PROTECTED BUSINESS INFORMATION

~~ARSENIC~~
~~TECHNICAL~~
~~ADVISOR COP~~Y

DRAFT

RECOVERY AND PURIFICATION OF ARSENIC OXIDE - GIANT MINE

DECEMBER 1999

MINING AND MINERAL SCIENCES LABORATORIES
J.E. Dutrizac, P.A. Riveros,
T.T. Chen and A. Dubreuil

Work performed for:
Department of Indian Affairs and
Northern Development, and
Royal Oak Mines Inc.

Job No. 601903

CONFIDENTIAL

MINING AND MINERAL SCIENCES LABORATORIES
REPORT MMSL 99-078 (CR)

CANMET

Gaëtan, Raymond

To: thompson@inac.gc.ca
Cc: Dutrizac, John
Subject: Report on Recovery and Purification of Arsenic Oxide-Giant Mine

Neill,

As mentioned in my last E-Mail to you, I have ready to be sent by courrier, a DRAFT version of the report. There are few gaps and these are as follows:
- Antimony analysis have to be confirmed;
- Results of Acid Leach are available at 50%. Remaining to come;
- A conclusion is being written and will be available early in January (next week); and
- No third party eduting was done on the draft report.

I hope this will be of immediate help for you at this specific moment.

Happy New Year.

INDIAN AND NORTHERN
AFFAIRS - CANADA
N.W.T. REGION

JAN 06 2000

WATER RESOURCES
DIVISION
YELLOWKNIFE, NT

INTRODUCTION

The Giant Mine, Yellowknife, Northwest Territories has been in operation for over fifty years and has produced 6,800,000 oz of gold in that period. Ore reserves, however, are nearly exhausted. In fact, at the present price of gold, calculated ore reserves are adequate for less than two years of operation. Until very recently, the mine was operated by Royal Oak Mines Inc., but that company was declared bankrupt in 1999. Accordingly, the mine is presently operating under a court-appointed receiver. At the Giant Mine, the ore is crushed, milled and then is floated to produce an arsenopyrite (FeAsS)-pyrite (FeS_2) concentrate. The concentrate is refractory, and accordingly, is subjected to roasting in a series of two slurry-feed Dorr-Oliver roasters to drive off the sulphur as SO_2 and the arsenic as As_2O_3. A two-stage roasting operation is required to ensure the total evolution of the arsenic as As_2O_3 and the compete liberation of the gold for subsequent cyanidation. Gases from the roaster train are passed through a hot electrostatic precipitator to collect any carried-over calcine, which is recycled to the gold extraction circuit. The gases are then cooled, by admitting dilution air, to condense the arsenic oxide. Finally, the As_2O_3 fume is collected in a baghouse, which operates with a solids collection efficiency of 99.9%. The collected As_2O_3-rich dust is easily fluidized and is subsequently transported pneumatically (1).

The As_2O_3-rich dusts produced since 1951 have been stored underground, initially in chambers in permafrost, but subsequently in chambers excavated in coherent bedrock. Presently, 265,000 tonnes of the As_2O_3-rich dust are stored underground in 15 chambers, and 8-15 t/day of new dust is accumulating. It is reported that, on average, the accumulated dust contains 76% As_2O_3 and 0.54 oz/t Au; however, localized gold concentrations as high as 2 oz/t Au have been analyzed. The dust presently produced is reported to contain 89% As_2O_3 (67.7% As), 1.04% Sb, 1.68% Fe and 0.14 oz/t Au. Recent mining activities have disturbed the permafrost seal in some of the chambers, and some arsenic contamination of the mine waters is occurring. Accordingly, the As-containing mine waters are pumped to the surface, where they are oxidized with hydrogen peroxide (H_2O_2) and then are treated with lime (CaO) and ferric sulphate ($Fe_2(SO_4)_3$) to precipitate an insoluble amorphous iron arsenate compound for storage in a residue pond (1).

The Department of Indian Affairs and Northern Development (DIAND) has the responsibility as regulator to ensure that the environment of the Northwest Territories is protected and that human health is maintained. Accordingly, DIAND is considering various options to reduce or eliminate the potential environmental and health impacts caused by the stored As_2O_3-rich dust. One of these options is the reprocessing of the dust to recover a purified arsenic oxide product which could be used in the wood preservative industry or for other applications. Although the value of As_2O_3 is only U.S. \$0.20-\$0.30/lb, the manufacture of any product would remove the arsenic from the mine site and convert it into a useful commodity. For such applications, it is claimed that the product must contain >98% As_2O_3, but less than 0.2% Sb and 0.02% Fe, although the need for such low Sb and Fe specifications for wood preservative applications is not clear.

One means to produce a marketable arsenic product from the As_2O_3-rich dust involves leaching with hot water to dissolve As_2O_3 selectively, filtration to reject insoluble matter, removal of any co-solubilized Sb from solution to meet product specifications, and crystallization of a pure As_2O_3 product from the aqueous medium. Preliminary testwork on the water leaching option was carried out by Royal Oak Mines (private communication of L. Connell, Royal Oak Mines Inc., 1998). Using a residence time of 30-240 minutes at 95°C, the company was able to achieve >90% As dissolution, while rejecting ~80% of the Sb to the residue. Negligible iron dissolution occurred. Over 80% of the mass of the initial dust dissolved; the residue amounted to about 17% of the initial mass and contained 39% As. The solution generated at 95°C analyzed 31 g/L As, 92 mg/L Sb and 6 mg/L Fe. The observed As solubility of 31 g/L As, however, is much less than the reported solubility of ~100 g/L As_2O_3 (~75 g/L As) (2). The reasons for the low solubilities over the As_2O_3-rich dusts are not known, but they could be partly attributable to the relatively short leaching times used (<4 h) or to the low pulp densities employed (~5% solids). Because of the low arsenic solubilities realized, the yield of As_2O_3 crystals during the subsequent cooling of the solution to ambient temperature was unacceptably low. In the Royal Oak work, this problem was addressed by evaporation of the ~95°C solution to about one-third of its initial volume prior to cooling to room temperature to crystallize As_2O_3. Efforts were also made to remove part of the co-dissolved Sb using two ion exchange resins and activated carbon. The use of the resins or activated carbon allowed the crystallization of a product containing ~100% As_2O_3, <0.2% Sb and <0.05% Fe. Hence, it appears that the simple water leaching-crystallization technique can yield an As_2O_3 product which satisfies the purity requirements of the marketplace. The major difficulty with this processing option seems to be the low As_2O_3 solubilities produced in the leaching part of the process that result in a commercially unacceptable yield of As_2O_3 crystals unless costly techniques, such as solution evaporation, are employed.

A second option to produce a pure As_2O_3 product is the controlled re-sublimation of the As_2O_3-rich dust to collect a pure As_2O_3 fume while leaving most of the impurities in a residue for subsequent treatment and stabilization. This option has also been pursued by Royal Oak Mines using the Warox process (1). Their test work showed that it was possible to re-sublime the As_2O_3-rich dust to yield a fume containing 99.3-99.8% As_2O_3, together with less than 0.05% Fe. Significantly, the Sb contents of the sublimates ranged from 0.13 to 0.59% Sb. Careful study of the low-Sb products, however, indicated that they tended to originate from low-Sb dusts. That is, there was little selective re-sublimation of As_2O_3 relative to Sb_2O_3. Although re-sublimation can control most of the impurities in the dust, the behaviour of antimony remains a concern with this option.

Within the above framework, CANMET was contracted to investigate the production of pure As_2O_3 using water leaching-crystallization and re-sublimation techniques. The initial contract was jointly funded by DIAND and Royal Oak Mines Inc. and was initiated in October, 1998. During that study, it became apparent that the originally proposed scope of work needed to be expanded, and as a consequence, the original project was amended and extended in February, 1999. The amendment was authorized only by DIAND as Royal Oak Mines Inc. was in receivership at that time.

The scope of the original and amended project involves the production of pure As_2O_3 by water leaching-crystallization and by re-sublimation of four As_2O_3-rich dust samples provided by the company. The water leaching work was intended to measure the solubility of As_2O_3 in water as a function of temperature on both heating and cooling. Because low solubilities were initially measured, they were subsequently determined at temperatures up to 200°C with the use of a high pressure autoclave. These latter tests suggested a possible processing procedure that involves autoclave leaching, cooling of the slurry to 95-100°C, followed by filtration and the subsequent cooling of the solution to room temperature to crystallize pure As_2O_3. Efforts were also made to leach the As_2O_3-rich dusts in acid media. Sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and nitric acid (HNO_3) were evaluated for this application, and subsequently, a number of leaching parameters were examined using hydrochloric acid or nitric acid as the leaching medium. Moderate As_2O_3 solubilities were realized in hydrochloric acid media, and hydrochloric acid leaching seems to offer some advantages over water leaching. Attempts were made to remove the low concentrations of co-dissolved Sb from the water and acid leach liquors using four ion exchange resins and activated carbon. These studies were done at various temperatures to try to optimize the level of antimony removal. Re-sublimation tests were carried out for different times at various temperatures and flow rates to try to enhance the vaporization of As_2O_3 relative to Sb_2O_3. The use of oxidizing, neutral and reducing atmospheres was explored. The initial results on the re-sublimation of As_2O_3 from the dusts indicated that the greatest selectivity of As_2O_3 over Sb_2O_3 occurred at the lowest temperatures, where unfortunately, mass transport of the vapour is also low. Consequently, the use of controlled re-sublimation at low temperatures was also investigated to try to obtain a high level of As_2O_3 selectivity over Sb_2O_3, together with an acceptable re-sublimation rate. To complement the re-sublimation activities, a preliminary mass spectrographic study of the vapour produced from one of the dusts was done to ascertain whether mixed $(As_{4-x}Sb_x)O_6$ molecules were present, or whether the vapour consisted only of As_4O_6 and Sb_4O_6 entities (3). In support of both the water leaching and re-sublimation activities, detailed mineralogical studies were carried out on the as-received As_2O_3-rich dust samples and on some of the intermediate products. The mineralogical activities focussed on the As-, Sb- and Fe-containing phases rather than on the gold content of the dusts. This report summarizes the results of the above exploratory investigations, and also offers some observations on their implications for the recovery of a marketable As_2O_3 product from the As_2O_3-rich dusts stored at the Giant Mine.

EXPERIMENTAL

Samples

Four samples of As_2O_3-rich dust from the Giant Mine were supplied by Royal Oak Mines Inc. Two of the dust samples were recent composites, and were identified as the January 98 Composite and the April 97 Composite. The remaining two samples were taken from the underground storage chambers, and were identified as 212 Chamber and 236 Chamber. All four samples were fine powders; three of the dusts were dry, but the 236 Chamber sample was slightly damp. All four samples, however, were used without further treatment. Reagent grade arsenious oxide (J.T. Baker, 99.95% As_2O_3) and reagent grade antimony trioxide (J.T. Baker, 101.4% Sb_2O_3) were sometimes used for comparative experimentation; the reagent grade oxides also were used in the as-received state.

Mineralogical Techniques

X-ray powder diffraction analyses were carried out on the four as-supplied samples, on the reagent grade As_2O_3, on some of the water leach and acid leach residues, and on some of the re-sublimation products using a Rigaku automated diffractometer with a water-cooled rotating copper anode. The detection limit of most crystalline compounds by this apparatus is 1-3%, depending on the number of phases present and their diffracting powers. Polished sections of the samples were prepared, and these were then examined using scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). Extensive use was made of the backscattered electron detector at high magnification to distinguish compositionally different phases. Some of the phases were analyzed quantitatively with a JEOL-8900 electron microprobe operated, generally, at 20 kV and a 20 nanoampere beam current. In some instances, loose powder mounts of the samples, wherein the material was sprinkled loosely on the stage of the electron microscope, were examined with the SEM to show the morphology of the dust particles more fully. Details of the various mineralogical procedures have been reported previously (4).

Solubility Measurements

The solubility experiments were done in a 2-L reaction vessel having a tight-fitting ground glass lid to prevent water evaporation during the course of the experiments. As shown in Figure 1, a thermometer (±0.1°C), a water-cooled condenser which was loosely stoppered, and a sampling tube closed at the bottom with a medium porosity glass frit were fitted in the lid of the vessel. The sampling tube with the fritted glass disk extended into the middle of the test slurry. The reaction vessel and its contents were heated in a temperature-controlled circulating oil bath regulated to better than ±0.1°C. The actual temperature of the solution was measured by the thermometer suspended in the slurry. The reaction vessel containing ~1.5 L of solution with an excess of dust (~150 g) rested on the bottom of the oil bath, and the slurry was stirred magnetically from beneath.

The solubility measurements were performed as follows. One and a half litres of water were placed in the 2-L reaction vessel together with an excess of the As_2O_3-rich dust or reagent grade As_2O_3 and Sb_2O_3. The contents were then stirred for ~3 days to attain equilibrium. Preliminary experiments showed that the dusts equilibrated slowly in water; three days were required to reach saturation at room temperature and one day was required at 60°C. Significantly, most of the solubility measurements carried out previously by Royal Oak Mines used equilibration times of <4 h. When equilibrium had been attained, a clean fritted sampling tube was immersed in the liquid and was thermally equilibrated. Saturated solution was then drawn through the frit into the sampling tube by the application of suction at the open end. When the sampling tube within the reaction vessel was partly filled with the filtered solution, the suction attachment, which fitted into the open end of the sampling tube in the lid of the vessel, was removed and samples of the hot solution were taken using 5 mL glass pipettes. The pipettes were previously calibrated as a function of temperature using pure water and the same sampling procedure as that employed for the As_2O_3-saturated solutions. A solution sample was taken at each temperature. The sample was diluted directly into 100 mL or 500 mL of 2% HNO_3 contained in a volumetric flask; the dilution factor was sufficiently large that crystallization of As_2O_3 or Sb_2O_3 never occurred. The contents of the volumetric flask were brought to volume, and the solution was analyzed for As by ICP analysis and for Sb and Fe by ICP-mass spectroscopy. In some instances, a second sample was taken at the various temperatures. These samples were discharged directly into a weighing bottle, sealed, cooled to room temperature, and weighed; this sample allowed the density of the saturated solution to be calculated.

After the samples were taken, the solution temperature was increased to 100°C in 10°C increments, with samples being taken at each incremental temperature. The solution was then cooled to ~95°C, and subsequently, in 10°C increments to room temperature or to 5°C to obtain saturation curves on both heating and cooling. Agreement between the data obtained on heating and cooling is necessary if "equilibrium" solubilities are to be reported.

The solubilities were calculated from the measured concentrations, the dilution factor and the volume of the calibrated pipette. The densities of the saturated solutions were calculated as a function of temperature by the measured weight of the sample and the calibrated volume of the pipette.

Autoclave Solubility-Leaching Tests

These experiments were carried out in a Parr 2-L titanium autoclave fitted with a glass liner and titanium internals. The As_2O_3-rich dust and water were placed in the autoclave, which was sealed and then heated rapidly to the desired reaction temperature of 125-200°C. Because of the high temperatures used in the autoclave solubility experiments, solution saturation was achieved in just a few hours. In this regard, retention times were measured from the moment that the operating temperature was reached, although it is recognized that some dissolution occurs during the heat-up period. The experiments were done without an applied gas pressure; that is, the tests were effected only under the steam pressure generated by the system. At the end of the reaction period, the autoclave was rapidly cooled (~5 min) to 95-100°C by the use of the internal water cooling coil. Of course, at temperatures <100°C, the pressure in the autoclave is that of the surrounding atmosphere. The autoclave was opened at 95-100°C, and the slurry was rapidly transferred to a solubility reactor heated to 95°C in its oil bath. The solubility reactor was sealed, and then equilibrated for 2-3 days at 95°C. A sample was taken for a solubility determination and the vessel was then cooled to room temperature. The procedure for determining the solubilities is described above.

In those experiments intended to produce As_2O_3 crystals, the autoclave slurry at 95-100°C was filtered hot using a Buchner vacuum filter with Whatman No. 3 paper; the apparatus was preheated to ensure that the temperature of the filtrate was always ~95°C. Following filtration, the solution was transferred to a beaker and was allowed to cool to room temperature while being gently agitated. It was found that As_2O_3 crystals formed spontaneously and without the need for As_2O_3 seed additions. When crystallization was complete (~16 h), the product was filtered using Whatman No. 3 paper. The various precipitates were collected, dried at 110°C, weighed, and sometimes, analyzed.

Antimony Removal by Ion Exchange or Activated Carbon

Four commercial ion exchange resins were selected on the basis of previous experiments carried out by Royal Oak Mines and on information published in the open literature. These resins were considered to be the most promising for the removal of antimony from concentrated As_2O_3-containing media under neutral or acid pH conditions. Samples of the resins were obtained from the manufacturers, and Table 1 presents a list of the four ion exchange resins used. The resins were hydrated for 24 h, washed with copious amounts of water and then used without additional treatment.

Table 1 - Ion Exchange Resins Tested for Antimony Removal

Resin	Type	Manufacturer
Gravex GR-2-0	Sulphonic	Graver Technologies
Amberlite IRC 120	Sulphonic	Rohm and Haas
Amberlite IRC 50	Carboxylic	Rohm and Haas
Duolite C467	Aminophosphonic	Rohm and Haas

Equilibrium extraction experiments were carried out by contacting appropriate amounts of the individual resins with the Sb-containing As_2O_3-rich solution, while applying gentle mechanical agitation. For most experiments, the amount of resin is expressed as the "wet settled volume", as is common practice in ion exchange applications. In some experiments, however, where a direct comparison with activated carbon was desired, the actual resin weight was used instead of the resin volume. In all the experiments, the extent of antimony removal was calculated from the Sb concentration of the aqueous solution before and after its contact with the resin. Total Sb was analyzed, and no effort was made to differentiate Sb(III) from Sb(V).

In addition to the four ion exchange resins given in Table 1, an activated carbon sample, Hycarb 6X12, was also evaluated for its Sb removal potential. The activated carbon was washed with water prior to use.

Re-Sublimation of the As_2O_3-Rich Dusts

The overall objective of this part of the investigation was to re-sublime the as-received As_2O_3-rich dusts to produce a pure As_2O_3 product. These experiments were carried out using a horizontal tube furnace which was 60 cm in length. A fused silica tube 90 cm long by 60 mm outside diameter was positioned in the tube furnace such that ~25 cm of the tube protruded on one side. The As_2O_3-rich dust was weighed and placed in an alumina crucible which was positioned in the constant temperature (±2°C) hot zone of the furnace. Rubber stoppers were used to seal the ends of the tube, and the stoppers were fitted with ports for the entry and exit of gases and for a temperature measuring thermocouple. Gas was sometimes passed through the tube to help transport the volatilized As_2O_3 to the cooler part of the tube where it condensed as a "ring" on the surface of the glass. At the completion of the experiment, the tube was removed from the furnace and was cooled. The condensed oxide product was removed and analyzed. The re-sublimation experiments were carried out at various temperatures and, sometimes, for different degrees of sublimation. Comparative tests were done using slowly-flowing oxygen, inert gas and hydrogen to assess the influence of the gaseous atmosphere on the relative transport of As_2O_3 and Sb_2O_3. Finally, screening experiments were done wherein the dust was heated with As metal to try to remove any vapourized antimony oxide from the gas stream prior to the condensation of the As_2O_3. To complement the vapourization studies and to provide a fundamental rationale for the co-sublimation of antimony at temperatures significantly below the 1550°C boiling point of Sb_2O_3, a preliminary mass spectrographic study of the vapours was carried out. This work was sub-contracted to the University of Montreal and was based on the use of a Micromass Autospec-OA time-of-flight mass spectrometer operating in the EI mode at 70 eV. The samples were heated to 300°C on a solid probe to vapourize the arsenic and antimony oxide species into the mass spectrometer.

