends on the solubility of the chemical compound in GI fluids (ICRP-54 1989, ICRP 2002, ICRP-78 1999, Skrabale et al. 1980). By the ICRP definition, the  $f_i$  value is the fraction of an ingested element directly absorbed to the body fluids (ICRP-30 1979, ICRP 2002).

The objective of this study was to assess workers exposure to Ta-bearing particles using experimental data and applying a metabolic model, to simulate Ta concentration in excreta samples from workers exposed to dust particles containing Ta. In order to evaluate the occupational exposure, this study used air samples, and urine and fecal samples from workers who were occupationally exposed to Th, U, Nb, and Ta bearing particles during routine tasks in a pyrochlore mine and metallurgical plant. The results from worker samples were compared to results from the control group samples. A metabolic model based on the ICRP model was applied to simulate the Ta concentrations in excreta samples, from the worker group and from the control group.

## **EXPERIMENTAL PROCEDURES**

### **Occupational exposure**

Samples were collected in mining and metallurgical plants located in the southwest of Goiás State, Brazil, that process pyrochlore to produce Fe-Nb alloys. These plants operated using two consecutive work regimens: the first work regimen

was three consecutive workdays followed by two days of rest, and the second work regimen consisted of three consecutive workdays followed by three days of rest. The two work regimens followed each other in sequence. The excreta samples were collected on the first rest day of both work regimens.

Particle size distributions in the workplace were determined using a six-stage Battelle-type cascade impactor (CI) with an operational flow rate of 12.5 L/min (Dias da Cunha et al. 1998 (a)). The CIs were located near the workers at sites with the highest total dust concentrations. The height of the first stage of the CIs was 1.5 m, to collect dust samples at nose height. Detailed information on CI placement within the facility can be found in the Ph.D. dissertation work of coauthor Dalia Periera (2006). Prior work showed no significant variation of particle size distributions within workrooms (Lipsztein et al. 2001; Dias da Cunha, et al. 1998 (a); Dias da Cunha 1998 (b); Dias da Cunha et al. 2002; Dalia Pereira 2006).

Eighteen workers used personal air samplers with cyclones, in order to evaluate their exposure to particles in the fine fraction of aerosols, and each worker used the air sampler over a 6-hour workday. These air samplers were calibrated and the flow rate was adjusted to obtain a cut-off equal to 2.5  $\mu\text{m}$ . Airborne particles smaller than 2.5  $\mu\text{m}$  were collected in a Nuclepore filter (pore size 0.4  $\mu\text{m}$ ) located above the cyclone, and coarse particles  $>2.5 \mu\text{m}$  were collected inside the cap at the end of cyclone; these coarse particles were not analyzed. Workers were asked for complete urine and fecal samples, corresponding to a 24-hour sample, that were taken on the first rest day following their work days. Water, food, and mineral samples were also collected.

Workers were required to wash hands before using the on-site restaurant, and food and drink were prohibited in the processing areas. They also showered in the plant before leaving, and work clothing worn inside the plant - boots, gloves, helmets, and uniforms - remained in the plant and were washed in a laundry room at the plant. Occupational exposure was estimated considering only fine particles that are deposited in alveolar regions while coarse particles deposited in upper regions of the lungs are removed from the lungs by mechanical processes (clearance) and ingested.

#### **Public exposure (control group)**

The control group was comprised of workers' spouses and/or other adults living at the workers' houses in a village about 100 km from the mine and metallurgical plant. Each individual of the control group was also asked for complete urine and fecal samples (24-hour samples). Drinking water samples were also collected at the village. The village is 100 km from the mine and plant, and the village is not located in the preferred wind direction that pass through the plant.

### **Sample preparation**

The fecal and food samples were pre-concentrated by burning for 48 h at 400° C, and the ashes were dissolved using heating and a solution of nitric acid and hydrofluoric acid. The 24-hour urine samples were concentrated by heating at 80° C until the volumes were reduced to 10 mL. At this point concentrated nitric acid was added to completely dissolve the urine samples. The dissolved samples (feces, urine, and food) were then heated on a hot plate to near dryness and then dissolved in a solution of 1M nitric acid. For the drinking water, 5 L water samples were concentrated to 10 mL using a hot plate at 80° C.

A drop of 2 µL of each sample was deposited on Mylar film for elemental analysis using Particle Induced X-ray Emission (PIXE). The airborne particles collected in personal air sampler filters and on the IC impact surface were fixed in a sample support disc for PIXE analysis without any preparation.

PIXE analyses were performed using a 2 MeV proton beam with a target current of ~20 nA from the 4.0 MV van de Graaff accelerator at the Pontifical Catholic University of Rio de Janeiro (PUC-Rio) van de Graaff Laboratory (Carvalho et al. 1988; Dias da Cunha 1997; Dias da Cunha et al. 1998 (a); (b)). The X rays emitted from the samples were detected using a Si-PIN detector with a 0.2 µm thick aluminum absorber foil. The X-ray spectra were analyzed using custom-designed software based on the stripping of a multi-element spectrum (Dias da Cunha et al. 1989 (a)).

For the mineral analysis, a 10 kg milled mineral sample was homogenized using a mechanical process, divided into four parts, and one part was selected for further homogenization and subsequent divisions in order to obtain an aliquot of 156 g. This was then sieved using a 400-mesh sieve and this fine fraction (< 400 mesh) was homogenized and further divided into three 50 g samples.

A sample of 28 g was measured using gamma-ray spectroscopy at The University of New Mexico's Low Activity Laboratory (LAL) without any pre-concentration procedure. The gamma rays from the sample were detected using a high purity Ge well detector, and the spectra were analyzed to assay <sup>232</sup>Th, <sup>238</sup>U, and their decay products.

### **Simulation**

An adaption (Nascimento 1994) of the mathematical model proposed by Bertelli and Lipsztein (1987) was used to calculate Ta concentrations in fecal and urine samples. In each simulation several inputs were considered: *i*) intake - inhalation, ingestion, or both as a route of intake; *ii*) the specific work regimes, to assess the occupational exposure; *iii*) chemical compound solubility; *iv*) during non-work hours workers were considered members of the public, with continuous exposure; *v*) each individual of the control group was considered a member of the public, with continuous



exposure and *vi*) period of exposure. When inhalation was considered as a pathway for Ta intake, then particle size (MMAD), concentrations, and solubility in lung fluid were also considered. When ingestion was deemed the main route, the solubility in gastrointestinal fluid was considered. The bioassay data interpretation was based on a comparison between experimental data and these theoretical calculations.

Daily Ta inhalation was calculated considering a daily air inhalation of 7.2 m<sup>3</sup> for each worker. This was calculated considering the ICRP reference man respiration rate of 0.02 m<sup>3</sup>/min during light work conditions (ICRP-23 1973, ICRP-66 1994) and 6 hours/day of work, as well as considering the Ta concentrations in the fine fraction of aerosols. Daily urine volume and feces mass were normalized to 1.4 L and 2.5 g of ash, respectively, for the calculations, which are the values adopted for reference man (ICRP-23 1973, ICRP-78 1999).