Arsenic Solubility in Acid Media

The intent of these experiments was to evaluate the possibility of enhancing the solubility of As_2O_3 over the As_2O_3-rich dusts by the use of acid media in place of water. All of these scoping experiments were done using the 236 Chamber sample. The acid leaching experiments were carried out in 2-L glass reaction kettles contained in a temperature-controlled oil bath. One litre of the acid solution was heated to 95°C, and at that point, a known mass of the As_2O_3-rich dust from the 236 Chamber was added and was stirred for the duration of the experiment, generally 2 h. The acids initially evaluated were 2.0 M HCl, 2.0 M HNO_3 and 1.0 M H_2SO_4 (i.e., 2.0 M H^+) . For the experiments using the different acids, solution samples were taken at various time intervals by drawing the liquid through an in-line filter. The collected solutions were stored in a water bath at 95°C. Subsequently, they were accurately pipetted, diluted to a known volume and finally analyzed to assess the extent of arsenic dissolution as a function of time. Based on these initial tests, nitric acid (HNO_3) and hydrochloric acid (HCl) were selected for further experimentation. The parameters investigated in this latter part of the study were the acid concentration (1.0, 2.0, 3.0 and 4.0 M HNO_3; 0.75, 2.0 and 3.0 M HCl) the leaching temperature (95°C, 75°C and 55°C) and the solids content of the slurry (75 g/L and 175 g/L solids). For the latter experiments, solution sampling as a function of time was not done. Rather, leaching was carried out for a constant 2-h period. At that time, the slurry was filtered while hot, and the filtrate was collected. The leach residue was then water-washed, dried at 110°C, and analyzed by X-ray powder diffraction methods. The filtrate was then cooled to room temperature to allow As_2O_3 to crystallize. The As_2O_3 crystals were filtered, dried at ~60°C, weighed and also analyzed by X-ray diffraction methods. In some tests, the solution remaining after filtration of the As_2O_3 crystals was neutralized to pH 9.0 with solid, reagent grade Na_2CO_3 to try to precipitate additional As_2O_3. The resulting precipitate was filtered, washed, dried at 110°C, and then analyzed by X-ray powder diffraction techniques to identify the arsenic compound precipitated.

RESULTS AND DISCUSSION

Samples

The four samples of As_2O_3-rich dust supplied by Royal Oak Mines were analyzed at CANMET; the results are presented in Table 2. The recent composite samples have As contents in excess of 66% As (>87% As_2O_3), but also contain modest amounts of Sb, Fe, Al, Ca, Mg and Si. The two samples from the underground chambers have much lower As contents (56-58% As), but also contain minor amounts of Sb, Fe, Al, Ca, Mg and Si. The Sb content is a concern for the marketing of any As_2O_3 product, and the Sb contents of the as-received dusts are variable. They range from 0.30 to 2.13% Sb. The data of Table 2 support the view that the stockpiled dusts have higher gold values than the dusts presently being generated.

Table 2 - Chemical Compositions of the Four As_2O_3-rich Dust Samples Provided by Royal Oak Mines (wt %)

Element	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As	68.2, 68.7	66.7, 69.6	56.2	58.0
Sb	0.87, 0.84	1.48, 1.49	2.13	0.30
Fe	1.23, 1.17	0.78. 0.81	2.62	1.66
Al	0.64, 0.64	0.33, 0.33	1.06	0.92
Ca	--	--	--	--
Mg	0.24, 0.26	0.13, 0.13	0.37	0.36
Si	1.05, 1.09	0.61, 0.61	2.07	1.81
Au(ppm)	2.2	2.4	11.0	5.1

Mineralogical Characterization of the Four Dust Samples

X-ray diffraction analyses of the two lots of reagent grade arsenic oxide indicated only As_2O_3 having the cubic arsenolite structure. Analogous X-ray diffraction analyses of the four dust samples showed them to be very similar, *inter alia,* despite the minor differences in chemical composition indicated in Table 2. The X-ray diffraction patterns of the four dust samples are presented in Appendix 1. All four samples consist of major amounts of As_2O_3 of the arsenolite structure, together with minor amounts of a chlorite-type mineral (chamosite?) having the general formula of $(Fe,Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$. A trace quantity of muscovite, $KAl_2(Si_3Al)O_{10}(OH,F)$, is also evident. Quartz is also present in trace amounts, but the detection of quartz is made difficult because the strong line of quartz overlaps that of muscovite. The amounts of chlorite, muscovite and quartz, relative to arsenolite, vary somewhat from sample to sample, but arsenolite is always the dominant phase. The four dust samples were supplied in large plastic pails. To investigate the possibility of sample segregation within the pails, X-ray diffraction analyses of material from the top and bottom of each pail were carried out. The spectra from the top and bottom of a given pail were identical, and the implication is that the supplied samples themselves are relatively homogeneous.

Characterization of the January 98 Composite Sample

Detailed SEM-EDX study of the dust provided considerably more insight into the phases present. Figure 2 presents a general view of the January 98 Composite sample. This sample consists mostly of As_2O_3 which commonly occurs as 1-3 μm free crystals or as somewhat larger crystal agglomerates. Many of the As_2O_3 crystals demonstrate an octahedral morphology characteristic of arsenolite. The large and darker appearing particles are chlorite (chamosite ?) or quartz. Tiny bright appearing grains of iron oxide having a minor As content are also present. The EDX study of the As_2O_3 particles commonly detected trace amounts of Sb; similar studies showed the chlorite to contain major amounts of Mg, Al and Si, along with traces of Fe, K and Na.

Figure 3 is a backscattered electron micrograph of the same sample as seen in polished section. The arsenolite (As_2O_3) occurs abundantly as tiny bright appearing crystals or crystal aggregates. The EDX study of the As_2O_3 commonly detected a trace-to-minor amount of Sb. The larger platy crystals are chlorite, whereas the dark appearing irregular grains are usually quartz. Of note are a number of 1-3 μm calcium arsenate particles having a minor or trace S content. Occasionally, large masses of As_2O_3 or $(As,Sb)_2O_3$ are detected, and one such mass is illustrated in Figure 4. Although the majority of the image shown in Figure 4 consists of 1-3 μm euhedral As_2O_3 crystals and somewhat larger grains of As-bearing iron oxide, a >50 μm mass of As_2O_3 having a trace Sb content is also evident. Such masses of As_2O_3 are moderately abundant in this sample, but nevertheless, constitute only a small percentage of the total As_2O_3 present. The mechanism of formation of these large masses of As_2O_3 is not known, but they may represent spalled accumulations from the roof or ducting of the baghouse.

Rarer masses of $(Sb,As)_2O_3$ are also detected, and one such occurrence is shown in Figure 5. The mass is 40-50 μm in size, and is irregular in form. Its brighter appearance reflects the elevated Sb content of this phase, which seems to be an As-bearing Sb-rich oxide; i.e., $(Sb,As)_2O_3$. The mechanism by which such Sb-rich oxide particles form in the baghouse is unknown.

An iron arsenic-oxide phase occurs in minor amounts in the January 98 Composite sample, and the iron arsenic-oxide ranges in composition from As-bearing iron oxide to compositions approaching iron arsenate. Figure 6 illustrates a ~20 μm mass of iron oxide containing minor amounts of As as well as traces of Sb. The iron oxide particle has a banded texture that may reflect the cyclical oxidation of a grain of pyrite. Variations in the grey level of the iron oxide reflect local variations in the As content. In this instance, it seems that the morphology of the original iron oxide particle has been faithfully preserved. Figure 7 illustrates a ~100 μm porous mass of iron arsenate that is associated with a large mass of As_2O_3 and numerous tiny As_2O_3 crystals. The iron arsenate phase contains major amounts of iron and arsenic, as well as a minor-to-major S content. It is likely an iron arsenate phase having a significant sulphate ion substitution for arsenate. The morphology suggests a complex formation mechanism that likely involves the diffusion of both As and Fe.

The SEM-EDX investigation of the January 98 Composite sample also detected trace amounts of a number of other phases. These phases are Mg silicate, Fe-Ca-Al silicate-sulphate, K-Mg-Al silicate, Na-Mg-Al silicate, Ca-Na-Mg-Al silicate, K-Al silicate (feldspar) and $PbSO_4$.

Quantitative electron microprobe analyses were carried out on the As- and Sb-containing phases in the January 98 Composite sample, and the detailed analyses are presented in Appendix 2.

Table 3 summarizes the electron microprobe data obtained for the major As_2O_3 phase. Thirty-nine particles of As_2O_3 were analyzed, and these particles included both the abundant tiny As_2O_3 crystals and the less common large masses of As_2O_3. Aside from its modest Sb content, the As_2O_3 is relatively pure, with only trace amounts of Fe and Pb being detected as impurities. Its general formula is $(As,Sb)_2O_3$. Given the abundance of the As_2O_3 phase in this sample and its high As and Sb content relative to the bulk composition of the dust (Table 2), it is clear that the As_2O_3 phase is the dominant As and Sb carrier in the January 98 Composite sample.

Table 3 - Electron Microprobe Determined Composition of the As_2O_3 Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
As	75.03	63.04 - 82.11
Sb	1.31	0.00 - 5.38
Fe	0.18	0.00 - 2.01
Pb	0.07	0.00 - 1.88
O	23.41	17.63 - 32.55

Table 4 presents the electron microprobe-determined compositional data for the Sb-rich oxide phase present in the January 98 Composite sample. Although this phase is a minor constituent of the dust, it has a high Sb and As content; that is, the phase is possibly best formulated as $(Sb,As)_2O_3$. The Sb-rich oxide seems to be relatively pure; only trace amounts of Fe and Pb are detected in its structure.

Table 4 - Electron Microprobe Determined Composition of the $(Sb,As)_2O_3$ Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Sb	44.65	40.50 - 47.77
As	35.16	28.94 - 38.95
Fe	0.05	0.01 - 0.09
Pb	0.01	0.00 - 0.07
O	20.12	14.41 - 30.52

The January 98 Composite sample contains both an As-bearing iron oxide phase as well as an iron arsenate phase. Table 5 summarizes the compositional data obtained on nine particles of the As-bearing iron oxide. The iron oxide phase contains major amounts of Fe and O, in addition to minor contents of As and Sb, and traces of Pb and S. The compositional data suggest a hematite-like compound, but complementary structural studies would be needed to collaborate this conclusion. Table 6 summarizes the analogous data obtained from 16 particles of the iron arsenate phase. This material has a relatively low Fe content but relatively high levels of As and S, which likely are present as AsO_4 and SO_4. There are also trace amounts of Sb, Pb, Ca and Bi detected. The composition suggests an iron arsenate compound having a significant degree of sulphate substitution for arsenate, but it should be appreciated that some of the analyses may be biased by intimately admixed As_2O_3.

Table 5 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Fe	59.11	57.51 - 61.11
As	4.68	3.15 - 5.87
Sb	1.67	1.15 - 2.10
Pb	0.10	0.05 - 0.17
S	0.04	0.00 - 0.08
O	34.39	33.67 - 35.23

Table 6 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the January 98 Composite Sample (wt %)

Element	Average Composition	Range
Fe	10.15	1.78 - 38.33
As	15.95	7.92 - 21.63
Sb	0.27	0.06 - 0.87
S	3.57	0.23 - 7.41
Pb	0.10	0.04 - 0.19
Ca	0.73	0.04 - 4.39
Bi	0.03	0.00 - 0.07
O	69.16	52.44 - 77.45

Characterization of the April 97 Composite Sample

In terms of its chemical composition (see Table 2) the April 97 Composite sample is similar to the January 98 Composite sample, although there are minor differences in the Sb contents as well as those of Fe, Al, Ca, Mg and Si. Both samples are more rich in As than the two samples collected from the storage chambers.

The SEM-EDX studies also indicated many similarities between the April 97 Composite sample and the January 98 Composite sample. In this regard, Figure 8 shows the general appearance of the April 97 Composite sample as seen in a loose powder mount. The sample consists predominantly of 1-3 μm crystals of As_2O_3, many of which have well developed external crystal faces. The EDX analysis showed major amounts of As, together with traces of Sb. The larger, irregular particles are chlorite, which consists mostly of Fe, Mg, Al, Si and O. Comparison with Figure 2 indicates that the general morphologies of the April 97 Composite and January 98 Composite samples are very similar.

Figure 9 shows the April 97 Composite sample in more detail and in polished section. Most of the field consists of 1-3 μm crystals of As_2O_3, which generally occur free but sometimes are intergrown into larger agglomerates. The large, bright appearing particle in the centre of the image is $(As,Sb)_2O_3$ containing about 13% Sb. As noted above, the mechanism by which such large arsenic-antimony oxide particles form is not known. The figure also indicates a number of small particles of quartz that passed through the electrostatic precipitator circuit and were collected in the baghouse along with the As_2O_3. Figure 10 shows an even larger mass of $(As,Sb)_2O_3$, the growth of which has sometimes encapsulated other species. Such large particles of $(As,Sb)_2O_3$ presumably formed on the walls or ducting of the baghouse where they accumulated to a considerable thickness before becoming dislodged and reporting with the baghouse dust. The large mass of $(As,Sb)_2O_3$ is associated with smaller crystals of As_2O_3, as well as with particles of quartz and chlorite. Notable is the presence of two ~10 μm particles of iron-calcium oxide containing only trace amounts of As or Sb. Figure 11 illustrates a ~5 μm compact particle of iron arsenate as well as a ~10 μm mass of $(As,Sb)_2O_3$, both of which are associated with 1-3 μm crystals of As_2O_3. Figure 12 illustrates a 10 μm zoned particle which was shown by EDX analysis to contain major amounts of Ca, As, S and O, as well as a trace amount of Fe. This phase is believed to be calcium arsenate-sulphate, and a number of such particles were identified in the April 97 Composite sample. The porous region of this figure is mounting medium.

In addition to the principal species discussed above, the detailed SEM-EDX studies also identified trace amounts of K-Al silicate and Na-Al silicate; these phases likely represent fragments of different feldspars which passed through the electrostatic precipitator circuit into the baghouse. A few particles of calcium oxide containing trace amounts of Fe, As and Sb were also noted.

Quantitative electron microprobe analyses were carried out on the principal As- and Sb-containing phases in the April 97 Composite sample. The detailed electron microprobe results are presented in Appendix 3.

Twenty-four particles of the As_2O_3 phase were analyzed with the electron microprobe, and the results are summarized in Table 7. The material is relatively pure As_2O_3 which contains only 0.23% Sb, in addition to trace amounts of Fe, Pb, Ca and S. The Sb content of the dominant As_2O_3 phase in the April 97 Composite sample is lower than that of the As_2O_3 crystals in the January 98 Composite sample, despite the higher total Sb content of the April 97 Composite sample.

Table 7 - Electron Microprobe Determined Composition of the As_2O_3 Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
As	76.29	71.45 - 82.70
Sb	0.23	0.00 - 0.54
Fe	0.18	0.02 - 0.52
Pb	0.04	0.00 - 0.52
Ca	0.04	0.00 - 0.19
S	0.03	0.00 - 0.18
O	23.15	16.97 - 28.15

In addition to the “normal” As_2O_3 crystals, the April 97 Composite sample contains a number of arsenic oxide particles having an elevated Sb content, but not containing enough Sb to constitute $(Sb,As)_2O_3$. Eight of these Sb-rich As_2O_3 particles were analyzed with the electron microprobe, and the results are given in Table 8. The average Sb content is 13.55%, a high enough concentration to warrant the differentiation of this phase from the “normal” As_2O_3 crystals which contain only 0.23% Sb. A small amount of iron, along with traces of Pb, Ca, Bi and S, is also detected in this material.

Table 8 - Electron Microprobe Determined Composition of the Sb-rich As_2O_3 Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
As	59.59	50.84 - 68.70
Sb	13.55	12.14 - 15.09
Fe	0.42	0.07 - 1.62
Pb	0.05	0.00 - 0.15
Ca	0.13	0.00 - 0.21
Bi	0.01	0.00 - 0.03
S	0.05	0.00 - 0.21
O	26.18	17.99 - 32.16

The April 97 Composite sample also contains an Sb-As oxide phase in which the amount of Sb equals or exceeds that of As; i.e., the phase has the general formula of $(Sb,As)_2O_3$. Thirty-two particles of the $(Sb,As)_2O_3$ phase were analyzed quantitatively with the electron microprobe, and the results are presented in Table 9. Comparison with the data of Table 4 suggests that the $(Sb,As)_2O_3$ phase in the April 97 Composite sample is very similar to that of the analogous phase in the January 98 Composite sample. In particular, the Sb and As contents of the $(Sb,As)_2O_3$ phase are virtually identical in the two samples.

Table 9 - Electron Microprobe Determined Composition of the $(Sb,As)_2O_3$ Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Sb	44.55	42.43 - 46.72
As	35.94	30.71 - 42.45
Fe	0.14	0.00 - 0.84
Pb	0.06	0.00 - 0.34
Ca	0.01	0.00 - 0.11
S	0.84	0.50 - 1.23
O	18.44	11.40 - 25.25

The SEM-EDX studies identified both an iron arsenate phase and a calcium arsenate-sulphate phase having a high Sb content. Electron microprobe analyses of four grains of each phase were carried out, and the data are summarized in Table 10 and Table 11, respectively. The iron arsenate phase contains major amounts of both As and Sb, but has only a very minor Ca and S content. This phase is clearly an iron arsenate-antimonate compound, although As always exceeds Sb in the structure. In contrast, the calcium arsenate-sulphate phase seems to have a major Sb content, but contains only minor amounts of Fe. It would be more fully described as a calcium-iron sulphate-antimonate-arsenate.

Table 10 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Fe	38.17	18.35 - 55.31
As	9.04	6.69 - 11.48
Sb	5.20	0.58 - 9.28
Pb	0.12	0.00 - 0.25
Ca	0.82	0.00 - 2.40
Bi	0.00	-
S	0.85	0.04 - 1.55
O	45.77	37.09 - 57.08

Table 11 - Electron Microprobe Determined Composition of the Calcium Arsenate-Sulphate Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Ca	11.47	10.22 - 12.26
Fe	2.24	1.91 - 2.55
Sb	15.43	11.15 - 20.28
As	8.46	7.73 - 9.57
S	8.93	7.41 - 9.89
Pb	0.14	0.12 - 0.16
O	53.30	50.27 - 56.27

A few particles of calcium oxide were detected during the SEM-EDX study of this sample, and four particles of this phase were analyzed by the electron microprobe. The results are given in Table 12. The phase is mostly calcium oxide, although there is a modest level of Fe present. Only minor amounts of As and Sb are detected. The low As and Sb contents, coupled with the rarity of this phase, make the calcium oxide a relatively unimportant carrier of either As or Sb in this sample.

Table 12 - Electron Microprobe Determined Composition of the Calcium Oxide Phase in the April 97 Composite Sample (wt %)

Element	Average Composition	Range
Ca	19.08	17.68 - 20.33
Fe	5.60	5.29 - 6.05
As	0.93	0.24 - 1.85
Sb	0.41	0.25 - 0.57
Pb	0.00	
S	0.52	0.20 - 0.80
O	73.43	72.67 - 74.54

Characterization of the 212 Chamber Sample

Table 2 indicates that the 212 Chamber sample has the highest Si, Al, Ca, Mg and Fe contents of any of the dusts studied. Accordingly, it would be expected that this sample contains more of the silicate impurity species. The sample also has the highest Sb content of any of the samples, and should, therefore, contain more Sb-rich arsenic oxide species.

Figure 13 illustrates the general appearance of the 212 Chamber sample as seen in a loose powder mount. Most of the sample consists of 1-3 μm crystals of As_2O_3, and many of the crystals show the development of octahedral crystal faces. A number of somewhat larger silicate particles are present in this sample, and Figure 13 shows several such grains of chlorite and muscovite.

A detailed SEM-EDX study of the 212 Chamber sample was carried out using polished section mounts, and Figure 14 illustrates the general appearance of the sample. Most of the bright appearing grains in the photomicrograph are As_2O_3 or As_2O_3 having a modest Sb content. Most of the darker grey grains are chlorite or other silicate species, but some of these particles are As-bearing iron oxide or As-bearing calcium oxide containing minor amounts of Fe and traces of S and Si. Relative to the two more recently collected samples discussed above, the 212 Chamber sample seems to have a higher Ca content. Figure 15 provides another general view of the dust from the 212 Chamber. Although a number of tiny bright appearing crystals of As_2O_3 are evident, there is also a large number of darker appearing particles. Various fragments of quartz and chlorite are evident, as is the situation for all the samples studied. Numerous particles of iron arsenate occur, and these tend to be present as ~10 μm free grains. Of interest is a ~10 μm particle of As-bearing iron oxide that is rimmed by very bright $(Sb,As)_2O_3$. A large grain of muscovite is rimmed by an Fe-Ca sulphate-arsenate phase. Relative to the initial two samples studied, there are more silicate and oxide phases present in the 212 Chamber sample, and several of these minerals seem to have undergone at least superficial alteration during roasting-gas cleaning.

Occasionally, large fragments of Sb-rich arsenic oxide or $(Sb,As)_2O_3$ are detected. Figure 16 illustrates one such occurrence. The bright appearing particle in the centre of the image has a high Sb content; it is likely $(Sb,As)_2O_3$. The particle is 20x40 μm in size. Such large particles were evident in the samples studied above, but the mechanism of formation of such large grains in the baghouse circuit is unknown. In Figure 16, the $(Sb,As)_2O_3$ particle is associated with tiny light grey crystals of As_2O_3 and slightly larger, and darker grey, particles of silicates and iron oxide or calcium oxide.

The 212 Chamber sample contains both iron arsenate and As-bearing iron oxide; the As-bearing iron oxide may be an intermediate phase in the formation of iron arsenate, although additional work would be required to substantiate this hypothesis. Figure 17 illustrates a large mass of iron arsenate, although smaller, typically ~10 μm particles, are more common. The large mass of iron arsenate seems to envelop smaller grains of As_2O_3, and the implication is that the iron arsenate mass "grew" in the baghouse system. In addition, there are two large grains of $CaSO_4$ evident in the image, and these particles support the contention that the dust in the 212 Chamber is Ca-rich. Figure 18 illustrates a 10x12 μm particle of As-bearing iron oxide that may reflect an oxidized pyrite crystal. The grain is distinctly zoned and contains major Fe and O, with minor As and a trace quantity of Sb. Also shown is a smaller, dark appearing grain of As_2O_3 containing minor amounts of Fe and Sb that is probably a reaction product between fine iron oxide particles and the As_2O_3 crystals.

Quantitative electron microprobe analyses were carried out on the As- and Sb-bearing phases present in the 212 Chamber sample. The detailed analyses are presented in Appendix 4, and the results are summarized below.

Table 13 presents the average electron microprobe-determined composition of 31 As_2O_3 crystals present in the 212 Chamber sample. This oxide consists mostly of As, but contains a modest amount of Sb that is consistent with the bulk Sb content of this sample given in Table 2. In addition, there is a modest amount of Fe detected, as well as traces of Pb, Ca, Si and S; some of the detected impurity content could arise from secondary fluorescence from associated impurity phases. That is, the As_2O_3 crystals are so small that penetration of the electron beam is likely.

Table 13 - Electron Microprobe Determined Composition of the As_2O_3 Crystals in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
As	76.01	70.24 - 82.42
Sb	1.19	0.08 - 3.52
Fe	0.56	0.25 - 1.72
Pb	0.03	0.00 - 0.22
Ca	0.05	0.00 - 0.30
Si	0.05	0.00 - 0.52
S	0.04	0.00 - 0.15
O	22.04	16.39 - 29.05

In addition to the "normal" As_2O_3 crystals, which contain ~1% Sb, there are arsenic oxide particles which have elevated contents of Sb. In the January 98 Composite and April 97 Composite samples discussed above, the amount of Sb often exceeded that of As, such that the phase could be described as $(Sb,As)_2O_3$. In the 212 Chamber sample, the Sb content of the arsenic oxide, although significant, generally does not exceed that of As. Consequently the Sb-rich oxide in the 212 Chamber sample is best described as $(As,Sb)_2O_3$. Table 14 summarizes the electron microprobe data obtained on the $(As,Sb)_2O_3$ phase.

The material has a significant As and Sb content, and also contains trace amounts of Fe, Pb and S.

Table 14 - Electron Microprobe Determined Composition of the $(As,Sb)_2O_3$ Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
As	50.46	42.57 - 56.72
Sb	24.44	20.93 - 31.10
Fe	0.33	0.12 - 1.49
Pb	0.03	0.00 - 0.11
S	0.01	0.00 - 0.02
O	24.71	17.14 - 27.82

The 212 Chamber sample contains numerous ~10 μm particles of As-bearing iron oxide as well as an iron arsenate phase exhibiting a modest level of SO_4 substitution for AsO_4. The electron microprobe-determined composition of the As-bearing iron oxide phase, as based on the analysis of 16 particles, is given in Table 15, from which it is apparent that modest amounts of both As and Sb are incorporated in the iron oxide. Other impurity elements, including S, are present only in trace amounts. Table 16 summarizes the analogous compositional data for the iron arsenate phase, as based on the analysis of 21 particles of this material. The iron arsenate phase has a significant content of both Fe and As, and also contains a minor amount of S, which is probably present as SO_4 replacing AsO_4 in the iron arsenate structure. Significantly, there are only trace amounts of Sb and other impurity elements in this material.

Table 15 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	52.41	44.90 - 57.53
As	8.54	3.51 - 14.88
Sb	3.09	0.77 - 9.89
Pb	0.38	0.16 -0.78
Ca	0.26	0.00 - 0.99
S	0.33	0.02 - 3.02
O	34.95	30.98 - 40.27

Table 16 - Electron Microprobe Determined Composition of the Iron Arsenate Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	12.60	11.34 - 13.21
As	31.67	26.19 - 37.33
Sb	0.49	0.38 - 0.73
Pb	0.72	0.50 - 1.10
Ca	0.86	0.64 - 3.46
S	1.58	1.12 - 2.21
O	51.99	45.84 - 57.46

The 212 Chamber sample contains a trace amount of an iron-calcium arsenate phase, and three particles of this compound were analyzed by the electron microprobe. As Table 17 indicates, this phase has a relatively low Sb content; it contains a minor amount of Pb as well as a trace of S.

Table 17 - Electron Microprobe Determined Composition of the Iron-Calcium Arsenate Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	6.62	5.08 - 9.59
Ca	3.03	2.03 - 4.12
As	35.21	29.93 - 41.34
Sb	1.09	1.75 - 2.05
Pb	2.55	2.30 - 3.00
S	0.48	0.08 - 1.30
O	50.17	47.39 - 52.37

A few particles of a Ca-Fe-As oxide phase were detected in the 212 Chamber sample, and three of the particles were analyzed by the electron microprobe. Table 18 summarizes the data obtained, and shows that this oxide consists mostly of Ca, Fe and As, together with trace amounts of Pb, Sb and S. The iron-calcium arsenate phase and the Ca-Fe-As oxide phase are rare constituents of the 212 Chamber sample, and accordingly, are relatively unimportant overall As carriers despite their high As contents.

Table 18 - Electron Microprobe Determined Composition of the Ca-Fe-As Oxide Phase in the 212 Chamber Sample (wt %)

Element	Average Composition	Range
Ca	13.93	8.39 - 18.65
Fe	8.75	8.03 -9.93
As	10.75	1.38 -20.76
Sb	0.53	0.06 - 0.82
Pb	0.24	0.06 - 0.34
S	0.50	0.04 - 1.08
O	65.26	60.29 - 69.85

Characterization of the 236 Chamber Sample

Unlike the other three As_2O_3-rich dusts supplied, the 236 Chamber sample was slightly moist when received, and the water content must affect its analysis to some extent. Nevertheless, the compositional data of Table 2 suggest that the 236 Chamber sample is similar to that of the 212 Chamber material in that it has a comparatively low As content, together with high levels of Fe, Si, Al, Ca and Mg. The 236 Chamber sample has the lowest Sb content of the four samples studied. The implication is that this sample will contain an abundance of low-Sb As_2O_3 crystals and numerous silicate and oxide particles.

Figure 19 shows the general morphology of the 236 Chamber sample as examined in a loose powder mount. The material consists of abundant As_2O_3 crystals ranging in size from 1 μm to over 10 μm. The large size of some of the As_2O_3 crystals differentiates this sample from the others studied. In many instances, the As_2O_3 crystals have well developed external crystal faces, and the crystals are sometimes intergrown into small clusters. Various silicate species are detected in this sample, and Figure 19 shows a small particle of chlorite as well as a larger fragment of muscovite.

Figure 20 illustrates the general morphology of the 236 Chamber sample as seen in polished section. The bright particles are mostly crystals of As_2O_3, and these range in size from 1 μm to 10 μm. The darker appearing particles are mostly silicates, and these include quartz, chlorite and muscovite. Figure 21 shows two of the larger As_2O_3 crystals in greater detail, and also illustrates a ~10 μm particle of As-bearing iron oxide. Most of the dark appearing particles in the image are quartz, chlorite and muscovite. The large As_2O_3 crystals are somewhat porous and seem to be intergrowths of two or three individual crystals. The euhedral habit of the large As_2O_3 crystals suggests that they developed directly in the vapour phase, as the gas from the roaster circuit was cooled with dilution air.

Figure 22 illustrates a particle of As-bearing iron oxide as well as grains of quartz, chlorite and muscovite. The SEM-EDX analyses of the quartz detected only Si and O. Complementary quantitative electron microprobe analyses of three quartz particles indicated ~40% Si and ~59% O; only traces of K, Fe, Mg, Ca and Al were detected, and these trace impurity contents could originate from secondary fluorescence from closely associated impurity phases. Similar SEM-EDX analyses of the chlorite phase indicated Fe, Mg, Al, Si and O, together with occasional traces of K. Electron microprobe analysis of nine particles of the chlorite detected 13-18% Fe, 7-11% Mg, 6-11% Al and 7-11% Si. The composition, together with the X-ray diffraction analyses, confirms that the chlorite mineral is chamosite. The SEM-EDX analyses of the muscovite indicated major amounts of K, Al, Si and O, together with trace quantities of Mg and Fe. Quantitative electron microprobe analyses of five grains of this mineral found 3-7% K, 10-17% Al and 13-21% Si. The compositional range, together with the X-ray diffraction results, confirm the presence of muscovite rather than a potassium feldspar.

Various other species were also detected in trace amounts during the SEM-EDX study of the 236 Chamber sample. These species include iron arsenate, calcium arsenate containing only trace Fe, K-Na-Mg-Al silicate, Ca-Mg-Al silicate, Na-K-Al silicate, iron oxide containing minor Cr and As, apatite and pyrite.

The principal As- and Sb-containing phases in the 236 Chamber sample were analyzed quantitatively with the electron microprobe. The individual analyses are given in Appendix 5, and the various results are summarized below.

Table 19 summarizes the electron microprobe analyses of 60 particles of As_2O_3 in the 236 Chamber sample. The As_2O_3 contains a major amount of As, but only a trace quantity of Sb. The low Sb content is consistent with low overall Sb content of this dust that is given in Table 2. There is also a trace amount of Fe present, but other impurities are nearly absent.

Table 19 - Electron Microprobe Determined Composition of the As_2O_3 Crystals in the 236 Chamber Sample (wt %)

Element	Average Composition	Range
As	76.78	71.43 - 79.87
Sb	0.19	0.00 - 0.99
Fe	0.27	0.08 - 1.13
Pb	0.02	0.00 - 0.13
Ca	0.01	0.00 - 0.09
Si	0.05	0.00 - 0.62
S	0.01	0.00 - 0.11
O	22.64	18.73 - 28.39

As noted above, a number of particles of As-bearing iron oxide are detected in the 236 Chamber sample, and 17 of these grains were analyzed quantitatively with the electron microprobe. Table 20 summarizes the results obtained. The iron oxide has a minor As content, but contains only a trace amount of Sb. Other impurity elements are detected only in low concentrations, but the presence of a small amount of Cr in the iron oxide in this sample is distinctive.

Table 20 - Electron Microprobe Determined Composition of the As-bearing Iron Oxide in the 236 Chamber Sample (wt %)

Element	Average Composition	Range
Fe	53.24	40.88-66.34
As	7.67	1.97 - 14.90
Sb	0.56	0.18 - 0.90
Pb	0.22	0.02 - 0.57
Ca	0.15	0.00 - 0.49
Cr	0.36	0.00 - 6.18
S	0.01	0.00 - 0.04
O	37.77	31.45 - 49.95

Comparison of the Four As_2O_3-Rich Dust Samples

From a mineralogical point of view, the four As_2O_3-rich dust samples are similar in that they contain, with only a few minor exceptions, the same species and in approximately the same amounts. These species are indicated qualitatively in Table 21. The two more recent samples, the January 98 Composite and the April 97 Composite, have high As_2O_3 contents and contain relatively small amounts of the impurity silicate phases. In contrast, the two older samples from the storage caverns, 212 Chamber and 236 Chamber, have relatively high silicate contents that possibly reflect less than optimum functioning of the electrostatic precipitators at the time of their production. The Sb contents of the dusts vary from 0.3 to 2.13% Sb, and this variation affects the Sb content of the As_2O_3 crystals, as well as the amount and composition of the $(Sb,As)_2O_3$ phase present. In all cases, the dominant As carrier is As_2O_3, which normally occurs as tiny euhedral crystals, but sometimes is present as large irregular masses. A minor amount of the As is also present as an Fe-bearing iron oxide or iron arsenate phase, in which the arsenic content varies from 1.9 to 38% As. The Ca arsenate or Ca-Fe arsenate phases are only minor As carriers in any of the dust samples. Most of the Sb in the samples is present in solid solution in the As_2O_3 crystals. The Sb content of the As_2O_3 varies from 0% to 47%. The more Sb-rich compositions are actually $(Sb,As)_2O_3$, and this phase often occurs as large irregular masses. A minor amount of the total Sb substitutes for As in the iron arsenate phase, and traces of Sb occur in the Ca arsenate, Ca-Fe arsenate and Fe arsenate-sulphate phases. Unlike As and Sb, most of the iron in the samples occurs in silicate form (chlorite) and as iron oxide. Lesser amounts of the total iron are present as iron arsenate or Ca-Fe arsenate, which contains 5-10% Fe.

Table 21 - Qualitative Comparison of the Phases Present in the Four As_2O_3-rich Dust Samples

Species	January 98 Composite	April 97 Composite	212 Chamber	236 Chamber
As_2O_3	major	major	major	major
Fe arsenate	minor	minor	minor	minor
$(Sb,As)_2O_3$	minor	minor	minor	trace
Ca-Fe arsenate	trace	trace	minor	trace
Fe arsenate-sulphate	trace	trace	trace	very rare
Iron oxide	trace	trace	trace	trace
Ca-Fe oxide	very rare	trace	trace	very rare
Ca sulphate	very rare	very rare	trace	very rare
Chlorite	minor	minor	minor	minor
Quartz	trace	trace	trace	trace
Muscovite	minor	minor	minor	minor

Solubility Measurements

The aqueous solubility of two lots of reagent grade As_2O_3 was determined over the temperature range from 20°C to 100°C. The results obtained are presented graphically in Figure 23 and Figure 24, and the detailed numerical data are given in Appendix 6. For the first sample, the results obtained on heating and cooling are identical, and the implication is that the measured values reflect the true equilibrium solubility of As_2O_3 in water. This conclusion is further supported by the close agreement of the current data with the published values of the solubility of As_2O_3 in water reported by Linke and Seidell (2). The results obtained for the second lot of reagent grade As_2O_3 are slightly higher at the higher temperatures and, for this sample, there is a slight difference between the heating and cooling data at the lower temperatures. This may indicate that the lower temperature values are not truly saturated, despite the fact that equilibration periods of 2-3 days were used. X-ray diffraction analysis of the solids in equilibrium with the solution at different temperatures indicated only the cubic arsenolite form of As_2O_3.

The valence state of the dissolved arsenic generated from the first lot of reagent grade As_2O_3 was determined by ion chromatography, and the detailed results are also presented in Appendix 6. At all temperatures, and on heating and cooling, only trace amounts of As(V) were detected. In fact, the concentration of As(V) never exceeded 0.1 g/L As(V), despite the fact that total arsenic concentrations as high as 63 g/L As were generated during the solubility measurements. Virtually all of the arsenic is present in the trivalent form; i.e., as As_2O_3, and the As(III) does not oxidize to any significant extent throughout the solubility measurements, which commonly lasted for over 30 days.

The solubility of reagent grade Sb_2O_3 was also measured to provide a comparison with the analogous data for As_2O_3. The results for the solubility of Sb_2O_3 in water are summarized graphically in Figure 25, and the numerical data are presented in Appendix 6. Unlike As_2O_3 which enjoys a moderate solubility in water, Sb_2O_3 is nearly insoluble over the entire temperature range from 25 to 95°C. The solubility at 25°C is <10 mg/L, and even at 95°C, it is only 55 mg/L Sb_2O_3. The data reveal a small difference between the solubilities measured on heating and those determined on cooling. Although the measured differences of <10 mg/L Sb_2O_3 could be due to analytical error at the low concentrations involved, equally they could reflect the partial oxidation of Sb(III) to Sb(V) during the course of the experiments. In any event, it is clear that the solubility of Sb_2O_3 is at least three orders of magnitude lower than that of As_2O_3. This conclusion is also supported by the limited solubility data published for Sb_2O_3 in water. For example, Linke and Seidell (2) report that the solubility of Sb_2O_3 is only 8.4 mg/L at 25°C, a value in general agreement with the results of this study. The inference is that the presence of even very modest amounts of Sb_2O_3 in solid solution in As_2O_3 will significantly reduce the solubility of the arsenic oxide.

The solubility of As_2O_3 over the four As_2O_3-rich dust samples was measured as a function of temperature on heating and cooling. The results are displayed graphically in Figures 26, 27, 28 and 29, and the detailed numerical data are presented in Appendix 6. The graphs also present the measured solubility of As over reagent grade As_2O_3 for comparative purposes.

In all instances, the solubility of As_2O_3 over the dust, measured on heating, is much lower than that determined over reagent grade As_2O_3. In fact, the solubility of As_2O_3 over the dust at any temperature during the heating cycle is about one-half of that over reagent grade As_2O_3, despite the fact that a 2 ½ -3 day equilibration period was employed at each temperature. Furthermore, there is a pronounced hysterisis between the data obtained on heating and those realized on cooling. The solubility increases systematically as the temperature is increased from 5°C to ~95°C. As the temperature is reduced, however, the solubility of As_2O_3 remains nearly constant until the solubility curve for reagent grade As_2O_3 is intersected. As the temperature is reduced further, the solubility curve then follows that of the reagent grade As_2O_3.

The solubilities of Sb over the As_2O_3-rich dusts were also measured as a function of temperature on heating and cooling. The individual solubility curves for the four As_2O_3-rich dust samples are presented in Figures 30, 31, 32 and 33; the detailed solubility data are given in Appendix 6. The measured solubilities of Sb are low at all temperatures studied; even at 95°C, the solubility is always less than 160 mg/L Sb. In many instances, the solubility of Sb over the As_2O_3-rich dust is greater than that over reagent grade Sb_2O_3. One possible explanation is that part of the Sb in the As_2O_3-rich dust is present as Sb(IV) or Sb(V) rather than as Sb(III), which is present in Sb_2O_3. The solubility data on cooling are consistently higher than the values realized on heating, and this trend could indicate some oxidation of the Sb during the experiments, although it could equally well be caused by the slow crystallization of the low concentrations of dissolved Sb(III) throughout the cooling cycle.

Although the measured solubility of As_2O_3 over reagent grade As_2O_3 is similar to the accepted value reported in the literature (2), the solubility of As_2O_3 over the four As_2O_3-rich dust samples is much lower than that expected from the bulk composition of the dusts and their abundance of As_2O_3. One possible cause of the lower than expected solubilities could be a very slow rate of dissolution of As_2O_3 from the dusts. To pursue this possibility, the solubility of reagent grade As_2O_3 was measured as a function of time at 25°C and 60°C, and that of the 212 Chamber sample was measured at 95°C. The results are summarized in Figures 34 and 35, respectively. Reagent grade As_2O_3 dissolves slowly, and at 25°C, ~70 h (3 days) is needed to achieve the equilibrium solubility. At 60°C, the time to reach saturation is about 24 h. The As_2O_3 dissolves relatively rapidly from the 212 Chamber sample at 95°C. Only about 8 h is needed to reach a steady state As_2O_3 concentration, which does not vary significantly for more extended heating times up to 170 h. As indicated by Figure 28, however, the solubility realized over the 212 Chamber sample is not that of pure As_2O_3, despite the constancy of the value. Because equilibration times of 2 ½-3 days were used in the present experiments, and even longer times were employed at temperatures lower than 30°C, the duration of the equilibration period at each temperature is not likely the cause of the low As_2O_3 solubilities from the As_2O_3-rich dust samples.

Additional support for this conclusion is provided by the data given in Table 22 that show the concentrations of As(III) and As(V) in the solutions in contact with the four As_2O_3-rich dust samples as a function of time. Clearly, the As concentration (as reflected by the sum of As(III) and As(V)) does not increase to any significant extent with increasing equilibration times, even for periods as long as 21 days.