## RESULTS

The results of gamma-ray spectroscopy showed that <sup>232</sup>Th, <sup>238</sup>U, and their decay products <sup>228</sup>Th, <sup>234</sup>U, <sup>214</sup>Pb, and <sup>214</sup>Bi, were identified in the mineral sample. <sup>232</sup>Th, <sup>228</sup>Th, and <sup>238</sup>U concentrations agreed with previous results from alpha-particle spectroscopy (Lima et al. 2007), however it was not possible to determine the <sup>234</sup>U, <sup>228</sup>Ra, and <sup>226</sup>Ra concentrations using gamma-ray spectroscopy. Lower concentrations of <sup>214</sup>Pb and <sup>214</sup>Bi compared with <sup>238</sup>U suggest that the decay chain was broken. <sup>228</sup>Ra is a daughter of <sup>232</sup>Th and <sup>226</sup>Ra is a decay product from <sup>238</sup>U, both radionuclides are soluble in water and <sup>220</sup>Rn, and <sup>222</sup>Rn are a noble gas and are decay products from Th and U natural series, respectively. Based on their chemical and physical characteristics two hypotheses can explain the lower concentration of <sup>214</sup>Pb and <sup>214</sup>Bi in mineral; the first hypothesis is that radium can be removed from mineral by natural leaching reaction caused by rainwater; the second hypothesis is that radon being a noble gas can escape from mineral. The concentrations of <sup>228</sup>Ra, <sup>226</sup>Ra, <sup>220</sup>Rn, and <sup>222</sup>Rn are thus reduced, and <sup>214</sup>Pb and <sup>214</sup>Bi concentrations are also reduced accordingly. However to confirm these hypotheses it would be necessary an in-depth geological study and this is beyond the scope of the present study.

Analyses of aerosol samples collected using the cascade impactors showed that workers were exposed to airborne particles containing Nb, Ta, Th, and U. The average elemental mass concentrations in the fine fraction of aerosols were determined considering only values above the detection limit, and are shown in Table 1. Ta concentrations varied from  $6.11 \times 10^{-4} \pm 1.62 \times 10^{-4}$  to  $2.40 \times 10^{-1} \pm 1.55 \times 10^{-1}$  µg/m<sup>3</sup>, and Nb concentrations varied from  $2.34 \times 10^{-3} \pm 0.39 \times 10^{-3}$  to  $1.67 \pm 1.29$  µg/m<sup>3</sup>. The flotation is a chemical reaction that occurs after the milling process and concentrates pyrochlore.

During this process particles with different size are generated and thus particle composition is not homogeneous. The flotation process occurred in a large, wall-less shed so the Ta and Nb air concentrations were not homogeneous. The aluminothermy is also a chemical reaction in which Fe-Nb alloy is obtained; this process also occurred in an open area. Airborne particles were collected in both areas at different sampling points and days, and the results showed a large variation Ta and Nb concentrations in air. Thorium and uranium concentrations varied from below the detection limit for both to  $6.57 \times 10^{-1} \pm 2.56 \times 10^{-1}$  and  $4.10 \times 10^{-1} \pm 2.07 \times 10^{-1}$   $\mu\text{g}/\text{m}^3$ , respectively. At the entrance of the industrial complex, Th and U concentrations were below the detection limit and Ta and Nb were at their lowest concentrations, indicating that the concentration of Ta-bearing particles outside the plant was lower than in the industrial area. The highest average concentrations of Th and U were determined during the slag crushing process, indicating that Th and U were concentrated in the slag. Concentrations of Ta and Nb particles were also high during the slag crushing process, indicating that the Ta and Nb remain in the slag. For this reason, after crushing the slag is mixed with the niobium concentrate at the aluminothermy stage. The highest total dust concentration was measured by Dalia Pereira (2006) during the slag crushing, so in order to reduce the dust concentration in this plant, slag was crushed inside a closed room with a special ventilation system and workers used respirators in this room. These workers were not included in the current study.

The MMAD and the geometric standard deviation ( $\sigma_g$ ) for particles containing Ta, Nb, Th, and U were determined and are presented in Table 2. During all processes - ore crushing, flotation, leaching, aluminothermy, and slag crushing - the MMAD values were smaller than  $2.5 \mu\text{m}$  for Ta-bearing particles. During leaching and slag crushing the MMAD values were above  $2.5 \mu\text{m}$  for particles containing Nb, Th, and U.

Thorium concentrations in air samples collected using personal air samplers were below the detection limit of  $1.22 \text{ ng}$ , and only 2 samples showed U concentrations above the detection limit of  $1.96 \text{ ng}$ . Ta and Nb concentrations in air are shown in Table 3.

Twenty-eight excreta samples from workers were analyzed, and Ta concentrations in urine and in fecal samples are shown in Table 3. In samples above the detection limit, Ta concentrations ranged from  $21.99$  to  $111.32 \mu\text{g}/\text{day}$  in urine samples and from  $96.13$  to  $878.66 \mu\text{g}/\text{day}$  in fecal samples.

Ta concentrations in the fine fraction of aerosols and in the urine samples from workers were compared using a non-parametric Spearman test with  $\alpha = 0.05$  (Zahr 1999). The results showed that there was no correlation between Ta concentrations in the air samples and in the urine samples. The same test was applied for Ta concentrations in

urine and fecal samples, and results indicated that there were also no correlations between Ta concentrations in urine and fecal samples. This indicated that inhalation was not the sole pathway of intake, though it should still be considered as a pathway for Ta incorporation.

Following this, Ta concentrations in excreta samples from workers were compared to Ta concentrations in excreta samples from each individual of the control group. From the control group, seventeen individuals provided urine samples and 15 individuals provided fecal samples. Ta concentrations ranged from 32.18 to 103.09  $\mu\text{g}/\text{day}$  in urine, and from 33.72 to 252.93  $\mu\text{g}/\text{day}$  in feces, for samples above the detection limit.

The Ta concentration results are shown in Table 3. Each worker was identified by a number between 01 and 30, and the same number was used for identification of the control group member who lives in the corresponding worker's residence. However, some results showed that the Ta concentrations in excreta from workers were lower than the concentrations in samples from the control group, even from the same house. Based on these results we conclude that the plant was not the only source of Ta exposure and that, beside occupational exposure, workers and the control group were exposed to the same source.

Ta concentrations in excreta samples from the control group and workers were compared using a Wilcoxon-Mann-Whitney non-parametric statistical test with  $\alpha=0.05$  (Zahr 1999). The results indicated no difference between the workers and the control group, suggesting that they were exposed to the same Ta source outside of the mine and plant. These results confirm the hypotheses that there were other sources of Ta exposure in this region in addition to occupational exposure, and that both the workers and the control group were exposed to the same source. Thus, ingestion of drinking water and/or food was considered a possible source of Ta intake.

Food consumed by workers in the work-site restaurant, by workers off site, and by the control group was supplied by a warehouse located in the village, and 8 complete meals were analyzed. Ta concentrations in the meals were below the detection limit of the analytical technique for Ta (0.15 ng). Thus the meals were not considered to be a source of Ta.

The second possible way of ingestion was through drinking water. At the industrial complex, the drinking water was mineral water obtained from a water source located far from the mine area and Ta concentrations were below the detection limit of the analytical technique (0.15 ng). In contrast, the village was supplied by a water source located downstream from the industrial complex. The average Ta concentration in the village drinking water was measured to be 112  $\mu\text{g}/\text{L}$ , in the same range as the Ta concentration in water used in the industrial process ( $191 \pm 3.52$   $\mu\text{g}/\text{L}$ ).

average), so the ingestion of drinking water could be considered a source of Ta intake.

Although 33 workers were monitored, only 8 workers provided a complete set of samples with Ta concentrations above the detection limit for urine, feces, and air samples. The daily Ta intake was calculated as described above. Ta concentrations in air and excreta samples are shown in Table 3.

## **MODELING**

In order to identify the possible pathway of Ta incorporation the mathematical model described above was applied to simulate Ta concentration in fecal and urine samples from each worker of the subset of 8 workers with complete samples and from individual of the control group. The data subset of workers and the respective control are included in Table 3.

Ta concentrations in urine and fecal samples depend on Ta intake and represent Ta incorporation. However, the ratio of the Ta concentrations in excreta samples for each individual depends on the metabolism of Ta compounds. Consequently this ratio is independent of the amount inhaled, and this ratio does not change based on intake quantities, and thus a nominal intake of 1  $\mu\text{g}$  was applied to calculate the theoretical concentration ratio in urine and feces.

The ICRP considers Ta compounds in minerals as insoluble compounds and the default parameters recommended by ICRP are: "fraction dissolved rapidly",  $f_r$ , for which a value of 0.001 is used, with a slow dissolution rate of 0.0001/day (ICRP 2002).

Several hypotheses on exposure were tested. The first hypothesis was occupational exposure of each worker considering inhalation of particles containing insoluble Ta compounds as the main source of occupational exposure. The experimental data that characterized each individual's dust particle exposure were: *i*) MMAD (Table 2) of Ta-bearing particles, *ii*) Ta concentrations in air samples collected using personal air samplers (Table 3), however as the urine/feces Ta ratios were determined, the nominal concentration of  $1\mu\text{g}/\text{m}^3$  was considered for each worker, *iii*) the worker regime describe above, *iv*) Ta in mineral dust, Ta oxide, is considered insoluble, and *v*) period of exposure.

These workers were occupationally exposed to Ta during approximately the same period of time, and MMAD values of the Ta-bearing particles varied very little (1.4-1.6  $\mu\text{m}$ ). These individual exposure variations were not enough to cause a significant variation of calculated Ta concentrations in urine and feces. The experimental and theoretical urine/feces Ta ratios for each worker are shown in Figure 1. The values of the theoretical ratios of urine/feces concentrations were 0.27 for each worker and did not agree with the experimental ratios. This indicates

that there should exist other sources beside inhalation of fine particles containing Ta. As the Ta concentration in excreta samples from some individuals of the control group was higher than Ta concentration in excreta samples from workers, as discussed above, it was concluded that both groups were exposed to the same source.

The second hypothesis considered ingestion as a pathway of Ta intake. However Ta concentration in food samples were below the detection limit, so for both groups ingestion of food was not considered a source of Ta contamination. As the average Ta concentration in drinking water at the village was 112 µg/L, ingestion of drinking water was considered to be a possible pathway of Ta intake.

The same model applied above, to calculate Ta concentration in excreta samples due to occupational exposure, was used to simulate ingestion of drinking water as the main pathway of Ta intake, and inhalation as a secondary pathway of Ta intake, for both the worker and control groups. Ta intake both for workers during rest days and for the control group was simulated considering ingestion of 1.4 L of drinking water per day.

Due to expected background aerosol levels in the village, it was assumed that inhabitants could be exposed to dust particles containing Ta. So it was assumed that individuals of the control group and workers during the resting hours were exposed to dust particles with MMAD equal to 1 µm, the value recommended by ICRP when the MMAD value was not determined (ICRP-66 1994, ICRP 2002).

This second hypothesis considering ingestion was split in two hypotheses. Hypothesis 2a considers inhalation of insoluble dust particles, class Y, and ingestion of insoluble Ta compounds in drinking water, with transfer factor of  $f_I = 0.001$  (ICRP 2002) adopted for insoluble compounds. Hypotheses 2b considers inhalation of insoluble dust particles but now ingestion of *soluble* Ta compounds in drinking water. As there is no  $f_I$  transfer factor adopted by ICRP for soluble Ta compounds,  $f_I = 0.1$  was assumed.

The ratios of urine/feces Ta concentrations for each worker and each individual of the control group based on experimental data are shown in Figure 2, with ratios from simulations. Theoretical ratios of urine/feces Ta concentrations were calculated considering inhalation and ingestion as the main pathway of Ta intake. The calculated urine/feces Ta concentration ratios in hypothesis 2a above, considering inhalation and ingestion of insoluble Ta compounds, showed that the ratios were about  $8.3 \pm 4.2$  for both groups, indicating that workers and individuals of the control group were exposed to the same Ta sources, and thus ingestion of drinking water was the main source of Ta exposure. However the predicted values did not agree with experimental ratios, and consequently this simulation did not represent the observed Ta incorporation. Hypothesis 2b above, treating Ta compounds as soluble predicts urine/feces Ta ratios of  $0.13 \pm 0.05$ . These

values were in the same range as the experimental values for both the worker and control groups, indicating that ingestion of soluble Ta compounds was the main source of Ta incorporation for both groups. However, the adopted model still did not represent the variation observed among the individuals of both the worker and control groups, indicating that the metabolic model adopted and the transfer factors should be reviewed for Ta compounds.

## CONCLUSIONS

Results from gamma-ray spectroscopy showed that  $^{232}\text{Th}$ ,  $^{238}\text{U}$ , and their decay products,  $^{228}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$ , were identified in pyrochlore mineral samples.  $^{232}\text{Th}$ ,  $^{228}\text{Th}$ , and  $^{238}\text{U}$  concentrations agreed with previous results from alpha spectroscopy (Lima et al. 2007), however it was not possible to determine the  $^{234}\text{U}$ ,  $^{228}\text{Ra}$ , and  $^{226}\text{Ra}$  concentrations using gamma spectroscopy. Lower concentrations of  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  compared to  $^{238}\text{U}$  suggest that the decay equilibrium chain was broken. As discussed above, radium solubility in water and radon escape can lead to the observed lower  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  concentrations

Workers were exposed to airborne particles containing Ta, Nb, Th, and U. The Ta concentrations varied from  $6.11 \times 10^{-4} \pm 1.62 \times 10^{-4}$  to  $2.40 \times 10^{-1} \pm 1.55 \times 10^{-1} \mu\text{g}/\text{m}^3$ , the Nb concentrations varied from  $2.34 \times 10^{-3} \pm 0.39 \times 10^{-3}$  to  $1.67 \pm 1.29 \mu\text{g}/\text{m}^3$ , while the thorium and uranium concentrations varied from below the detection limit to  $6.57 \times 10^{-1} \pm 2.56 \times 10^{-1}$  and to  $4.10 \times 10^{-1} \pm 2.07 \times 10^{-1} \mu\text{g}/\text{m}^3$ , respectively. The highest average Th and U air concentrations were determined during slag crushing, showing that Th and U were concentrated in the slag. It is noted that during all processes - ore crushing, flotation, leaching, aluminothermy, and slag crushing - the workers were exposed to particles smaller than  $2.5 \mu\text{m}$ .