Another possible cause of the lower solubility of arsenic from the As_2O_3-rich dust samples could be an enhanced rate of oxidation of As(III) in the presence of the diverse solid species in the dust. To evaluate this possibility, the As_2O_3-rich dust samples were equilibrated with water at room temperature for times up to 21 days, about the total duration of the individual solubility tests. Samples were taken periodically and the solutions were analyzed for As(III) and As(V) using liquid chromatography. The results, which are summarized in Table 22, indicate that the concentration of As(V) is always less than 5% of the total As concentration, and that the As(V) concentration does not increase in any significant way with increasing retention time in the presence of water, air and the various solid phases present in the dust. Clearly, the oxidation of the dissolved arsenic is not the cause of the lower than expected As_2O_3 solubilities from the As_2O_3-rich dust samples.

Table 22 - Relative Concentrations of As(III) and As(V) in the Saturated Solutions Generated From the As_2O_3-rich Dust Samples

Sample	Temperature (°C)	Time (days)	As(III) (g/L)	As(V) (g/L)
January 98 Composite	26.3	7	9.02	0.07
		9	9.06	0.07
		21	9.55	0.08
April 97 Composite	26.4	7	13.7	0.07
		9	13.7	0.07
		21	13.8	0.09
212 Chamber	23.4	7	9.13	0.30
		9	9.09	0.30
		21	9.48	0.32
236 Chamber	26.6	7	13.9	0.33
		9	13.9	0.32
		21	14.3	0.34

The above discussion suggests that the low As_2O_3 solubility from the As_2O_3-rich dust samples is an inherent property of the dust itself, and is not a consequence of the measuring technique. Further support for this hypothesis comes from Figure 36 which compares the As_2O_3 solubilities over the four As_2O_3-rich dust samples, as obtained on heating only. Although all the solubilities are low relative to that of reagent grade As_2O_3, there are significant solubility variations among the four As_2O_3-rich dust samples themselves. There is some indication that the observed solubility differences are related to the total Sb content of the dust, and possibly, to the solid solution Sb content of the As_2O_3 crystals present in the dust. In this regard, Figure 37 shows the As_2O_3 solubility at 65°C and 95°C as a function of the total Sb content of the dust for the four As_2O_3-rich dust samples (Table 2), as well as for reagent grade As_2O_3. These solubilities were calculated by fitting the experimental solubility data obtained on heating to a second order polynomial equation of the form:

$$\text{Solubility (g/L } As_2O_3) = a + bt + ct^2 \qquad (1)$$

where t is the temperature in °C. The relevant equations are given below.

Reagent Grade As_2O_3: $S = 14.78 + 0.0626\ t + 0.00649\ t^2$ (2)
January 98 Composite: $S = 5.41 + 0.1094\ t + 0.00223\ t^2$ (3)
April 97 Composite: $S = 6.12 + 0.2012\ t + 0.00123\ t^2$ (4)
212 Chamber: $S = 6.31 + 0.0888\ t + 0.00167\ t^2$ (5)
236 Chamber: $S = 9.77 + 0.2414\ t + 0.00151\ t^2$ (6)

The data given in Figure 37 suggest that the solubility of As_2O_3 is related to the Sb content, and that small amounts of Sb have a significant effect on the solubility of As_2O_3. In this regard, a similar trend is observed when the solubility of As_2O_3 is plotted against the solid solution Sb content of the As_2O_3 crystals in the four As_2O_3-rich dust samples (see Figure 38). Presumably, the presence of Sb in the As_2O_3 crystals causes a significant reduction in the thermodynamic activity of As_2O_3 that, in turn, results in a reduction in the aqueous solubility of the oxide. Based on the data presented in Figures 37 and 38, the effect is most pronounced for Sb contents in the 0.0 - 0.5% Sb range, but more experimentation would be required to substantiate this hypothesis.

The mineralogical characterization studies of the four As_2O_3-rich dust samples showed that the dominant As_2O_3 crystal phase has solid solution Sb contents ranging from zero to several percent. Based on the hypothesis that only the low-Sb As_2O_3 crystals dissolve readily, the addition of greater amounts of solid As_2O_3-rich dust should increase the measured solubility of As_2O_3 over the dust. That is, the addition of more dust to the solubility vessel consequentially results in the addition of more low-Sb As_2O_3 to the system. The low-Sb As_2O_3 is postulated to dissolve readily, and should, therefore yield higher As_2O_3 solubilities over the dust. To test this hypothesis, various amounts of the April 97 Composite sample were added to 1L of water heated to 70°C in a 2-L solubility reactor (see Figure 1). After 96 h of agitation at 70°C, the solution was sampled, diluted and analyzed for As and Sb. The results of this part of the investigation are summarized in Table 23. When an initial pulp density of 75 g/L solids was employed, the measured solubility over the April 97 Composite sample was 41.55 g/L As_2O_3. It is important to recognize that, based on the overall composition of the April 97 Composite sample presented in Table 2 and assuming that all of the contained As is present as As_2O_3, an initial pulp density of 75 g/L corresponds to 130% of the As_2O_3 required to achieve the ~51 g/L As_2O_3 solubility of reagent grade As_2O_3 at 70°C. Increasing the pulp density to 150 g/L solids yields a solubility of 48.03 g/L As_2O_3, and a pulp density of 300 g/L gives a solubility of 51.76 g/L As_2O_3. The latter value is essentially that of reagent grade As_2O_3 at 70°C (50.96 g/L As_2O_3). The implication is that a large excess of the solid As_2O_3-rich dust will result in an As_2O_3-saturated solution, even during the heating cycle. In contrast, the Sb concentration of the solution appears to be nearly independent of the pulp density, and this implies the rapid saturation of all the solutions with respect to Sb.

Table 23 - The Aqueous Solubility of As_2O_3 and Sb at 70°C for Various Pulp Densities of the April 96 Composite Sample

Pulp Density (g/L)	Solubility of As_2O_3 (g/L)	Solubility of Sb (mg/L)
75	41.55	41
150	48.03	37
225	48.87	34
300	51.76	37
Reagent Grade As_2O_3	50.96	-

Support for the hypothesis that only the low-Sb As_2O_3 crystals dissolve readily at temperatures below 100°C comes from the mineralogical characterization of the leach residues from the above experiments done at various pulp densities. Figure 39 illustrates the general morphology of the leach residue from the test done using an initial pulp density of 75 g/L, and Figure 40 shows the morphology of the analogous residue from the experiment done using an initial pulp density of 150 g/L of the April 97 Composite sample. Both residues consist of tiny particles of As_2O_3 having a low but detectable Sb content, and of larger bright appearing particles of $(Sb,As)_2O_3$. The darker appearing grains are chlorite, muscovite, quartz, iron oxide and iron arsenate. Relative to the unleached material (see Figures 9 and 11), the As_2O_3 crystals in the water leached residues are significantly reduced in size. This reduction in particle size is believed to result from the rapid dissolution of the low-Sb As_2O_3 crystals. In contrast, the $(Sb,As)_2O_3$ particles appear to have the same size and morphology as they possessed in the original sample. Of course, water leaching does not affect the morphology of the silicate species.

Quantitative electron microprobe analyses of the As_2O_3 crystals remaining in the water leach residues were carried out. All the data are presented in Appendix 7, and the results are summarized in Table 24. The As_2O_3 crystals in the as-received April 97 Composite sample have a solid solution Sb content of 0.238%. Leaching of this sample at 70°C and at a pulp density of 150 g/L solids (i.e., with a ~250% excess of the As_2O_3-rich dust), results in an increase in the average solid solution Sb content of the As_2O_3 crystals to 0.819%. When a pulp density of 75 g/L solids was employed, the residual As_2O_3 crystals have an average Sb content of 1.64%. The implication is that the low-Sb As_2O_3 crystals dissolve readily. As the dissolution of the As_2O_3 proceeds, the Sb content rises in the residual particles and, eventually, the Sb content impedes the dissolution reaction. This trend is also reflected in the expanded range of the Sb contents of the As_2O_3 crystals in the leach residues, especially that from the 75 g/L pulp density experiment.

Table 24 - Electron Microprobe Determined Composition of the As_2O_3 Crystals After Leaching at Various Pulp Densities and 70°C (wt %)

Condition	As Content	Range	Sb Content	Range
April 97 Composite sample	76.29	71.45-82.70	0.238	0.000-0.545
150 g/L Solids Leach	74.63	70.48-83.33	0.819	0.122-4.254
75 g/L Solids Leach	74.77	70.20-81.82	1.648	0.279-7.445

High Temperature Leaching of the As_2O_3-Rich Dusts

The experiments presented above indicate that the As_2O_3-rich dusts from the Giant Mine do not dissolve extensively in water at temperatures <100°C. As a result, the concentration of As_2O_3 in solution generally does not exceed 50 g/L As_2O_3, a value significantly lower than the ~90 g/L As_2O_3 concentration realized at 95-100°C for reagent grade As_2O_3. Although the concentration of dissolved arsenic over the four As_2O_3-rich dusts is relatively low, it increases with increasing temperature. Accordingly, the use of temperatures >100°C should generate a more concentrated As_2O_3 solution, and this option was investigated using an autoclave at 125-200°C.

Table 25 shows the As_2O_3 aqueous solubilities achieved when ~100 g/L of each of the four As_2O_3-rich dusts was heated in water in an autoclave for 2 h at 125, 150, 175 and 200°C, followed by cooling to 95°C and sampling. Heating the As_2O_3-rich dusts to 125-200°C results in a significant increase in the As_2O_3 solubility at 95°C, and in this regard, it should be recalled that the apparent solubility achieved by heating any of the dusts directly to 95°C is only ~45 g/L As_2O_3. Heating of the As_2O_3-rich dusts to 125°C, followed by cooling to 95°C, results in a significantly enhanced solubility relative to the solubility values realized by directly heating the slurries to 95°C. Heating to a higher temperature results in a further As_2O_3 solubility increase for the April 97 Composite and the 212 Chamber samples, but has little effect on the solubility of the January 98 Composite or 236 Chamber samples. All of the dusts yield As_2O_3-saturated solutions at 95°C, after heating to 175°C or 200°C. Furthermore, the 212 Chamber sample seems to reach saturation at 150°C, and both the January 98 Composite and 236 Chamber samples give As_2O_3-saturated solutions after heating to only 125°C.

Table 25 – Solubility of As_2O_3 in Water at 95°C After a Two-hour Heating Period at Elevated Temperatures in an Autoclave (g/L As_2O_3)

Sample	Heating Temperature			
	125°C	150°C	175°C	200°C
January 98 Composite	87.1	79.7	80.9	83.8
April 97 Composite	73.9	73.9	82.6	87.1
212 Chamber	67.4	81.2	80.6	80.2
236 Chamber	85.1	84.9	80.8	81.6

Based on the data given in Table 25, the procedure outlined in Figure 41 was developed to produce a significant yield of "pure" As_2O_3 crystals by hot water leaching of the As_2O_3-rich dusts. The procedure consists of leaching the As_2O_3-rich dusts in water, in an autoclave, for 2 h at 150ºC and under the "neutral" atmosphere generated by the air in the vessel plus the significant steam pressure produced at the leaching temperature. After 2 h of leaching at the elevated temperature, the slurry was cooled to 95°C, and was filtered while hot. The clear, As_2O_3-saturated liquor was then cooled to room temperature to crystallize As_2O_3. An autoclave temperature of 150°C was employed, but it is possible that further test work could reduce this temperature somewhat, at least for some of the As_2O_3-rich dust samples. Also, additional refinement of the procedure possibly could shorten the time needed to achieve As_2O_3 saturation at the elevated temperatures used.

Table 26 summarizes the results obtained when the four As_2O_3-rich dust samples were leached at 150°C under the conditions given in Figure 41 and at various pulp densities. For any of the samples, decreasing the initial pulp density results in a higher dissolution of As_2O_3 from the dust, and a lower As content in the leach residue. The maximum extraction of 93% was achieved using 48 g/L of the January 98 Composite sample, and the lowest extraction of 75% was obtained when 91 g/L of the 212 Chamber sample was treated. For any of the samples, a relatively constant level of As_2O_3 dissolution is achieved for pulp densities up to ~80 g/L, but the extractions decrease at still higher pulp densities. Clearly, the decreasing solubility reflects the point at which an As_2O_3-saturated solution is produced; any additional As_2O_3-rich dust simply accumulates in the leach residue, thereby lowering the total percentage of As_2O_3 dissolved. Impurities, such as Fe, Sb and Au accumulate in the residue as the As_2O_3 dissolves, and this observation is consistent with the low water solubility of these species. The Au content of most of the leach residues is commercially interesting.

Following filtration at ~95°C, the clear filtrates were cooled to room temperature, while being gently stirred, to crystallize a pure As_2O_3 product. The resulting crystals were filtered and then dried in an oven at 110°C. The crystals were weighed to give the yield of product, and were analyzed for As, Sb and Fe. As shown in Table 27, the yield of product depends on the degree of saturation at 95°C, which in turn depends on the pulp density employed in the initial leaching stage at 150°C. The experiments done using high pulp densities produce nearly saturated solutions at 95°C, and in turn, these result in high yields of the As_2O_3 product. Comparison with Table 26, however, shows that the tests done at high pulp densities also result in relatively low overall levels of dust dissolution. In practice, it will be necessary to strike a compromise between the pulp density needed to give a high level of dust dissolution and that required to produce a highly concentrated As_2O_3 solution at 95°C. Because, in any commercial process, the cold As_2O_3-bearing solution from the crystallization of the As_2O_3 product would likely be recycled as "water" to the pressure leaching stage, the optimum pulp density should be re-determined using recycled As_2O_3-bearing solutions.

Table 26 – Results Obtained by Leaching the As_2O_3-rich Dusts for 2 h at 150°C, Followed by Cooling and Filtration at ~95°C

Sample	Pulp Density (g/L)	Dust Dissolved (%)	Residue Composition (%) As	Sb	Fe	Au (ppm)
January	94	85.7	34.5	3.3	10.1	25.9
98	87	88.5	23.7	6.4	12.4	37.6
Composite	79	91.2	14.5	3.8	15.8	40.1
	66	91.3	14.1	4.7	16.2	39.2
	57	91.2	12.4	5.0	16.3	40.1
	48	93.0	9.4	3.0	17.1	43.4
April 97	78	91.1	25.1	15.1	9.4	29.9
Composite	71	91.7	23.7	13.8	9.7	32.0
212	102	77.4	21.4	7.4	14.2	54.7
Chamber	91	75.5	18.7	7.5	15.0	56.6
236	91	88.4	11.6	1.3	17.7	57.4
Chamber	83	89.0	8.4	1.1	18.0	43.9

The As_2O_3 crystals produced on cooling were shown by X-ray diffraction analysis to consist only of the cubic arsenolite form of As_2O_3; no other phases were detected. The As_2O_3 was generally of high chemical purity; in many cases the product consisted of >99% As_2O_3, and "water" is likely the major impurity as the crystals were dried at only 60°C. Contamination of the As_2O_3 with Sb or Fe was generally low, except for those experiments where the leach solution was not saturated with As_2O_3. In many of the experiments, the Sb content was <0.2% and the Fe content was <0.005%. Hence, it is believed that the high temperature leaching procedure outlined in Figure 41 could yield a commercially acceptable As_2O_3 product.

Table 27 – Arsenic Concentrations and the Purity of the As_2O_3 Crystals Made Using the High Temperature Leaching Procedure

Sample	Pulp Density (g/L)	[As] at 95°C (g/L)	[As] at 25°C (g/L)	Yield (g/L)	As_2O_3 Crystals As_2O_3 (%)	Sb (%)	Fe (%)
January 98	94	59.7	17.4	57.7	98.3	0.06	0.003
Composite	87	59.0	21.0	52.5	95.8	0.03	0.005
	79	54.9	18.5	48.9	99.9	0.07	0.002
	66	46.0	17.7	37.4	99.1	0.16	0.001
	57	39.2	16.7	30.6	99.5	0.28	0.002
	48	28.5	22.0	9.7	97.9	0.97	0.005
April 97	91	62.8	21.5	51.1	98.7	0.11	0.008
Composite	83	56.5	19.3	47.3	97.7	0.13	0.008
212	102	55.8	19.4	47.5	98.3	0.06	0.008
Chamber	91	49.5	16.8	47.4	99.0	0.10	0.008
236	78	61.0	18.6	50.9	97.7	0.18	0.004
Chamber	71	50.2	16.6	44.6	99.0	0.22	0.002

In the hot water leaching procedure illustrated in Figure 41, the arsenic is distributed among the As_2O_3 crystals, the high temperature leach residue and the cold solution. Mass balances were carried out to determine the relative distribution of arsenic among the three phases, and the results are given in Table 28. Only 1-9% of the total arsenic remains in the high temperature leach residue, and the amount of residual arsenic increases as the pulp density increases. For the preferred range of pulp densities likely to be used in a commercial process, however, the amount of residual arsenic seems to be only 2-4% of the total. Under the same preferred pulp density conditions, about 25-30% of the total arsenic remains in the cold solution. In a commercial application, however, this solution would almost certainly be recycled as "water" for the high temperature leaching operation. Hence, negligible amounts of the total arsenic leached would report to the cold solution in a continuous operation. Accordingly, it can be concluded that 96-98% of the total arsenic would report as

As_2O_3 crystals in a commercial hot water leaching process wherein the cold solution after As_2O_3 crystallization was recycled.

Table 28 – Relative Arsenic Distribution in the Hot Water Leaching Procedure

Sample	Pulp Density (g/L)	Relative Arsenic Distribution		
		In Leach Residue (%)	In Cold Solution (%)	In As_2O_3 Crystals (%)
January 98 Composite	94	7.3	25.3	67.4
	87	3.9	32.4	63.7
	79	1.8	30.9	67.3
	66	1.8	36.2	62.0
	57	1.6	39.8	58.6
	48	1.0	64.8	34.2
April 97 Composite	78	2.9	32.7	64.3
	71	2.6	32.8	64.6
212 Chamber	102	8.5	30.9	60.6
	91	7.5	28.1	64.4
236 Chamber	91	2.2	27.0	70.8
	83	1.5	30.8	67.6

Mineralogical Characterization of the Hot Water Leach Residues

Samples of the four As_2O_3-rich dusts were leached for 2 h at 150°C, at various pulp densities, as noted above. The slurry was rapidly cooled in the autoclave to 95-100°C, and the vessel was then opened. The hot slurry was filtered, and the solids were washed with a small amount of water to displace the nearly As_2O_3-saturated processing solution. The washed solids then were dried at 110°C for a few hours prior to mineralogical study.

X-ray diffraction analysis of the residue from the leaching of the January 98 Composite sample, obtained using an initial pulp density of 95 g/L solids, indicated an As_2O_3-type compound, quartz, chlorite, muscovite and traces of other unidentifiable species. Similar X-ray diffraction analyses of the April 97 Composite sample leached at a pulp density of 77 g/L or 85 g/L solids detected an As_2O_3-type compound, quartz, chlorite, muscovite, hematite (maghemite?) and other unidentifiable phases.

The SEM-EDX studies of the latter two samples provided complementary mineralogical information and phase confirmation. Figure 42 shows the residue from the leaching experiment done using a pulp density of 77 g/L solids. The bright appearing grains are rich in both Sb and As; they are likely $(Sb,As)_2O_3$, which is the As_2O_3-type compound identified by X-ray diffraction analysis. Relative to the $(Sb,As)_2O_3$ particles in the as-received As_2O_3-rich dust, the $(Sb,As)_2O_3$ particles in the leach residue are better crystallized. In fact, many of the particles show well developed external crystal forms, possibly indicating the localized dissolution-crystallization of the $(Sb,As)_2O_3$ phase. The low-Sb As_2O_3 crystals prevalent in the as-received As_2O_3-rich dust are lacking, and this behaviour is not unexpected given the low pulp density used for this leaching experiment. The various dark appearing grains are mostly chlorite, muscovite or quartz, although a number of fragments of As-bearing iron oxide were also detected. Figure 43 shows the analogous leach residue from the experiment done using a pulp density of 85 g/L solids; the leach residue contains 25.1% As, 15.1% Sb and 9.4% Fe. Most of the bright appearing particles are crystals of $(Sb,As)_2O_3$, whereas the darker appearing particles are chlorite, muscovite, quartz and As-bearing iron oxide. Both figures suggest that the low-Sb As_2O_3 crystals dissolve during hot water leaching. In contrast, the Sb-rich oxides, iron oxides and silicate species are poorly soluble and accumulate in the leach residue.

X-ray diffraction analyses were also carried out on the residues from the water leaching of the 212 Chamber sample for 2 h at 150°C. The residues were generated for pulp densities ranging from 100 to 113 g/L, but all the residues were virtually identical. They consist of an As_2O_3-type compound (likely $(Sb,As)_2O_3$), chlorite, muscovite, quartz and iron oxide (hematite and maghemite(?)).