Ta concentrations in workers' excreta ranged from 21.99 to 111.32  $\mu\text{g}/\text{day}$  for urine samples and from 96.13 to 878.66  $\mu\text{g}/\text{day}$  for fecal samples. Statistical analyses showed that there was no correlation between Ta concentrations in air samples and in urine samples, as well as no correlation between Ta concentrations in urine and fecal samples. Based on these results it was concluded that workers were exposed to other sources of Ta outside of any occupational exposure to airborne particles.

Daily Ta concentrations in excreta from the control group were in the range of 32.18 to 103.09  $\mu\text{g}/\text{day}$  in urine samples and 33.72 to 252.93  $\mu\text{g}/\text{day}$  in fecal samples. Statistical analyses showed that there was no difference between Ta concentrations in excreta samples from workers and from the control group, indicating that both groups were exposed to the same source. Ta concentrations in food samples were below the detection limit (0.15 ng),

however the average Ta concentration in drinking water at the village where both the workers and the control group lived was 112 µg/L, presenting a possible source of ingestion.

A metabolic model based on ICRP model was used here to calculate Ta concentrations in urine and fecal samples from 8 workers due to inhalation of airborne particles containing insoluble Ta compounds. The theoretical urine/feces Ta concentration ratios were 0.27 for the workers and did not agree with variations in experimental ratios. Therefore, new simulations of Ta intake were performed considering inhalation of insoluble compounds of Ta as well as ingestion of drinking water containing either insoluble or soluble Ta.

In the first hypothesis (1) in which simulations considered only inhalation of insoluble Ta compounds, the theoretical values and the experimental ratios did not agree, and analysis of measured values showed that the workers and individuals of the control group were probably exposed to the same source. The second hypothesis (2a) considered inhalation of insoluble particles and ingestion of water containing insoluble Ta compounds, but this also did not agree with the experimental data. Following this, the second hypothesis was modified (2b) to consider inhalation of insoluble Ta-bearing particles, as before, but also ingestion of *soluble* Ta compounds. Theoretical Ta concentration ratios for excreta ( $0.13 \pm 0.05$ ) were in the same range as the experimental values for both the worker and control groups, indicating that ingestion of soluble Ta compounds was the main source of Ta incorporation for both groups. However, the adopted model did not represent the variation observed among the individuals of both the worker and control groups, indicating that the GI transfer factors should be reviewed for Ta compounds.

Based on these results it was concluded that the main source of Ta exposure of both the workers and the control group was ingestion of drinking water containing soluble compounds of Ta, and that some Ta compounds should be considered soluble inside the human body. Thus, the ICRP metabolic model and transfer factor for Ta should be reviewed and the solubility of Ta compounds inside the human body should be determined. Further studies should be developed to determine the values of specific transfer factors for Ta inside of the human body.

## **ACKNOWLEDGEMENTS**

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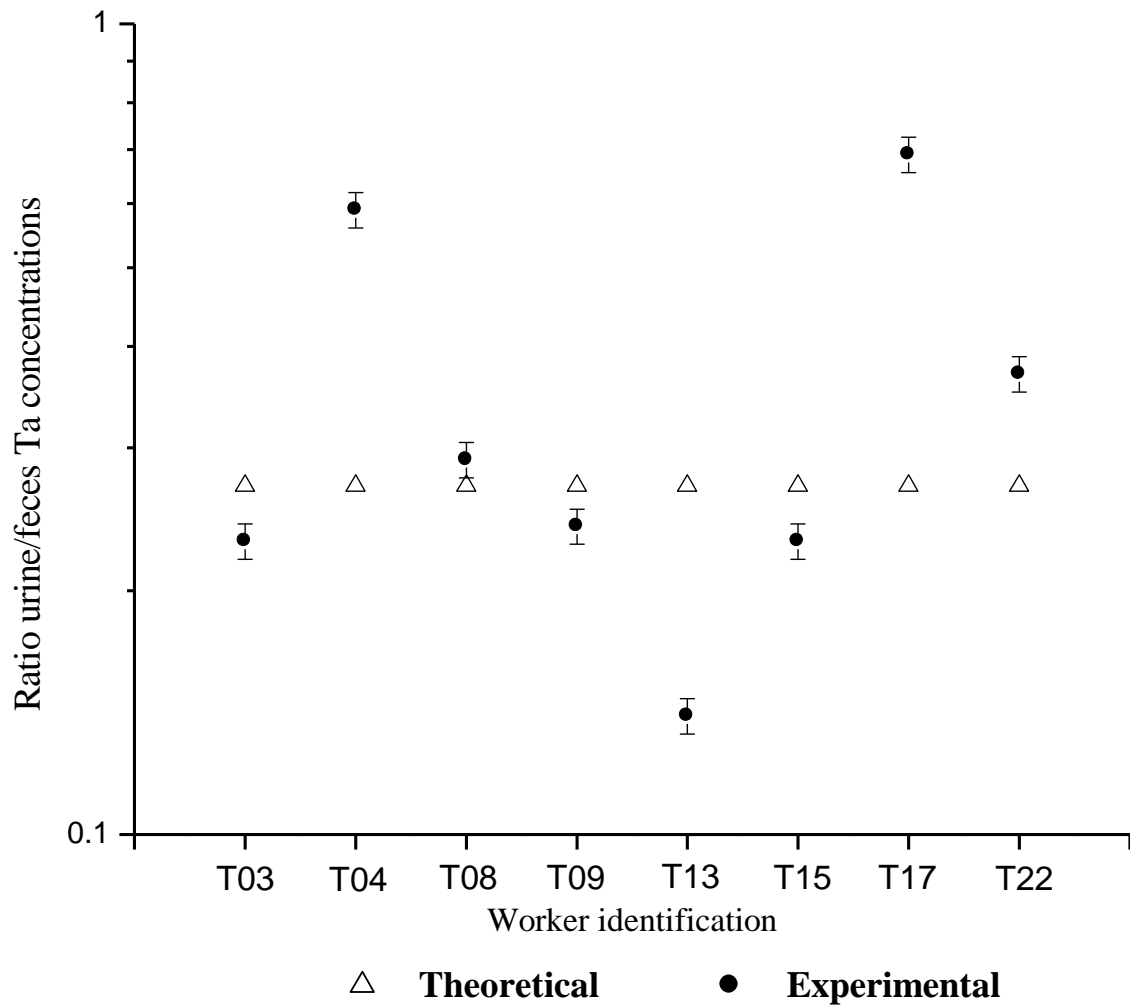


Figure 1. Theoretical and experimental values of the ratios of Ta concentrations in urine and fecal samples from workers. The theoretical values of 0.27 were calculated assuming only inhalation of insoluble Ta compounds.