Removal of Antimony From the Water Leach Solutions

Preliminary research on the water leaching option was carried out by Royal Oak Mines. In their studies, leaching was done at 100°C, and it is now known that such temperatures are inadequate to saturate the water with As_2O_3. In the Royal Oak work, the solution was evaporated to ~30% of its volume to increase the concentration of As_2O_3, and the evaporated solution was cooled to crystallize As_2O_3. In the Royal Oak work, the crystals contained 99.6% As_2O_3, 0.33 % Sb and 0.08% Fe. The Sb content was considered to be excessive, and accordingly, tests were done to remove the Sb from solution using either ion exchange or activated carbon. Those experiments, however, were inconclusive, and accordingly, additional work was done at CANMET on the use of ion exchange resins or activated carbon for antimony control.

Table 29 illustrates the composition of a solution which was made by leaching 100 g/L of the 212 Chamber sample with hot water at 100°C. The hot slurry was filtered, and the filtrate was analyzed. The solution was then cooled to room temperature and was held at room temperature for 72 h. The Sb concentration at 90°C is about that expected from the measured solubility data (Figure 32), but the solubility decreases significantly as the temperature is lowered. The measured concentration of Sb at 25°C is about three times greater than the reported solubility of antimony at 25°C which is 0.0084 g/L Sb_2O_3 (5). It is not known whether this discrepancy is due to the presence of some Sb(V) in the 212 Chamber sample, or whether it reflects a persistent level of Sb_2O_3 supersaturation in water. The latter explanation may be more likely as it was noted that the Sb_2O_3 tended to remain in solution, in a supersaturated state, for several hours when the solution was cooled from 90°C to 25°C.

Table 29 - Composition of the Solution Resulting From the Hot Water Leaching of the 212 Chamber Sample

Time (h)	Temperature (°C)	As Concentration (g/L)	Sb Concentration (g/L)
0	90	24.5	0.0643
24	25	21.0	0.0272
72	25	21.4	0.0263

The data of Table 30 show the Sb concentrations resulting when the As_2O_3-rich dust samples were subjected to the hot water leaching procedure (Figure 41) for 2 h at 150°C, and were then cooled to 95°C and subsequently to room temperature. The Sb concentrations in the 95°C solutions vary widely, and seem to depend on both the dust sample used and its pulp density. There is an inverse correlation between the Sb and As concentrations of the hot solution, although the correlation is not precise. The Sb concentration of the solutions cooled to 25°C varies widely, from 0.029 to 0.194 g/L Sb. This observation could reflect the presence of variable amounts of Sb(V) in the dust samples, or more likely, an erratic level of Sb_2O_3 supersaturation in the cooled solutions. In any event, a modest amount of Sb dissolves along with the As_2O_3, and the Sb persists in solution at room temperature.

Table 30 - Antimony Concentrations Produced in the Hot Water Leaching Procedure

Sample	Pulp Density (g/L)	Sb Concentration at 95°C (g/L)	As Concentration at 95°C (g/L)	Sb Concentration at 25°C (g/L)
January 98 Composite	94	0.075	59.7	0.030
	87	0.094	59.0	0.093
	79	0.113	54.9	0.081
	66	0.139	46.0	0.086
	57	0.154	39.2	0.080
	48	0.130	28.5	0.048
April 97 Composite	78	0.130	-	0.075
	71	0.118	-	0.068
212 Chamber	102	0.191	-	0.181
	91	0.171	-	0.194
	91	0.121	-	0.029
236 Chamber	83	0.134	-	0.049

Although Royal Oak Mines reported some success in removing Sb from water leach solutions using Gravex GR-2-0 ion exchange resin or activated carbon, their results might simply reflect the delayed crystallization of the antimony on the surface of the resin or carbon during the cooling of the solutions in their experiments. In an effort to confirm the preliminary results obtained by Royal Oak Mines, the removal of Sb was studied using the four ion exchange resins presented in Table 1 as well as Hycarb 6x12 activated carbon. As shown in Table 31, however, none of the resins extracted any significant amount of Sb from the water leach solutions at room temperature and their natural pH of ~4. For these experiments, the 212 Chamber sample was leached at 95°C in water for several hours to generate an As- and Sb-bearing solution. The leach slurry was filtered and then was cooled to room temperature for ~24 h. The cooled solution analyzed 21 g/L As and 0.0263 g/L Sb. One hundred millilitre samples of the cooled solution were contacted with 2 mL of the various resins, and the mixtures were gently agitated overnight at room temperature using an orbital shaker. The solutions were then analyzed for As and Sb; the results are summarized in Table 31. None of the resins is effective for extracting Sb from the water leach solution; less than 10% of the total Sb was removed in any of the experiments.

Table 31 - Concentrations of As and Sb After Prolonged Contact With Different Ion Exchange Resins

Resin	As Concentration (g/L)	Sb Concentration (g/L)
Feed solution	21	0.0263
Gravex GR-2-0	21	0.0247
Amberlite IRC-120	21	0.0266
Amberlite IRC-50	21	0.0024
Duolite C-467	21	0.0232

Efforts were also made to extract the Sb from a hot aqueous leach solution. For these experiments, the 212 Chamber sample was leached for 2 h at 150°C in the autoclave. The autoclave was cooled to 95-100°C, and the slurry was then filtered hot. The filtrate was transferred to a reaction vessel which was maintained at 95°C. Next, 250 mL samples of the hot solution were contacted with 10-g portions of three of the resins and with activated carbon, and the resin-solution slurries were held at ~95°C for 2 h prior to sampling to assess the extent of Sb adsorption. The results of these experiments are summarized in Table 32. The results possibly suggest a minor amount of As extraction, but the differences in As concentration could be the consequence of minor, and undetected, changes in the volume of the samples during the 2-h equilibration period (compare the analyses for the "blank" test). Clearly, none of the ion exchange resins extracts any significant amount of Sb. In contrast, activated carbon seems to adsorb a minor amount of Sb, but unfortunately, the carbon co-sorbs a more significant amount of the associated arsenic. Of the reagents tested, however, only the activated carbon seems to offer any potential for Sb removal from the As_2O_3-containing water leach solutions.

Table 32 - Extraction of Antimony From the Hot (95°C) Water Leach Solutions

Resin	Concentration of the Hot Solution Before the Addition of the Resin or Carbon		Concentration of the Hot Solution After 2 h of Contact with the Resin or Carbon	
	As	Sb	As	Sb
Blank	56.6	0.243	55.5	0.235
Gravex GR-2-0	56.6	0.243	55.4	0.231
Duolite C-467	56.8	0.237	55.9	0.231
Hycarb 6x12	56.8	0.237	52.7	0.168

The generally negative extraction results are probably related to the aqueous chemistry of antimony. If any cationic resin is to extract antimony, the element must be present as a cationic species. It is known that Sb(V) does not form water soluble cationic species. Although Sb(III) can form an antimonyl ion, SbO^+, the species exists only in acid media (6). Consequently, it is unlikely that antimony can be extracted with cationic exchange resins unless the pH of the solution is lowered. To pursue this option, the 212 Chamber sample was leached in hot water, the slurry was filtered and the filtrate was cooled to room temperature. One hundred millilitre aliquots of the solution were acidified to pH 3.0 or pH 1.0 with H_2SO_4. The acidified solutions were contacted with 2 mL of the various resins and agitated gently for 2 h prior to sampling. The results of these studies are given in Table 33, in which the Sb concentrations should be compared to the initial concentration of 0.0245 g/L Sb. Minimal Sb extraction occurs at pH 3.0, but a more significant level of extraction is observed at pH 1.0. In particular, the Duolite C-467 ion exchange resin extracted >90% of the Sb from the pH 1.0 solution. Although acidification coupled with ion exchange likely could be used to control antimony, the use of strongly acid media is not compatible with the simple hot water leaching option outlined in Figure 41.

Table 33 - Extraction of Antimony by Various Ion Exchange Resins at Room Temperature and pH 3.0 or pH 1.0

Resin	pH	Sb Concentration in Raffinate (g/L)	Total Sb Extracted (%)
Gravex GR-2-0	3.0	0.0246	0.0
Amberlite IRC-120	3.0	0.0238	0.2
Amberlite IRC-50	3.0	0.0232	2.1
Duolite C-467	3.0	0.0236	0.5
Gravex GR-2-0	1.0	0.0229	11.9
Amberlite IRC-120	1.0	0.0229	11.9
Amberlite IRC-50	1.0	0.0226	13.1
Duolite C-467	1.0	0.0022	91.7

Re-Sublimation of the As_2O_3-Rich Dusts

The underlying objective of this part of the study is to produce a marketable As_2O_3 product by the re-sublimation of the as-received As_2O_3-rich dusts. The index of success of the re-sublimation process is the purity of the re-sublimed As_2O_3, and to a lesser extent, the total percentage of arsenic sublimed. As will be seen, iron and the silicate minerals do not sublime, and as a result, Sb is the only impurity of any significance in the re-sublimed As_2O_3 product.

The effect of the re-sublimation temperature and the sublimation atmosphere (oxidizing, neutral or reducing) on the As/As+Sb ratio of the re-sublimed oxide product is illustrated in Table 34 and Figure 44. These data were generated for the 212 Chamber sample which analyzes 45.20% As and 2.13% Sb. It is apparent that the purity of the oxide depends directly on the temperature. As the re-sublimation temperature increases from 250°C to 550°C, the As/As+Sb ratio decreases from ~99.5% to 96-97%. Significantly, the Sb contents of the re-sublimed oxide are 0.15 - 0.66% Sb; accordingly, many of the re-sublimed products contain >0.2% Sb and might be difficult to market. All of the products made at temperatures greater than the boiling point of As_2O_3 (~350°C) had unacceptably high Sb contents. It also appears that the gaseous atmosphere affects the relative purity of the re-sublimed oxide, although there is some scatter of the data obtained. Oxidizing atmospheres, such as those produced using air or O_2 gas, seem to yield the highest purity products, and the products made under oxidizing conditions were consistently white. Neutral atmospheres (N_2 or He gases) and reducing atmospheres (H_2 gas) seem to yield oxide products having similar purities. Although the products made using neutral atmospheres were also white, those generated under reducing conditions were consistently grey. Nevertheless, X-ray diffraction analysis showed all the re-sublimed oxide products to consist only of As_2O_3 having the cubic arsenolite structure. Based on the results presented above, the decision was made to carry out all subsequent re-sublimation tests using an air atmosphere.

The results presented above indicate that low sublimation temperatures yield higher purity oxide products. Accordingly, the re-sublimation reaction was monitored as a function of time at 259°C using the 212 Chamber sample, which analyzes 56.2% As and 2.13% Sb. Figure 45 illustrates the extent of reaction, reported as the percentage of the original sample mass remaining unsublimed, as a function of the heating time at 259°C. The sublimation takes place in a nearly linear manner for the first 5-6 h of heating, but subsequently, the reaction slows and eventually levels off after about 10 h of heating. Still longer heating times have no significant effect on the amount of sample sublimed. Ultimately, about 25% of the original mass of the sample remains in the residue at 259°C. Table 35 presents the compositional data of the various samples produced in the heating experiments outlined in Figure 45. In total, about 75% of the initial mass of the sample sublimes; however, 93% of the initially present arsenic sublimes under the same conditions. This reflects the significantly higher volatility of As_2O_3 relative to the silicate minerals and iron oxide impurities present in the sample. As will be shown later, the residual ~7% As is present in the residue as poorly volatile $(Sb,As)_2O_3$ and iron arsenate ($Fe_2As_4O_{12}$) species. The compositional data indicate that the initially re-sublimed oxide has the highest purity and that the purity decreases with prolonged heating times. In fact, there is an almost linear correlation between the As_2O_3 content of the re-sublimed oxide with the duration of heating, at least for heating periods up to 20 h. Likely,

Table 34 - Influence of Temperature and the Type of Atmosphere on the Purity of the Re-sublimed Arsenic Oxide

Temperature (C)	Oxidizing Atmosphere		Neutral Atmosphere		Reducing Atmosphere	
	As/As+Sb	Sb (wt %)	As/As+Sb	Sb (wt %)	As/As+Sb	Sb (wt %)
299	99.46	0.16	99.47	0.39	-	-
	99.80	0.15	-	-	-	-
	99.78	0.39	-	-	-	-
	99.67	0.24	-	-	-	-
	99.10	0.66	-	-	-	-
272	-	-	99.47	0.41	-	-
386	-	-	97.61	1.82	-	-
400	-	-	97.50	1.85	-	-
450	-	-	97.18	2.18	-	-
459	98.35	1.41	-	-	-	-
472	-	-	-	-	96.27	2.91
475	-	-	97.54	1.89	-	-
513	-	-	-	-	97.00	2.31
519	-	-	96.97	2.33	-	-
545	98.67	0.96	-	-	-	-

a heating time of 10-12 h would be required to re-sublime most of the arsenic present in the 212 Chamber sample at 259°C.. For such heating periods, it appears that the re-sublimed oxide would contain ~99.6% As_2O_3 and ~0.4% Sb. Clearly, only the very initial products meet the stipulated antimony content of <0.2% Sb.

Table 35 – Effect of Heating Time at 259°C on the Percentage of the Total Arsenic Sublimed From the 212 Chamber Sample, and the Purity of the Re-sublimed Product

Heating Time (h)	Residue Mass (% of Initial)	As Sublimed (% of Initial)	Product Composition As_2O_3 (%)	Product Composition Sb (%)
0	100	0	–	–
2	79.5	32.1	99.80	0.15
4	60.1	–	–	–
6	44.5	69.9	99.71	0.21
8	32.6	–	–	–
10	29.2	–	–	–
12	28.2	91.9	99.57	0.31
20	27.8	93.3	99.46	0.39
30	27.0	–	–	–

Although most of the re-sublimation studies were done using the 212 Chamber sample, a direct comparison of the thermal behaviour of all four As_2O_3-rich dusts was made. For these comparative tests, samples of each dust were heated at 545°C for 10 h in static air. The sublimates were collected and analyzed; the results are summarized in Table 36. In all instances, the re-sublimation process yields a relatively pure oxide product, which consistently has a higher As/As+Sb percentage relative to the starting material. In fact, Figure 46 suggests that there is a nearly linear relationship between the percentage of As/As+Sb in the re-sublimed product and As/As+Sb percentage of the original As_2O_3-rich dust. This behaviour implies that the Sb in all the As_2O_3-rich dusts behaves in a similar manner during thermal processing. Accordingly, the trend identified in Figure 46 might be useful for predicting the re-sublimation response of other dust samples. The re-sublimation procedure reduces the Sb content of the As_2O_3 product, but aside from the 236 Chamber sample, all the re-sublimed products have Sb contents greater than the specified 0.2% Sb limit. The Au analyses also presented in Table 36 demonstrate that gold collects almost quantitatively in the re-sublimation residues. As a consequence, all of the re-sublimed oxide products contained <0.03 ppm Au, the detection limit of the analytical procedure used.

Table 36 – Purities of the Re-sublimed As_2O_3 Products Made When the Four As_2O_3-rich Dusts were Heated to 545°C for 10 h in Static Air

Sample	% As/As+Sb in Sample	% As/As+Sb in Product	% As in Product	% Sb in Product	ppm Au in Product
January 98 Composite	98.74	99.57	72.3	0.31	16.82
April 97 Composite	97.83	98.90	70.4	0.78	28.84
212 Chamber	96.35	98.67	71.4	0.96	42.90
236 Chamber	99.49	99.94	71.7	0.04	26.64

The results presented above indicate a modest level of Sb_2O_3 re-sublimation along with that of As_2O_3, despite a significant difference in the vapour pressures of the two end-member oxides. The limited mass spectrographic work carried out in support of the project helps to explain the unexpected transport of Sb_2O_3 along with As_2O_3. It is known that both As_2O_3 and Sb_2O_3 exist as dimers in the vapour state; i.e., the vapour species are predominantly As_4O_6 and Sb_4O_6 (3). The mass spectrographic analysis of the sublimed vapour from the 212 Chamber sample detected the presence of mixed As-Sb oxide species, notably, As_3SbO_6. Such mixed As-Sb oxide species presumably have a vapour pressure lower than that of end-member As_2O_3, but significantly higher than that of end-member Sb_2O_3. The result is the significant transport of Sb_2O_3 at temperatures much lower than those needed to vapourize end-member Sb_2O_3. As a result, the re-sublimed As_2O_3 has a significant Sb content although the As/As+Sb ratio of the sublimate is consistently higher than that of the starting As_2O_3-rich dust.

In an effort to eliminate Sb from the mixed vapour species, such as As_3SbO_6, the As_2O_3-rich dust was mixed with metallic arsenic and was re-sublimed in a flowing H_2 gas stream. The intent was to reduce the amount of Sb transported by utilizing the following reaction.

$$As_3SbO_6 + As \rightarrow As_4O_6 + Sb \qquad (7)$$

To investigate this option, 2.21 g of 99.99% As metal powder was mixed with 8.78 g of the 212 Chamber dust, and the mixture was heated for 16 h at 545°C. A hydrogen atmosphere was employed to prevent the possible oxidation of the elemental arsenic. The presence of the arsenic metal increases the As_2O_3 content of re-sublimation product, but only to a limited extent. With the arsenic metal present in the system, the re-sublimed product contained 98% As_2O_3; in the absence of the arsenic metal the product consisted of 97% As_2O_3. Although the presence of arsenic metal improves the quality of the re-sublimed As_2O_3 product, the improvement is not likely great enough to warrent the pursuit of this option.

Mineralogical Investigations of the Sublimation Residues

Mineralogical studies were carried out on the residues produced by heating the January 98 Composite, the April 97 Composite and 236 Chamber samples for 10 h at 545°C in static air, and the 212 Chamber sample for 20 h at 610°C in static air.

X-ray diffraction analyses of the four sublimation residues were carried; the individual diffraction patterns are presented in Appendix 8. The sublimation residue from the January 98 Composite sample consists of an As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$), anhydrite ($CaSO_4$) and quartz. The corresponding residue from the heating of the April 97 Composite sample consists of an As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$), anhydrite ($CaSO_4$), quartz and muscovite. A trace amount of As metal was also detected in this sample, but the presence of elemental arsenic requires independent confirmation. The sublimation residue from the heating of the 236 Chamber sample was shown to contain abundant muscovite, chlorite, quartz and iron oxide (FeO_3), in addition to the As_2O_3-type compound, iron arsenate ($Fe_2As_4O_{12}$) and anhydrite ($CaSO_4$). A trace amount of $Fe_8(AsO_4)_6(OH)_6.5H_2O$ may also be present, but the occurrence of this phase requires confirmation. The sublimation residue from the heating of the 212 Chamber sample was shown by X-ray diffraction analysis to consist of hematite, maghemite (Fe_2O_3), anhydrite ($CaSO_4$), chlorite, muscovite, K-feldspar and quartz. Significantly, the As_2O_3-type compound and iron arsenate ($Fe_2As_4O_{10}$) were not detected in this sublimation residue by X-ray diffraction analysis. Their absence could be a consequence of the somewhat higher temperature (610°C versus 545°C) and longer heating time (20 h versus 10 h) used to generate this material.

Figure 47 shows the general appearance of the sublimation residue from the January 98 Composite sample. The residue clearly has sintered into 100-500 μm in aggregates which have irregular outlines. The brighter masses are rich in As, but also contain minor amounts of O, as well as traces of Sb and Fe. This phase is presumably $(As,Sb)_2O_3$, although the presence of finely dispersed As metal cannot be precluded. The darker appearing masses are mostly silicates, iron arsenate and iron oxide; one such occurrence is shown in more detail in Figure 48. The sintered agglomerate contains bright appearing particles of iron arsenate (presumably $Fe_2As_4O_{12}$), as well as darker appearing grains of $CaSO_4$, muscovite and quartz. The various particles clearly have sintered together, but there is not an obvious agglomerating phase. In some instances, the particles may be sintered by $(Sb,As)_2O_3$. Overall, the SEM-EDX studies of this sublimation residue showed it to consist of major iron arsenate ($Fe_2As_4O_{12}$ or $FeAs_2O_3$ having a minor Sb content), $CaSO_4$, muscovite and quartz. The iron arsenate phase commonly contains trace amounts of Ca, K, S, Si and Al, but some of the impurities detected may originate from dispersed silicate grains. Minor amounts of As_2O_3, containing traces of Sb, were present along with trace amounts of elemental As. Isolated particles of calcium arsenate having a minor Fe and trace S content were detected, and a few grains of Na-Al silicate were evident.