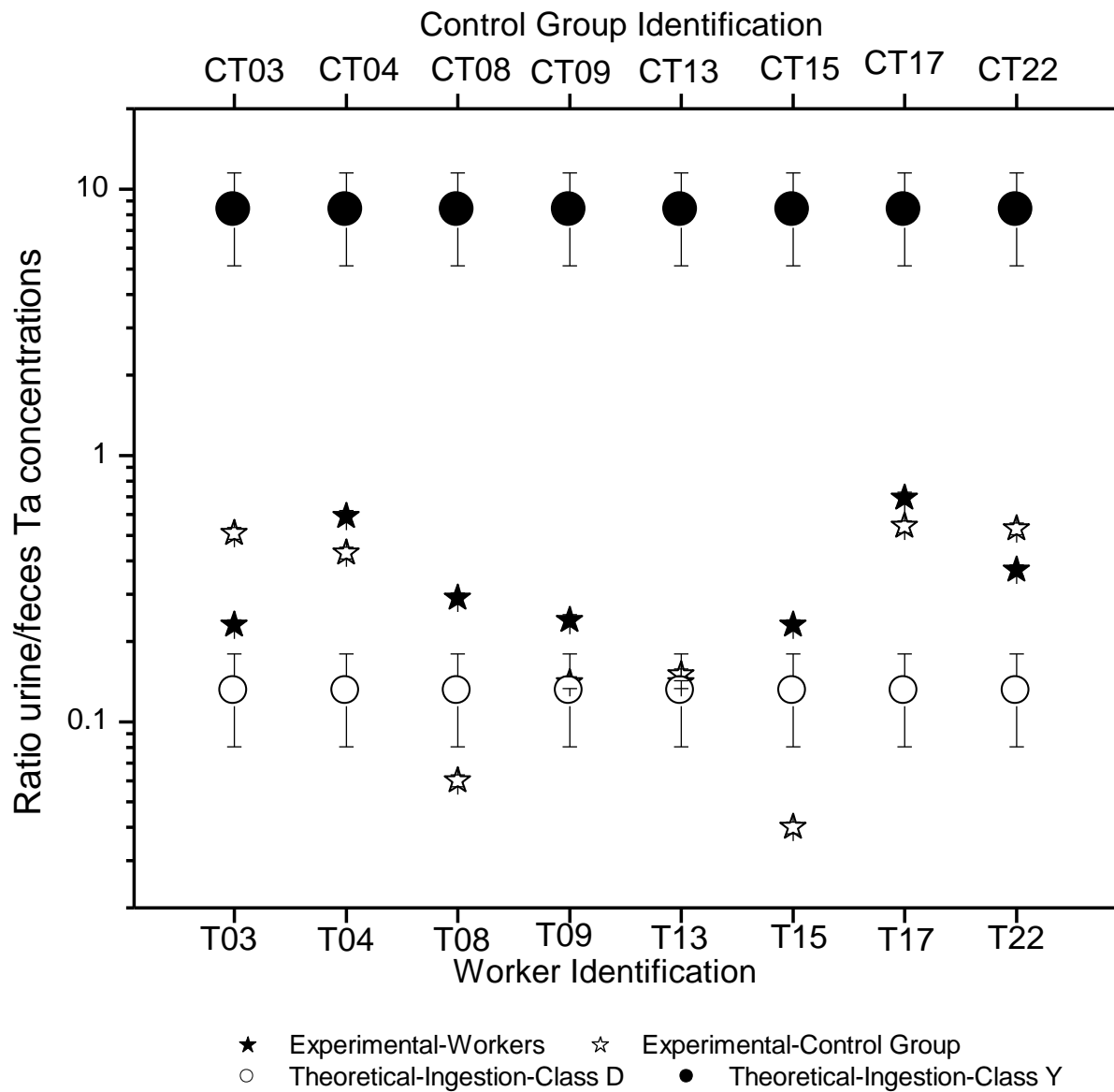


Figure 2. Experimental and theoretical urine/feces Ta concentration ratios. Theoretical values calculated for each worker and for each individual of the control group assuming Ta incorporation by ingestion and treating the Ta compounds as either soluble (Class D) or insoluble (Class Y).

Table 1. Ta, Nb, Th, and U average mass concentrations in the fine fraction of aerosols. Samples collected using a cascade impactor at different steps of mineral processing.

Site	Step of process	Average Concentrations in Fine Fraction ( $\mu\text{g}/\text{m}^3$ )			
		Ta	Nb	Th	U
Crushing	Ore crushing	$2.03 \times 10^{-2}$ $\pm 1.33 \times 10^{-2}$	$2.95 \times 10^{-1}$ $\pm 1.58 \times 10^{-1}$	$3.89 \times 10^{-2}$ $\pm 1.04 \times 10^{-2}$	$1.96 \times 10^{-2}$ $\pm 1.40 \times 10^{-2}$
	Slag crushing	$2.40 \times 10^{-1}$ $\pm 1.55 \times 10^{-1}$	1.67 $\pm 1.29$	$6.57 \times 10^{-1}$ $\pm 2.56 \times 10^{-1}$	$4.10 \times 10^{-1}$ $\pm 2.07 \times 10^{-1}$
Concentration	Flotation	$3.11 \times 10^{-3}$ $\pm 3.33 \times 10^{-3}$	$2.17 \times 10^{-1}$ $\pm 3.04 \times 10^{-1}$	$1.15 \times 10^{-2}$ $\pm 8.3 \times 10^{-3}$	$7.60 \times 10^{-3}$ $\pm 5.30 \times 10^{-3}$
	Leaching	$2.94 \times 10^{-3}$ $\pm 1.71 \times 10^{-3}$	$6.98 \times 10^{-1}$ $\pm 2.64 \times 10^{-1}$	$1.56 \times 10^{-2}$ $\pm 1.25 \times 10^{-2}$	$6.40 \times 10^{-3}$ $\pm 2.53 \times 10^{-3}$
Metallurgy	Aluminothermy	$3.40 \times 10^{-3}$ $\pm 1.30 \times 10^{-3}$	$3.43 \times 10^{-1}$ $\pm 3.93 \times 10^{-1}$	$5.76 \times 10^{-3}$ $\pm 2.76 \times 10^{-3}$	<DL
Outer area	Entrance	$6.11 \times 10^{-4}$ $\pm 1.62 \times 10^{-4}$	$2.34 \times 10^{-3}$ $\pm 0.39 \times 10^{-3}$	<DL	<DL

<DL = Below detection limit of analytical technique.

U detection limit =  $1.96 \times 10^{-3} \mu\text{g}/\text{m}^3$ . Th detection limit =  $1.22 \times 10^{-3} \mu\text{g}/\text{m}^3$ .

Table 2. Mass Median Aerodynamic Diameter (MMAD) values and geometric standard deviation ( $\sigma_g$ ) of particles containing Nb, Ta, Th, and U. Samples collected using a cascade impactor at different steps of mineral processing.

Step of process	MMAD ( $\mu\text{m}$ )							
	Ta		Nb		Th		U	
	MMAD	$\sigma_g$	MMAD	$\sigma_g$	MMAD	$\sigma_g$	MMAD	$\sigma_g$
Ore crushing	1.4	1.8	1.7	1.7	2.7	1.4	2.4	-
Flotation	1.4	1.8	1.5	1.4	1.3	1.5	1.1	1.2
Leaching	1.6	1.9	2.6	1.7	2.5	1.6	9.9	-
Aluminothermy	1.4	1.8	1.6	1.5	2.3	1.2	-	-
Slag crushing	2.4	1.5	3.2	1.3	3.4	1.3	3.4	1.4
Entrance	1.3	1.9	1.0	-	-	-	-	-



Table 3. Ta concentrations in air, urine, and fecal samples.

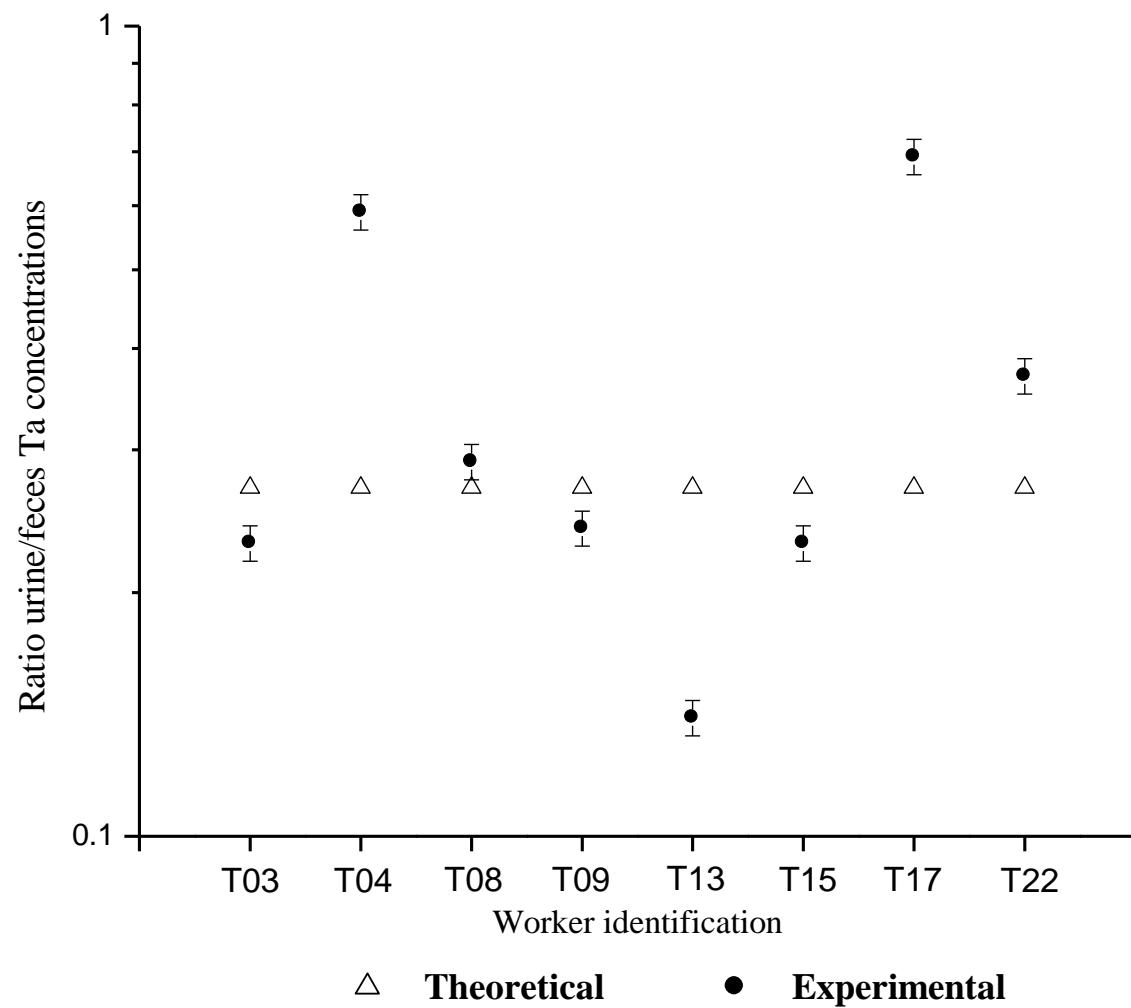
Worker identification	Workers				Control group		
	Air concentration [ $\mu\text{g}/\text{m}^3$ ]		Ta daily concentration [ $\mu\text{g}/\text{day}$ ]		Control identification	Ta daily concentration [ $\mu\text{g}/\text{day}$ ]	
	Ta	Nb	Urine	Feces		Urine	Feces
T01	N	N	35.76 $\pm$ 7.165	288.16 $\pm$ 57.736	CT01	51.40 $\pm$ 10.298	94.66 $\pm$ 18.966
T02	N	N	68.30 $\pm$ 13.685	265.57 $\pm$ 53.210	CT02	80.83 $\pm$ 16.195	76.68 $\pm$ 15.364
<b>T03</b>	0.03 $\pm$ 0.006	0.40 $\pm$ 0.080	111.32 $\pm$ 22.304	98.77 $\pm$ 19.790	CT03	55.20 $\pm$ 11.060	<DL
<b>T04</b>	0.01 $\pm$ 0.002	0.16 $\pm$ 0.032	47.94 $\pm$ 9.605	190.28 $\pm$ 38.124	CT04	77.03 $\pm$ 15.434	100.90 $\pm$ 20.216
T05	N	N	50.09 $\pm$ 10.036	417.93 $\pm$ 83.736	CT05	81.00 $\pm$ 16.229	N
T06	0.01 $\pm$ 0.002	<DL	66.59 $\pm$ 13.342	N	CT06	N	N
T07	N	N	57.51 $\pm$ 11.523	878.66 $\pm$ 176.048	CT07	78.14 $\pm$ 15.656	78.89 $\pm$ 15.806
<b>T08</b>	0.02 $\pm$ 0.004	<DL	60.65 $\pm$ 12.1523	116.56 $\pm$ 23.354	CT08	32.18 $\pm$ 6.448	81.96 $\pm$ 16.421
<b>T09</b>	0.03 $\pm$ 0.007	0.50 $\pm$ 0.100	100.38 $\pm$ 20.112	389.77 $\pm$ 78.094	CT09	N	N
T10	N	N	<DL	254.63 $\pm$ 51.018	CT10	32.29 $\pm$ 6.470	252.93 $\pm$ 50.677
T11	<DL	0.43 $\pm$ 0.086	<DL	196.42 $\pm$ 39.355	CT11	N	N
T12	0.03 $\pm$ 0.006	0.52 $\pm$ 0.104	59.80 $\pm$ 11.982	N	CT12	N	N
<b>T13</b>	0.02 $\pm$ 0.003	<DL	70.09 $\pm$ 14.043	226.23 $\pm$ 45.327	CT13	N	N
T14	<DL	<DL	100.24 $\pm$ 20.084	380.01 $\pm$ 76.139	CT14	36.67 $\pm$ 7.347	N
<b>T15</b>	0.02 $\pm$ 0.004	0.60 $\pm$ 0.120	88.54 $\pm$ 17.740	403.86 $\pm$ 80.917	CT15	N	N
T16	<DL	<DL	42.86 $\pm$ 8.587	170.17 $\pm$ 34.095	CT16	69.02 $\pm$ 13.829	150.75 $\pm$ 30.204
<b>T17</b>	0.02 $\pm$ 0.003	0.33 $\pm$ 0.066	51.48 $\pm$ 10.315	281.74 $\pm$ 56.449	CT17	101.90 $\pm$ 20.417	45.29 $\pm$ 9.074
T18	N	N	56.51 $\pm$ 11.322	218.96 $\pm$ 43.871	CT18	74.54 $\pm$ 14.935	134.58 $\pm$ 26.964
T19	DL	0.62 $\pm$ 0.124	54.22 $\pm$ 10.864	329.66 $\pm$ 66.051	CT19	N	N
T20	0.03 $\pm$ 0.005	0.69 $\pm$ 0.138	<DL	96.13 $\pm$ 19.261	CT20	<DL	38.40 $\pm$ 7.694
T21	<DL	0.50 $\pm$ 0.100	21.99 $\pm$ 4.46	111.93 $\pm$ 22.426	CT21	61.72 $\pm$ 12.366	33.72 $\pm$ 6.756
<b>T22</b>	0.02 $\pm$ 0.004	0.43 $\pm$ 0.086	65.75 $\pm$ 13.174	134.66 $\pm$ 26.980	CT22	N	N
T23	N	N	29.52 $\pm$ 5.915	397.77 $\pm$ 79.697	CT23	N	N
T24	N	N	53.46 $\pm$ 10.711	123.56 $\pm$ 24.756	CT24	103.09 $\pm$ 20.655	70.79 $\pm$ 14.183
T25	N	N	93.05 $\pm$ 18.643	296.26 $\pm$ 59.359	CT25	55.83 $\pm$ 11.186	93.59 $\pm$ 18.752
T26	N	N	34.73 $\pm$ 6.958	138.75 $\pm$ 27.800	CT26	N	N
T27	<DL	<DL	79.83 $\pm$ 15.995	162.05 $\pm$ 32.468	CT27	38.24 $\pm$ 7.662	98.99 $\pm$ 19.834
T28	N	N	32.40 $\pm$ 6.492	804.11 $\pm$ 161.111	CT28	N	N
T29	0.26 $\pm$ 0.052	<DL	N	131.40 $\pm$ 26.327	CT29	N	N
T30	0.27 $\pm$ 0.054	<DL	N	407.66 $\pm$ 81.679	CT30	N	N