The SEM-EDX study of the sublimation residue from the heating of the April 97 Composite sample showed this material to be similar to the residue from the January 98 Composite sample. Figure 49 shows the detailed texture of the sublimation residue from the April 97 Composite sample. This material consists of bright grains of iron arsenate ($Fe_2As_4O_{12}$or $FeAs_2O_3$) having a minor Sb content. The abundance of the iron arsenate species reflects their significant stability at elevated temperatures. A few particles rich in Sb, As and Fe may be iron arsenate-antimonate compounds. Most of the grey appearing particles in Figure 49 are muscovite, whereas the dark grains are $CaSO_4$ or quartz. Other species detected in trace amounts include As-bearing iron oxide and elemental arsenic. Minor amounts of As_2O_3 having a low Sb content were also detected, and as shown in Figure 50, the As_2O_3 phase tends to occur as large masses enveloping smaller particles of iron arsenate, muscovite and quartz.

The 236 Chamber sample contains less As_2O_3 but more silicate and oxide species than the January 98 Composite and April 97 Composite samples. As a result, the sublimation residue from the heating of the 236 Chamber sample contains more abundant oxide and silicate species. Figure 51 illustrates a number of iron arsenate ($Fe_2As_4O_{12}$) particles which are associated with needle-like grains of As_2O_3 containing minor amounts of Fe. Particles of $CaSO_4$, about 10 μm in size and having a modest As content, and dark appearing fragments of quartz are also evident. Most of the grey appearing grains are chlorite or muscovite. Other species detected in this sample include As-bearing iron oxide, calcium arsenate having a minor Fe content, and possibly, elemental arsenic.

Of the resublimed samples, the 212 Chamber sample was heated to be highest temperature and for the longest time. Despite this fact, the sublimation residue from the heating of the 212 Chamber dust still contained a few large fragments of arsenic oxide. One such fragment is illustrated in Figure 52 which shows a ~500 μm mass of arsenic oxide agglomerating various silicate and iron arsenate particles. EDX analysis showed the arsenic oxide to contain minor amounts of O, but only traces of Sb. The reasons for the persistence of large arsenic oxide masses at temperatures well above the sublimation temperature of As_2O_3 (465°C) are not clear. It may be that the oxide has a reduced O content and, consequently, a lower vapour pressure than stoichiometric As_2O_3. Alternatively, it is possible that the large masses form during the removal of the sample from the furnace, although the morphology really does not support such a mechanism. Figure 53 shows a number of the finer grain constituents of the sublimation residue from the 212 Chamber sample in greater detail. The bright appearing grains are either iron oxide or iron arsenate. In this regard, both $Fe_2As_4O_{12}$ and $Fe_2As_4O_{12}$ containing trace Sb were detected. A few tiny bright grains of $(Sb,As)_2O_3$ were also evident, but this phase is surprisingly rare given the abundance of Sb in the 212 Chamber sample. Figure 53 illustrates some particles of Ca arsenate having a modest Fe content and of $CaSO_4$. Most of the dark appearing particles are chlorite, muscovite or quartz. Figure 54 provides a different view of the same sublimation residue. In addition to the phases identified above, the figure illustrates several particles of $CaSO_4$ and quartz, as well as a few grains of a rare Fe-Zn arsenate phase containing minor Sb. The fine grained residues presented in Figures 53 and 54 illustrate the non-volatile phases which are concentrated when the arsenic-antimony oxide species are sublimed.

CONCLUSIONS

ACKNOWLEDGEMENTS

The authors of this report wish to acknowledge the valuable assistance provided by CANMET staff members A. Kuiper and D.J. Hardy, with the solubility and leaching experiments, and Dr. J.-P. Charland and P. Carrière, with the X-ray diffraction studies. Special thanks are extended to Lorna Paquette for her assistance with the preparation of this report.

REFERENCES

1. "Giant Mine Arsenic Trioxide Technical Workshop / Final Summary Report", Dillon Consulting, Yellowknife, Northwest Territories, November 1999.

2. W.F. Linke and A. Seidell, "Solubilities: Inorganic and Metal Organic Compounds", 4th Edition, Van Nostrand, New York, NY, U.S.A. (1965).

3. J.E. Mauser, "Heteronuclear Compounds of Arsenic and Antimony", Metallurgical Transactions 13B, 511-513 (1982).

4. T.T. Chen and J.E. Dutrizac, "Practical Mineralogical Techniques for the Characterization of Hydrometallurgical Products". In: Process Mineralogy IX, W. Petruk and R.D. Hagni, eds., The Minerals, Metals and Materials Society, Warrendale, PA, U.S.A., pp. 289-309 (1990).

5. K.H. Gayer and A.B. Garrett, "The Equilibria of Antimonous Oxide (Rhombic) in Dilute Solutions of Hydrochloric Acid and Sodium Hydroxide at 25°C", J. Am. Chem. Soc., 74, 2353-2354 (1952).

6. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", John Wiley and Sons, New York, NY, U.S.A. (1980).

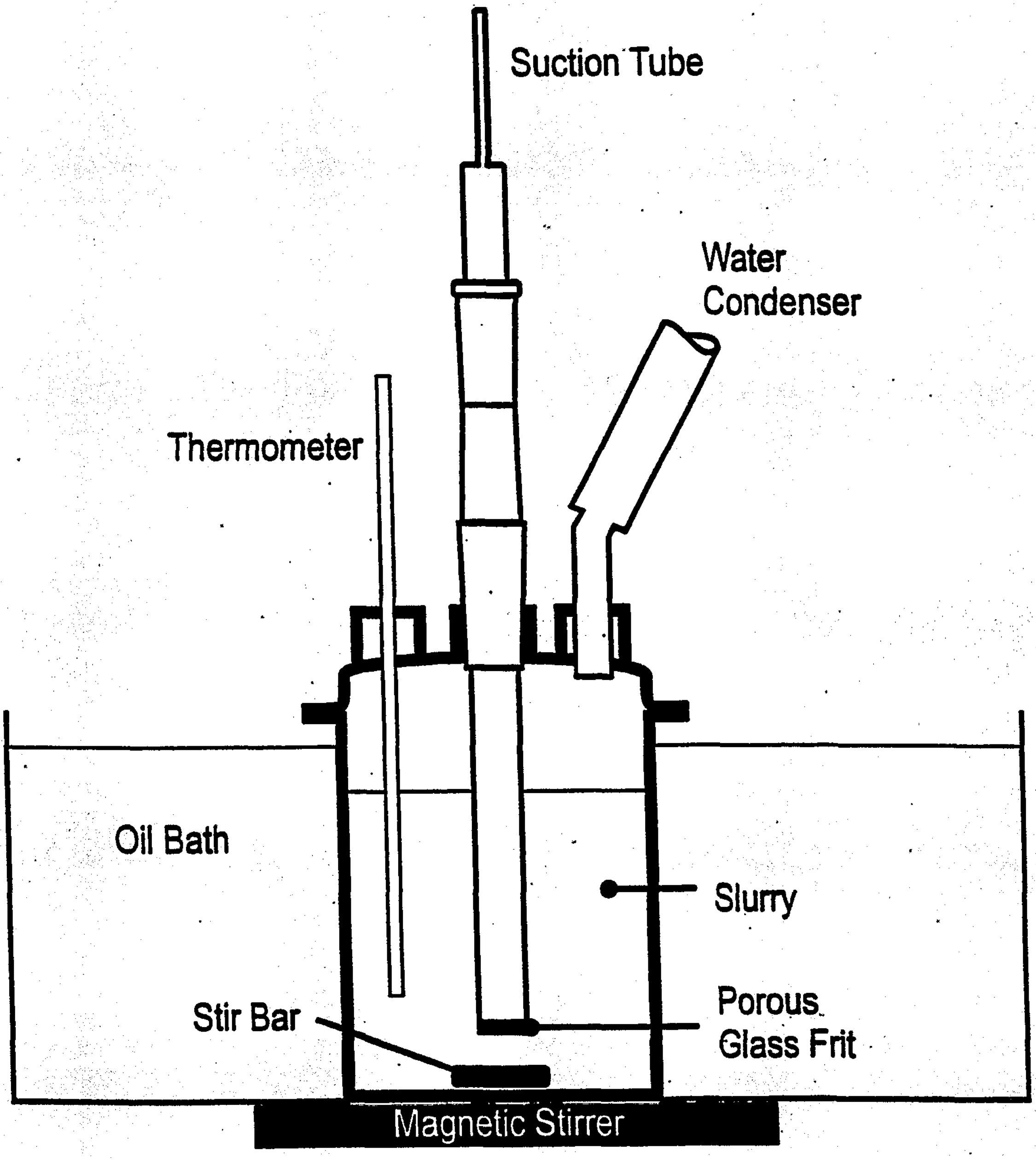


Fig. 1 - Schematic representation of the apparatus used to measure the solubilities of the As_2O_3-rich dusts.

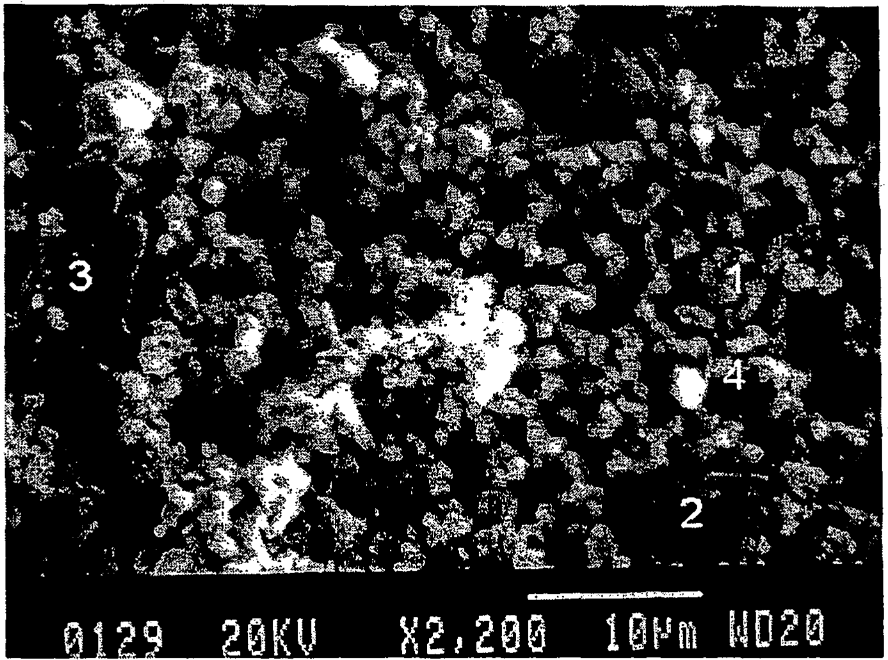


Fig. 2 - Secondary electron micrograph of a loose powder mount of the January 98 Composite sample that shows the general appearance of this material. 1- As_2O_3, 2- chlorite, 3- quartz, 4- As-bearing iron oxide

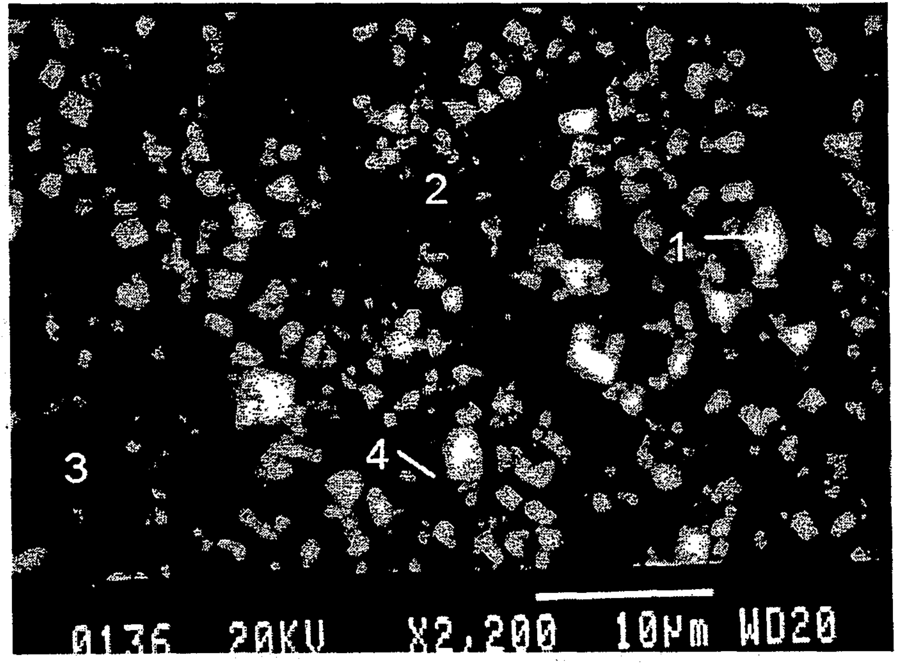


Fig. 3 - Backscattered electron micrograph of a polished section of the January 98 Composite sample. 1- As_2O_3, 2- chlorite, 3- quartz, 4- Ca arsenate

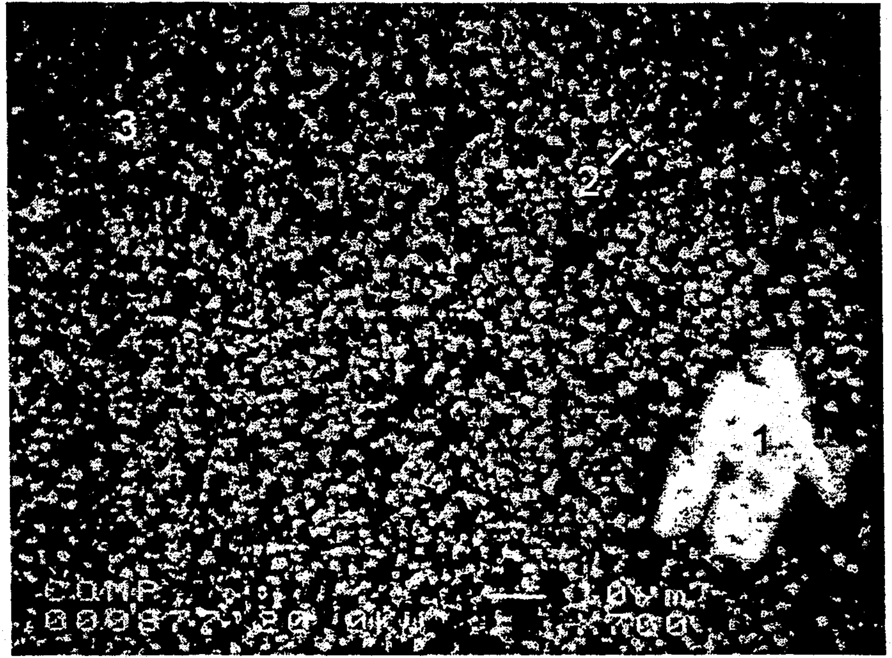


Fig. 4 – Backscattered electron micrograph illustrating a large mass of As_2O_3 in the January 98 Composite sample. 1- large mass of As_2O_3, 2- As_2O_3, 3- As-bearing iron oxide

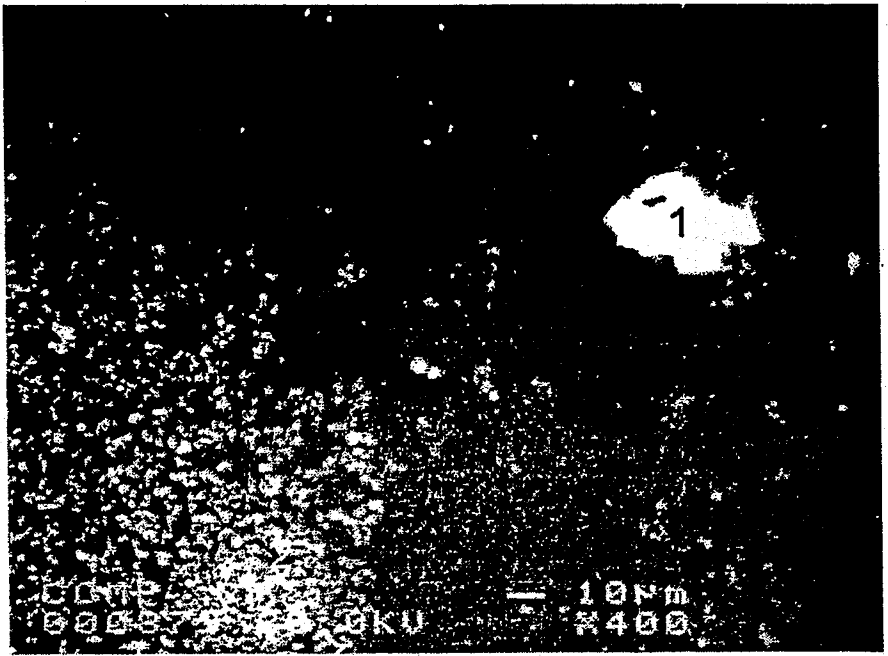


Fig. 5 - Backscattered electron micrograph showing a large mass of As-bearing Sb-rich oxide. 1- Sb-rich oxide, 2- As_2O_3

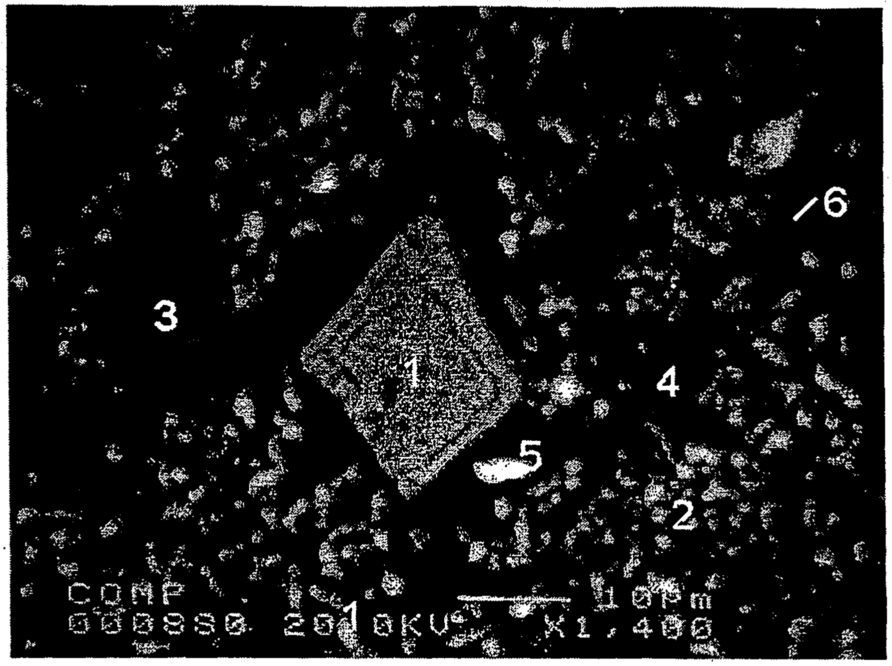


Fig. 6 – Backscattered electron micrograph of an As-bearing iron oxide particle in the January 98 Composite sample. 1- As-bearing iron oxide, 2- As_2O_3, 3- muscovite, 4- quartz, 5- rare grain of $PbSO_4$, 6- chlorite

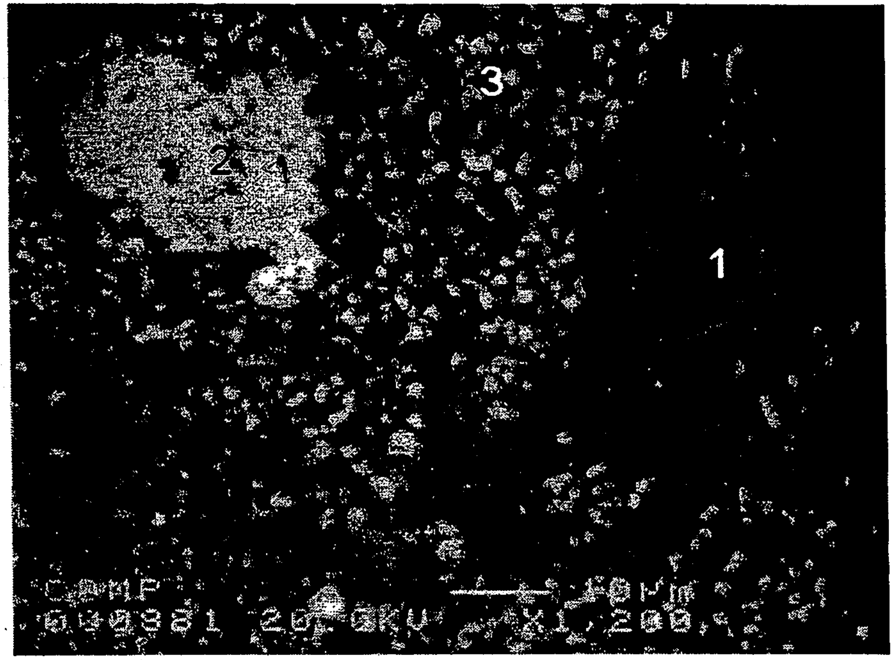


Fig. 7 – Backscattered electron micrograph of the iron arsenate phase in the January 98 Composite sample. 1- iron arsenate, 2- large mass of As_2O_3, 3- As_2O_3

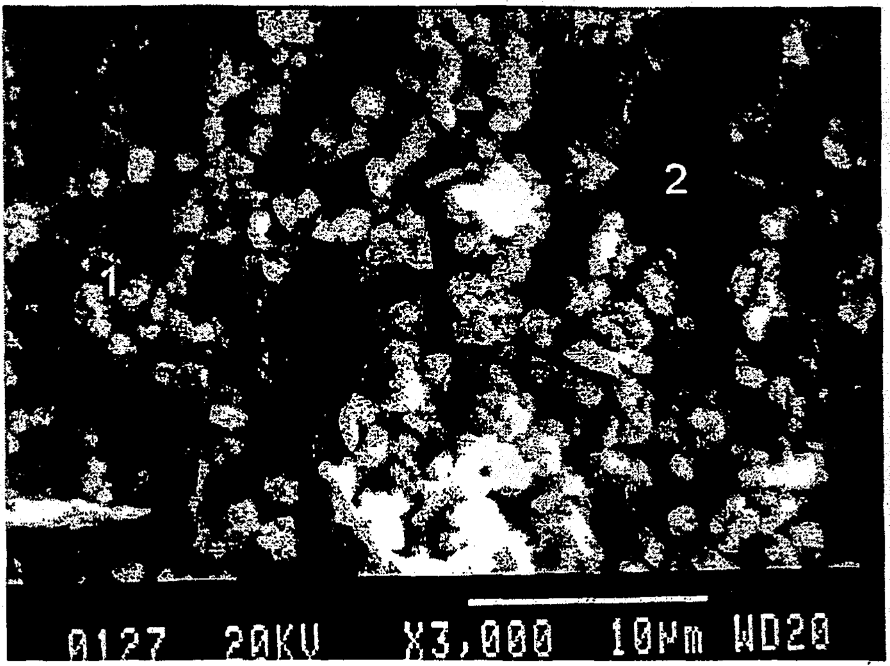


Fig. 8 – Secondary electron micrograph of a loose powder mount of the April 97 Composite sample that shows the general appearance of this material. 1- As_2O_3, 2- chlorite

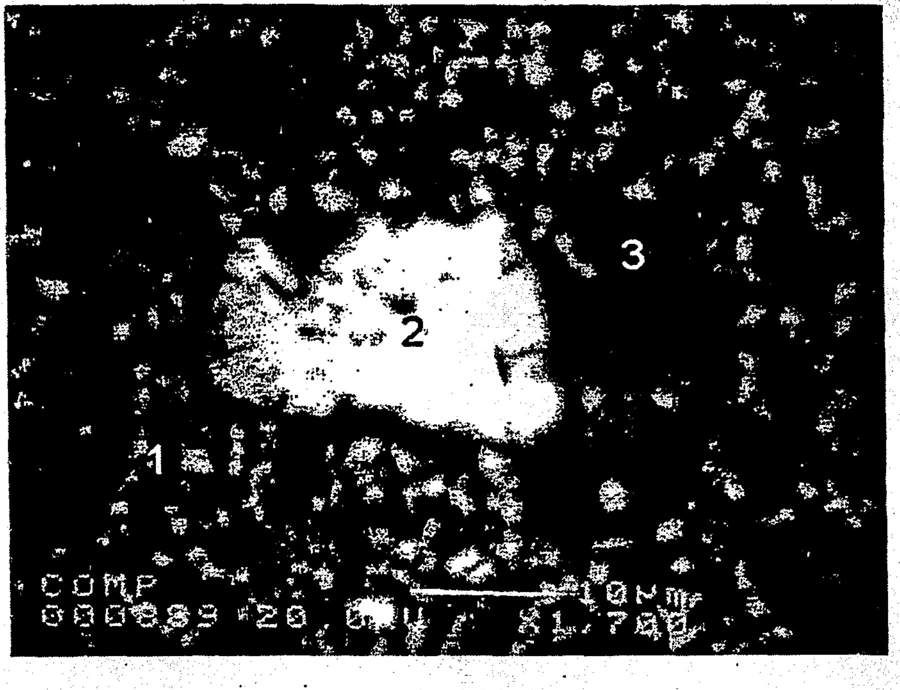


Fig. 9 – Backscattered electron micrograph showing the detailed morphology of the April 97 Composite sample. 1- As_2O_3, 2- $(As,Sb)_2O_3$ containing 13% Sb, 3- quartz

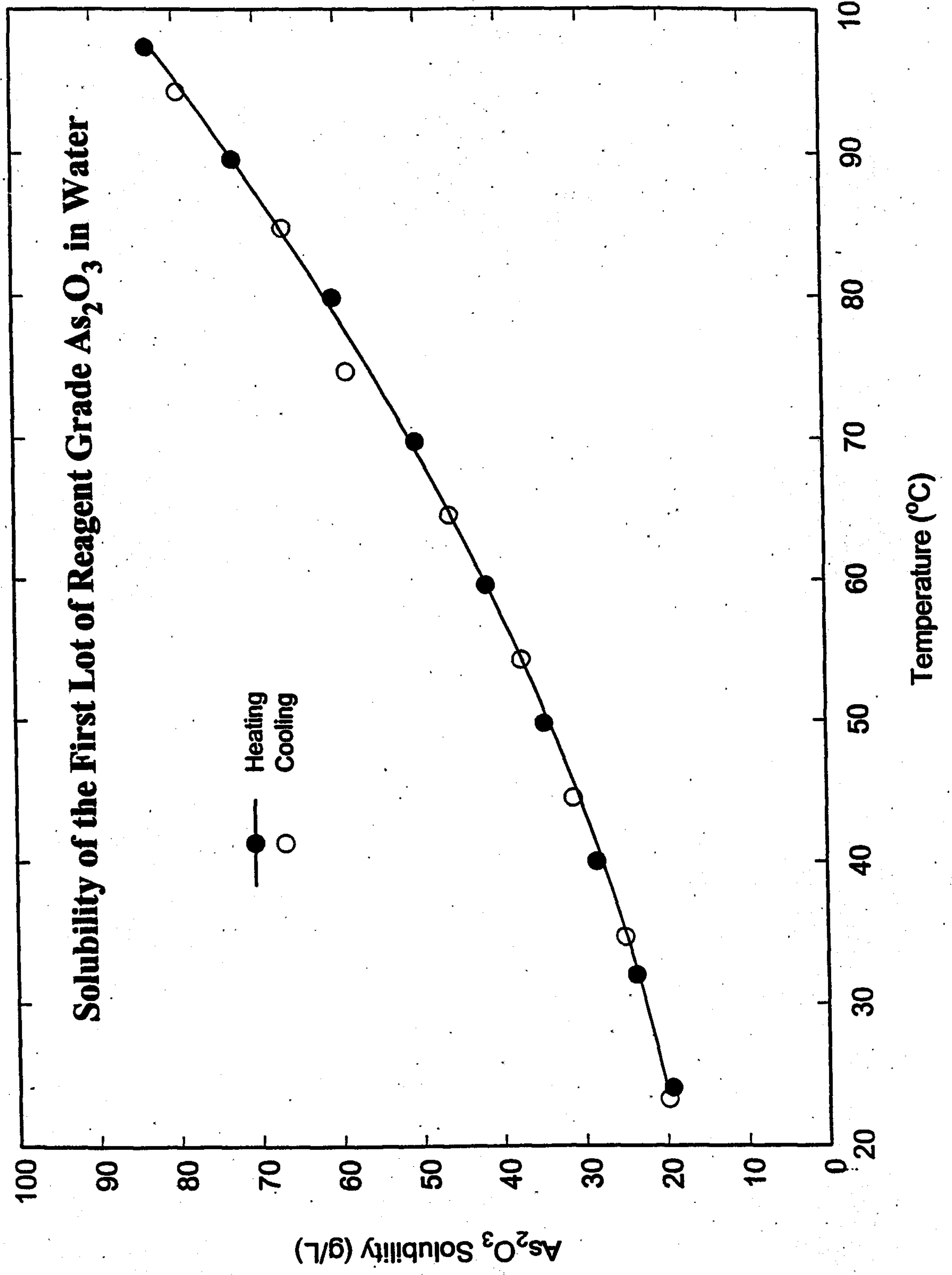


Fig. 23 - Experimentally determined solubility of As_2O_3 over the first lot of reagent grade As_2O_3.

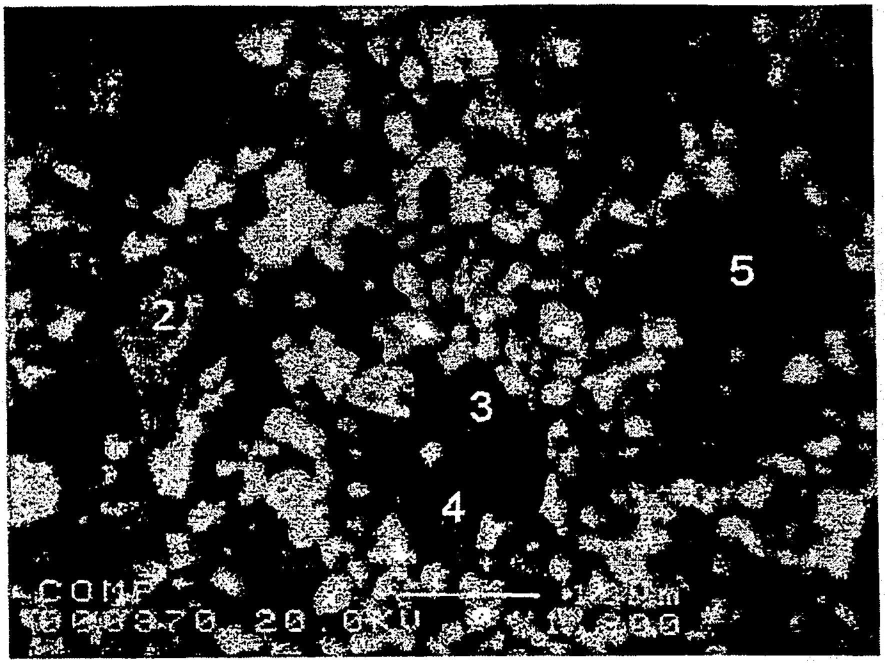


Fig. 22 – Backscattered electron micrograph showing the presence of As-bearing iron oxide and various silicate species in the 236 Chamber sample. 1- As_2O_3, 2- As-bearing iron oxide, 3- quartz, 4- chlorite, 5- muscovite

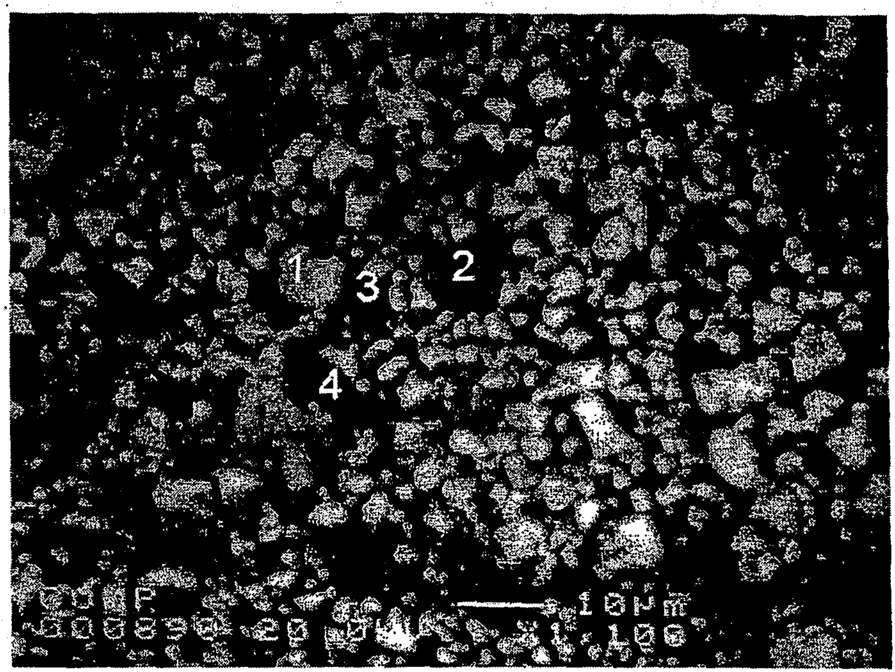


Fig. 20 - Backscattered electron micrograph showing the general morphology of the 236 Chamber sample in a polished section. 1- As_2O_3, 2- quartz, 3- chlorite, 4- muscovite

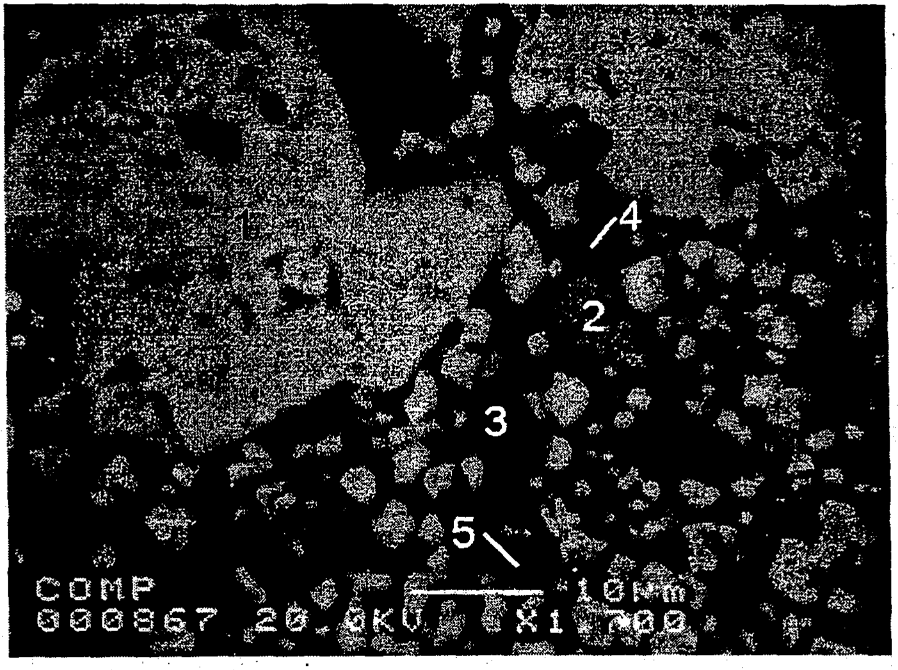


Fig. 21 - Backscattered electron micrograph showing the detailed morphology of the large As_2O_3 crystals in the 236 Chamber sample. 1- As_2O_3, 2- As-bearing iron oxide, 3- quartz, 4- chlorite, 5- muscovite

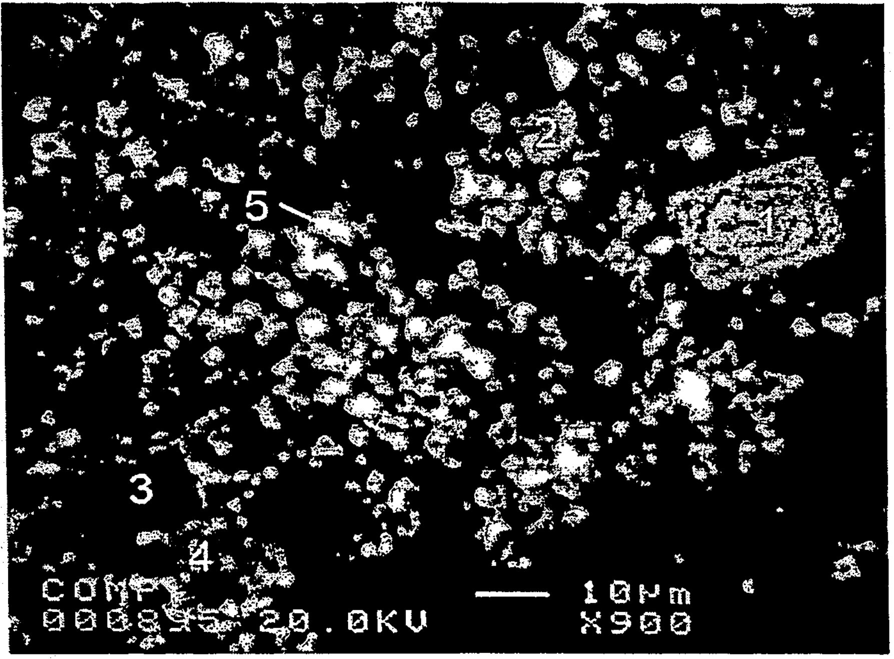


Fig. 18 - Backscattered electron micrograph showing a large particle of As-bearing iron oxide in the 212 Chamber sample. 1- As-bearing iron oxide, 2- As_2O_3 with minor Fe and Sb, 3- quartz, 4- chlorite, 5- As_2O_3

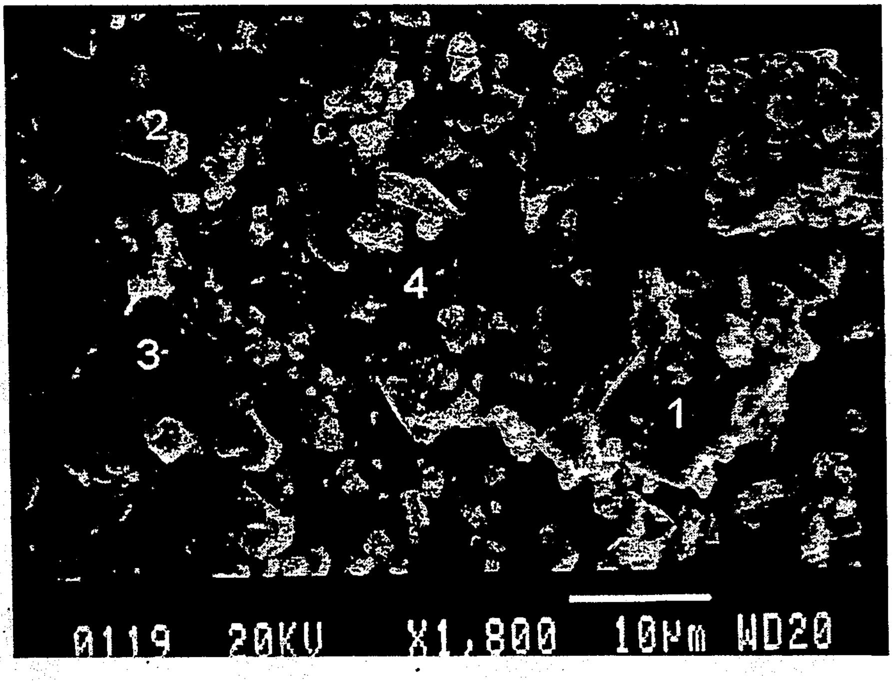


Fig. 19 - Secondary electron micrograph showing the general morphology of the 236 Chamber sample as seen in a loose powder mount. 1- As_2O_3, 2- chlorite, 3- muscovite, 4- As-bearing iron oxide