<DL = Below detection limit of analytical technique.

N = No sample.



Figure 1. Theoretical and experimental values of the ratios of Ta concentrations in urine and fecal samples from workers. The theoretical values of 0.27 were calculated assuming only inhalation of insoluble Ta compounds.



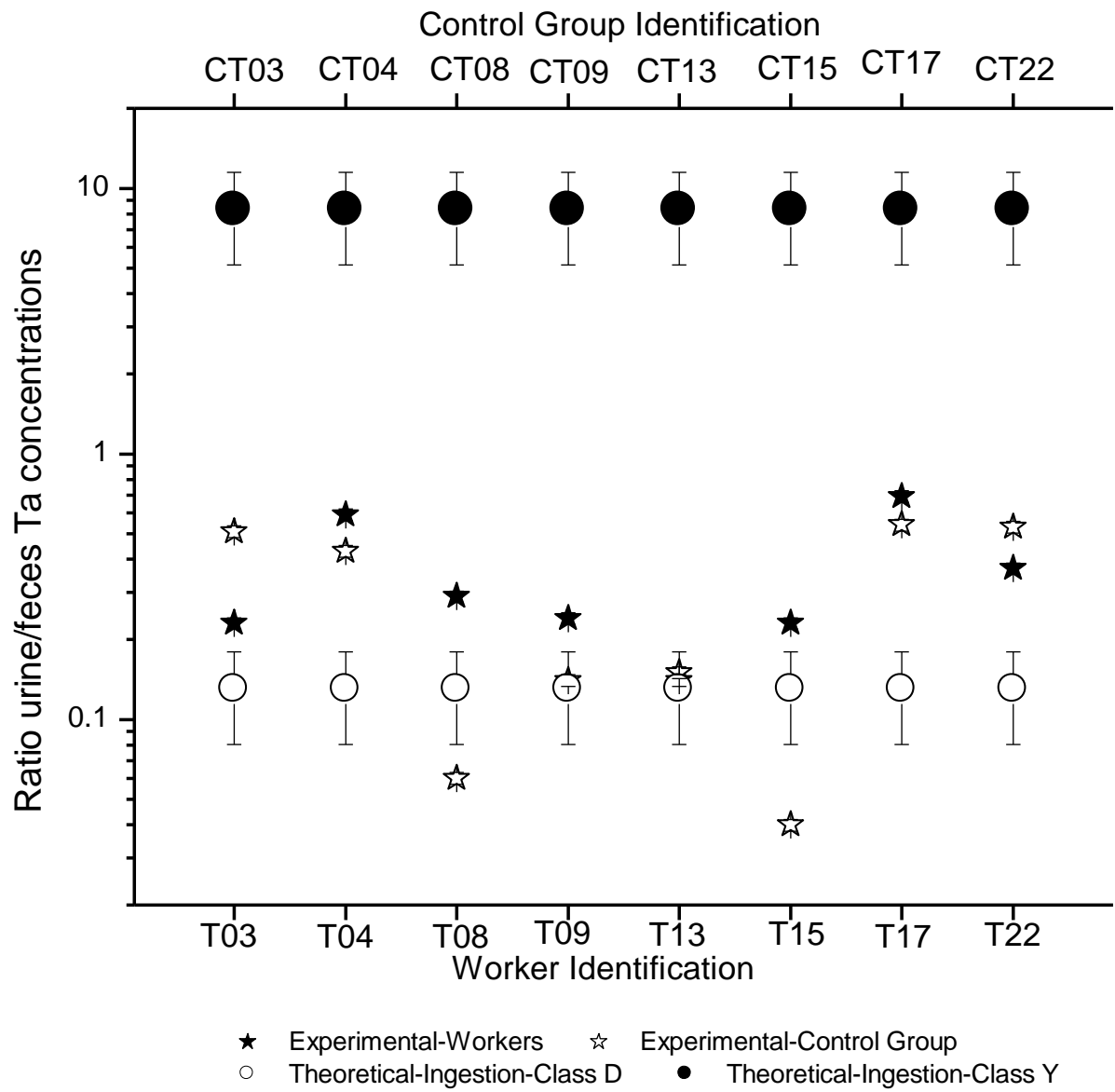


Figure 2. Experimental and theoretical urine/feces Ta concentration ratios. Theoretical values calculated for each worker and for each individual of the control group assuming Ta incorporation by ingestion and treating the Ta compounds as either soluble (Class D) or insoluble (Class Y).

Site	Step of process	Average Concentrations in Fine Fraction ( $\mu\text{g}/\text{m}^3$ )			
		Ta	Nb	Th	U
Crushing	Ore crushing	$2.03 \times 10^{-2}$ $\pm 1.33 \times 10^{-2}$	$2.95 \times 10^{-1}$ $\pm 1.58 \times 10^{-1}$	$3.89 \times 10^{-2}$ $\pm 1.04 \times 10^{-2}$	$1.96 \times 10^{-2}$ $\pm 1.40 \times 10^{-2}$
	Slag crushing	$2.40 \times 10^{-1}$ $\pm 1.55 \times 10^{-1}$	1.67 $\pm 1.29$	$6.57 \times 10^{-1}$ $\pm 2.56 \times 10^{-1}$	$4.10 \times 10^{-1}$ $\pm 2.07 \times 10^{-1}$
Concentration	Flotation	$3.11 \times 10^{-3}$ $\pm 3.33 \times 10^{-3}$	$2.17 \times 10^{-1}$ $\pm 3.04 \times 10^{-1}$	$1.15 \times 10^{-2}$ $\pm 8.3 \times 10^{-3}$	$7.60 \times 10^{-3}$ $\pm 5.30 \times 10^{-3}$
	Leaching	$2.94 \times 10^{-3}$ $\pm 1.71 \times 10^{-3}$	$6.98 \times 10^{-1}$ $\pm 2.64 \times 10^{-1}$	$1.56 \times 10^{-2}$ $\pm 1.25 \times 10^{-2}$	$6.40 \times 10^{-3}$ $\pm 2.53 \times 10^{-3}$
Metallurgy	Aluminothermy	$3.40 \times 10^{-3}$ $\pm 1.30 \times 10^{-3}$	$3.43 \times 10^{-1}$ $\pm 3.93 \times 10^{-1}$	$5.76 \times 10^{-3}$ $\pm 2.76 \times 10^{-3}$	<DL
Outer area	Entrance	$6.11 \times 10^{-4}$ $\pm 1.62 \times 10^{-4}$	$2.34 \times 10^{-3}$ $\pm 0.39 \times 10^{-3}$	<DL	<DL

Table 1. Ta, Nb, Th, and U average mass concentrations in the fine fraction of aerosols. Samples collected using a cascade impactor at different steps of mineral processing.

Step of process	MMAD ( $\mu\text{m}$ )							
	Ta		Nb		Th		U	
	MMAD	$\sigma_g$	MMAD	$\sigma_g$	MMAD	$\sigma_g$	MMAD	$\sigma_g$
Ore crushing	1.4	1.8	1.7	1.7	2.7	1.4	2.4	-
Flotation	1.4	1.8	1.5	1.4	1.3	1.5	1.1	1.2
Leaching	1.6	1.9	2.6	1.7	2.5	1.6	9.9	-
Aluminothermy	1.4	1.8	1.6	1.5	2.3	1.2	-	-
Slag crushing	2.4	1.5	3.2	1.3	3.4	1.3	3.4	1.4
Entrance	1.3	1.9	1.0	-	-	-	-	-

Table 2. Mass Median Aerodynamic Diameter (MMAD) values and geometric standard deviation ( $\sigma_g$ ) of particles containing Nb, Ta, Th, and U. Samples collected using a cascade impactor at different steps of mineral processing.

Worker identification	Workers				Control group		
	Air concentration [ $\mu\text{g}/\text{m}^3$ ]		Ta daily concentration [ $\mu\text{g}/\text{day}$ ]		Control identification	Ta daily concentration [ $\mu\text{g}/\text{day}$ ]	
	Ta	Nb	Urine	Feces		Urine	Feces
T01	N	N	35.76 $\pm$ 7.165	288.16 $\pm$ 57.736	CT01	51.40 $\pm$ 10.298	94.66 $\pm$ 18.966
T02	N	N	68.30 $\pm$ 13.685	265.57 $\pm$ 53.210	CT02	80.83 $\pm$ 16.195	76.68 $\pm$ 15.364
T03	0.03 $\pm$ 0.006	0.40 $\pm$ 0.080	111.32 $\pm$ 22.304	98.77 $\pm$ 19.790	CT03	55.20 $\pm$ 11.060	<DL
T04	0.01 $\pm$ 0.002	0.16 $\pm$ 0.032	47.94 $\pm$ 9.605	190.28 $\pm$ 38.124	CT04	77.03 $\pm$ 15.434	100.90 $\pm$ 20.216
T05	N	N	50.09 $\pm$ 10.036	417.93 $\pm$ 83.736	CT05	81.00 $\pm$ 16.229	N
T06	0.01 $\pm$ 0.002	<DL	66.59 $\pm$ 13.342	N	CT06	N	N
T07	N	N	57.51 $\pm$ 11.523	878.66 $\pm$ 176.048	CT07	78.14 $\pm$ 15.656	78.89 $\pm$ 15.806
T08	0.02 $\pm$ 0.004	<DL	60.65 $\pm$ 12.1523	116.56 $\pm$ 23.354	CT08	32.18 $\pm$ 6.448	81.96 $\pm$ 16.421
T09	0.03 $\pm$ 0.007	0.50 $\pm$ 0.100	100.38 $\pm$ 20.112	389.77 $\pm$ 78.094	CT09	N	N
T10	N	N	<DL	254.63 $\pm$ 51.018	CT10	32.29 $\pm$ 6.470	252.93 $\pm$ 50.677
T11	<DL	0.43 $\pm$ 0.086	<DL	196.42 $\pm$ 39.355	CT11	N	N
T12	0.03 $\pm$ 0.006	0.52 $\pm$ 0.104	59.80 $\pm$ 11.982	N	CT12	N	N
T13	0.02 $\pm$ 0.003	<DL	70.09 $\pm$ 14.043	226.23 $\pm$ 45.327	CT13	N	N
T14	<DL	<DL	100.24 $\pm$ 20.084	380.01 $\pm$ 76.139	CT14	36.67 $\pm$ 7.347	N
T15	0.02 $\pm$ 0.004	0.60 $\pm$ 0.120	88.54 $\pm$ 17.740	403.86 $\pm$ 80.917	CT15	N	N
T16	<DL	<DL	42.86 $\pm$ 8.587	170.17 $\pm$ 34.095	CT16	69.02 $\pm$ 13.829	150.75 $\pm$ 30.204
T17	0.02 $\pm$ 0.003	0.33 $\pm$ 0.066	51.48 $\pm$ 10.315	281.74 $\pm$ 56.449	CT17	101.90 $\pm$ 20.417	45.29 $\pm$ 9.074
T18	N	N	56.51 $\pm$ 11.322	218.96 $\pm$ 43.871	CT18	74.54 $\pm$ 14.935	134.58 $\pm$ 26.964
T19	DL	0.62 $\pm$ 0.124	54.22 $\pm$ 10.864	329.66 $\pm$ 66.051	CT19	N	N
T20	0.03 $\pm$ 0.005	0.69 $\pm$ 0.138	<DL	96.13 $\pm$ 19.261	CT20	<DL	38.40 $\pm$ 7.694
T21	<DL	0.50 $\pm$ 0.100	21.99 $\pm$ 4.46	111.93 $\pm$ 22.426	CT21	61.72 $\pm$ 12.366	33.72 $\pm$ 6.756
T22	0.02 $\pm$ 0.004	0.43 $\pm$ 0.086	65.75 $\pm$ 13.174	134.66 $\pm$ 26.980	CT22	N	N
T23	N	N	29.52 $\pm$ 5.915	397.77 $\pm$ 79.697	CT23	N	N
T24	N	N	53.46 $\pm$ 10.711	123.56 $\pm$ 24.756	CT24	103.09 $\pm$ 20.655	70.79 $\pm$ 14.183
T25	N	N	93.05 $\pm$ 18.643	296.26 $\pm$ 59.359	CT25	55.83 $\pm$ 11.186	93.59 $\pm$ 18.752
T26	N	N	34.73 $\pm$ 6.958	138.75 $\pm$ 27.800	CT26	N	N
T27	<DL	<DL	79.83 $\pm$ 15.995	162.05 $\pm$ 32.468	CT27	38.24 $\pm$ 7.662	98.99 $\pm$ 19.834
T28	N	N	32.40 $\pm$ 6.492	804.11 $\pm$ 161.111	CT28	N	N
T29	0.26 $\pm$ 0.052	<DL	N	131.40 $\pm$ 26.327	CT29	N	N
T30	0.27 $\pm$ 0.054	<DL	N	407.66 $\pm$ 81.679	CT30	N	N

Table 3. Ta concentrations in air, urine, and fecal samples.