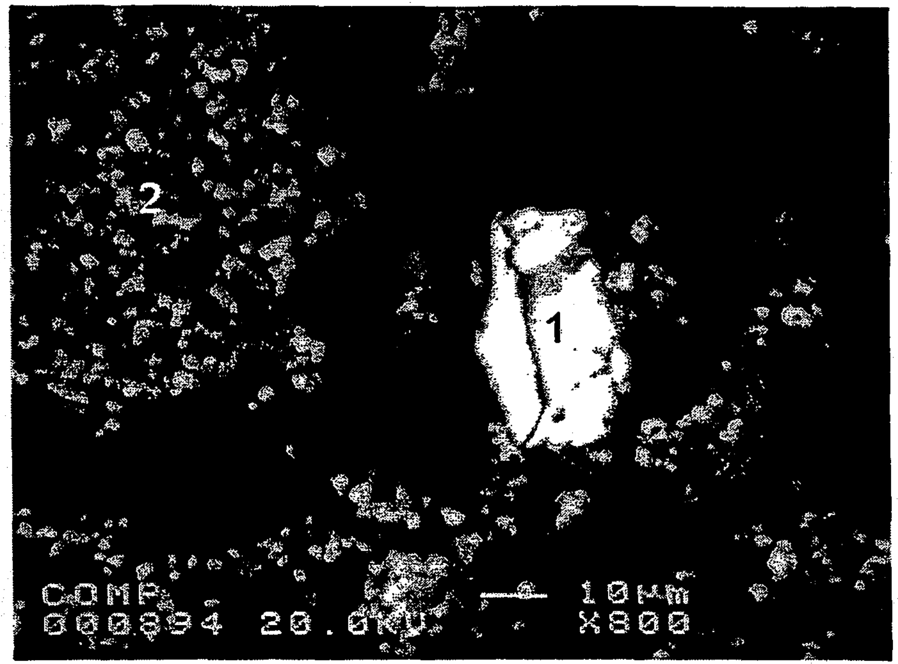


Fig. 16 – Backscattered electron micrograph of a large mass of $(Sb,As)_2O_3$ in the 212 Chamber sample. 1- $(Sb,As)_2O_3$, 2- As_2O_3 + silicates

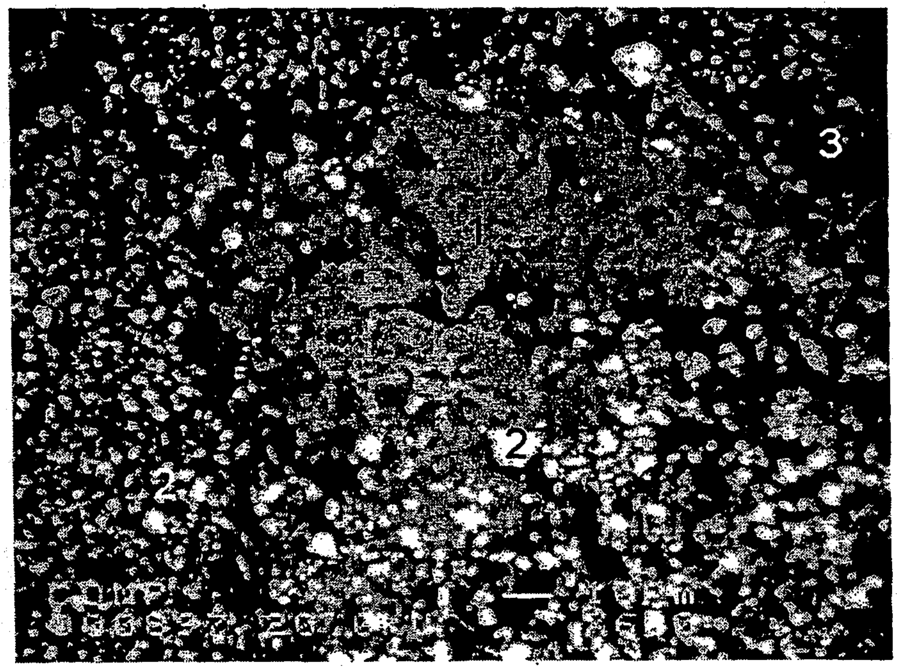


Fig. 17 – Backscattered electron micrograph showing a mass of iron arsenate in the 212 Chamber sample. 1- iron arsenate, 2- As_2O_3, 3- calcium sulphate

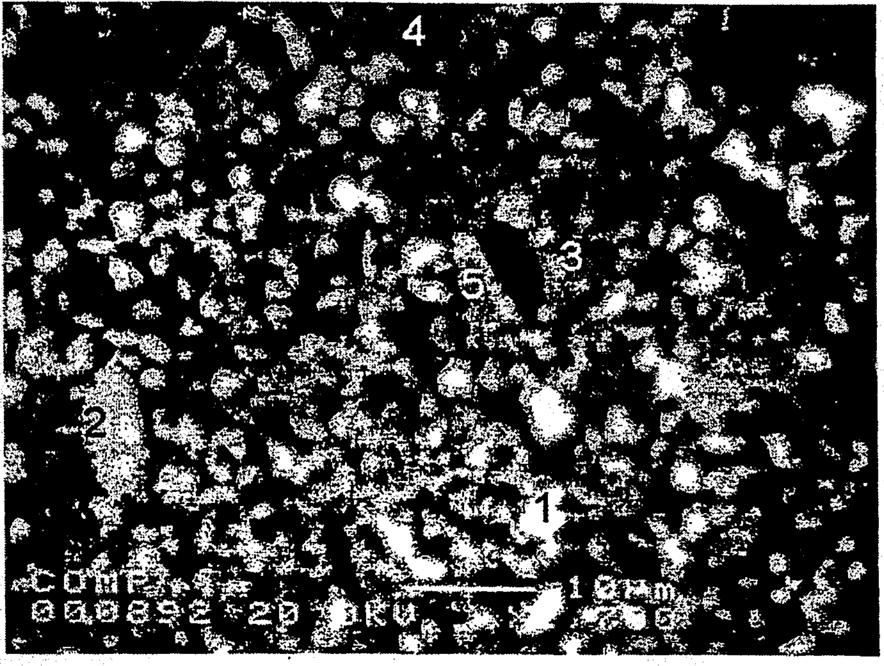


Fig. 14 – Backscattered electron micrograph showing the general appearance of the 212 Chamber sample in polished section. 1- As_2O_3, 2- As-bearing iron oxide, 3- As-bearing Ca-Fe oxide, 4- muscovite, 5- chlorite

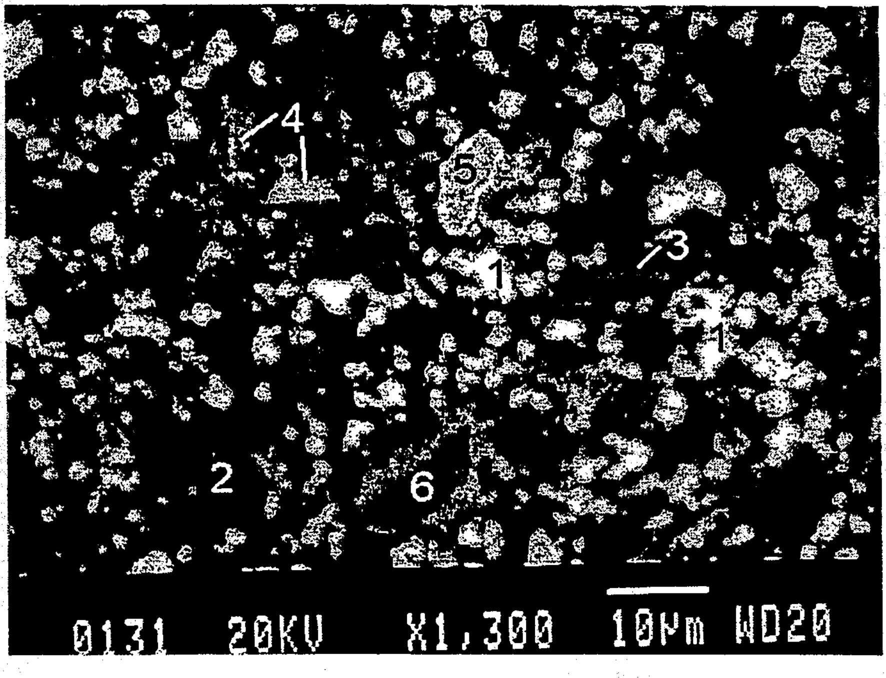


Fig. 15 – Backscattered electron micrograph showing the general appearance of the 212 Chamber sample. 1- As_2O_3, 2- quartz, 3- chlorite, 4- Fe arsenate, 5- As-bearing iron oxide rimmed by $(Sb,As)_2O_3$, 6- muscovite rimmed with Fe-Ca sulphate-arsenate

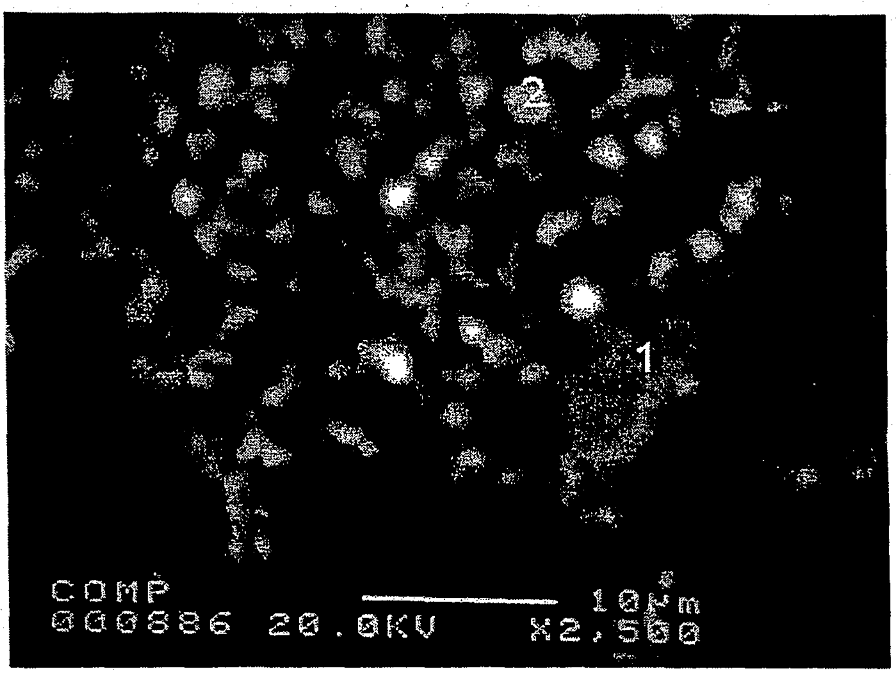


Fig. 12 - Backscattered electron micrograph illustrating a zoned particle of calcium arsenate in the April 97 Composite sample. 1- calcium arsenate-sulphate, 2- As_2O_3

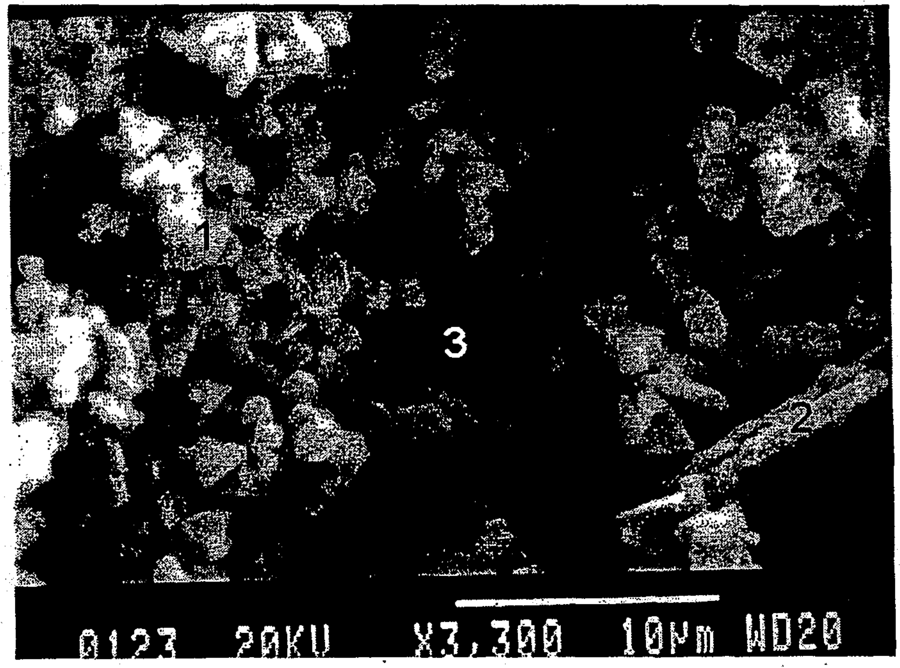


Fig. 13 - Secondary electron micrograph of a loose powder mount of the 212 Chamber sample. 1- As_2O_3, 2- chlorite, 3- muscovite

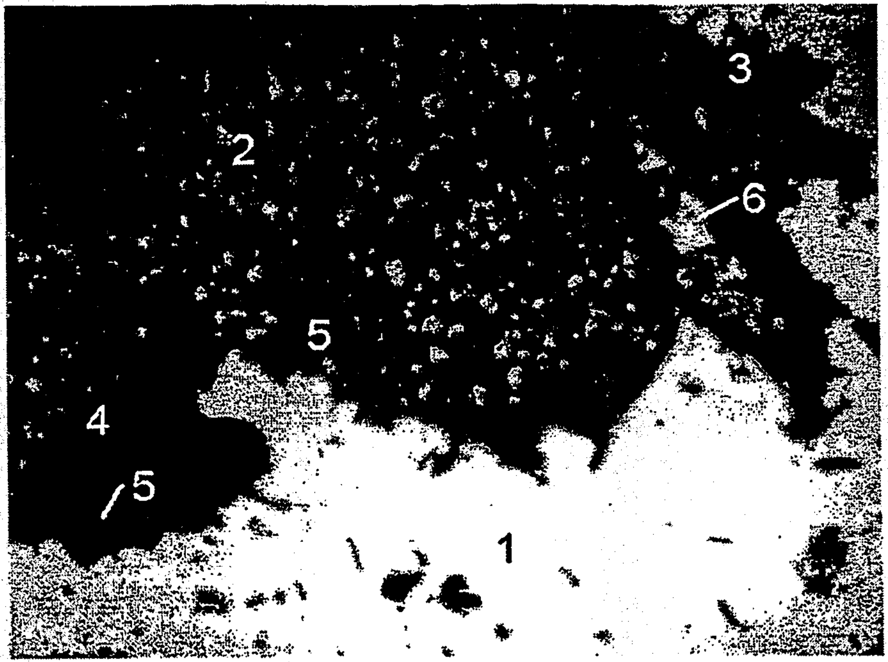


Fig. 10 - Backscattered electron micrograph of a large mass of $(As,Sb)_2O_3$ oxide in the April 97 Composite sample. 1- $(As,Sb)_2O_3$, 2- As_2O_3, 3- quartz, 4- chlorite, 5- Fe-Ca oxide, 6- (As,Sb,Fe) oxide

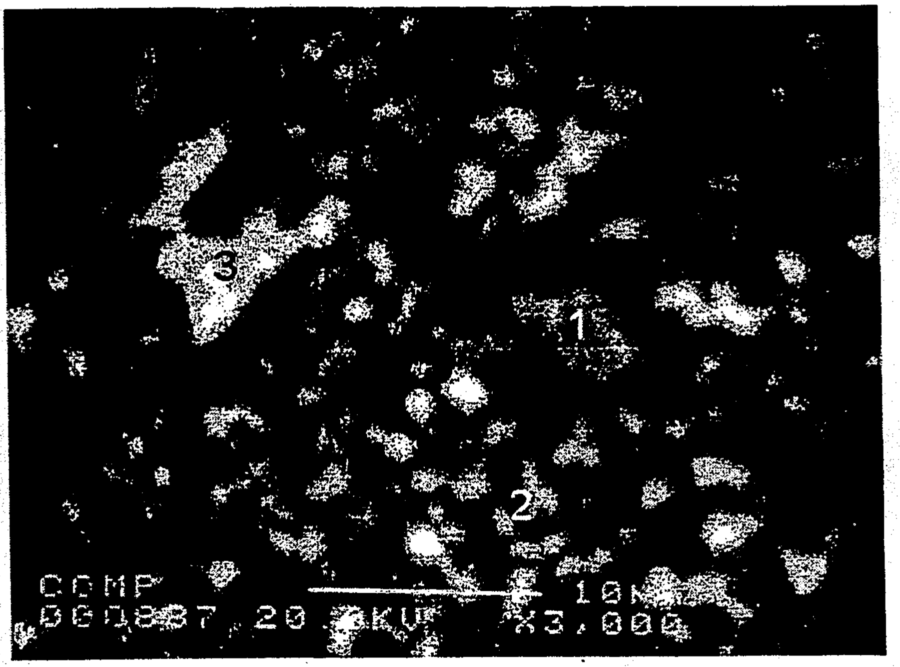


Fig. 11 - Backscattered electron micrograph showing a particle of iron arsenate in the April 97 Composite sample. 1- iron arsenate, 2- As_2O_3, 3- $(As,Sb)_2O_3$

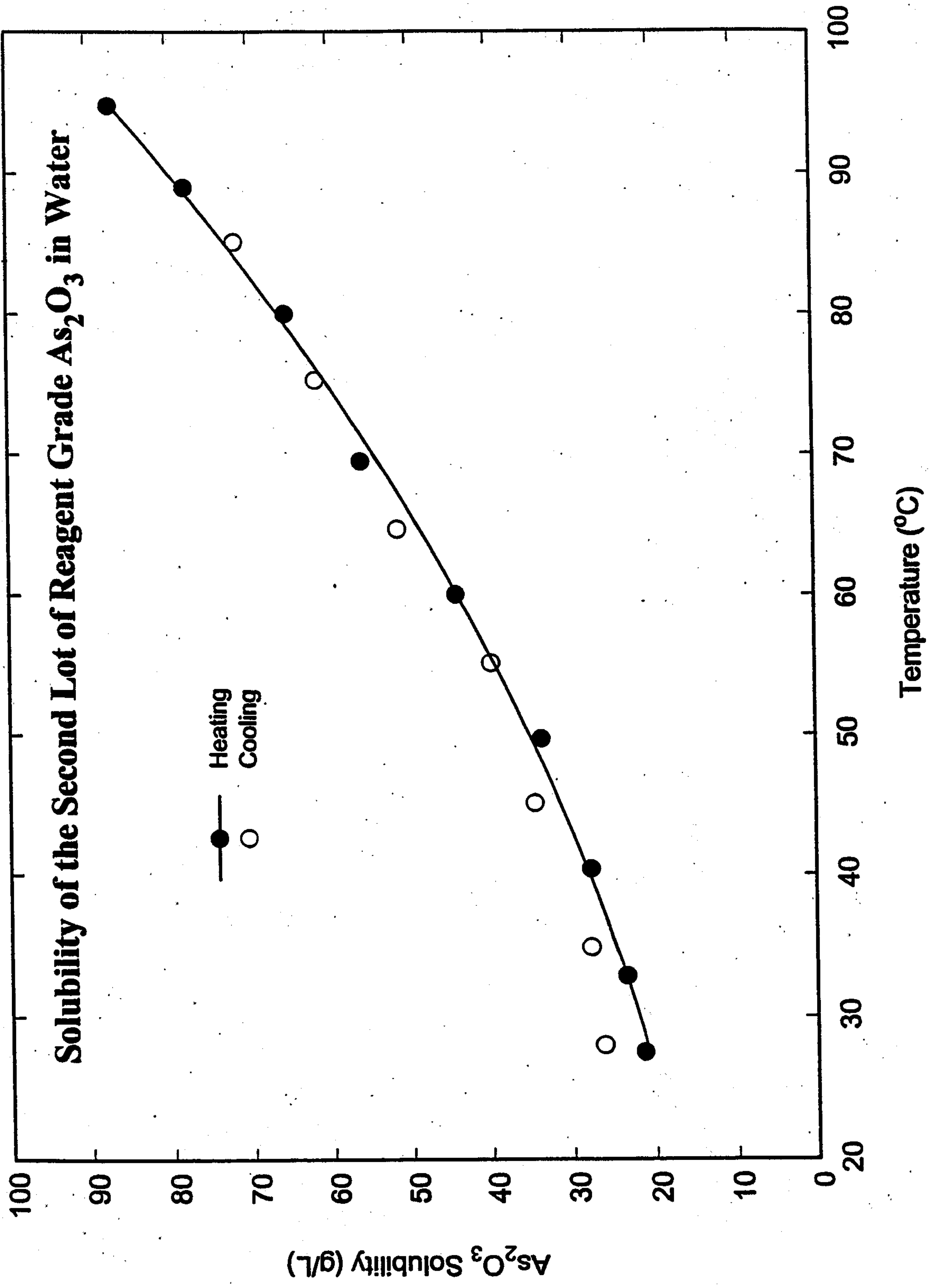


Fig. 24 - Experimentally determined solubility of As_2O_3 over the second lot of reagent grade As_2O_3.

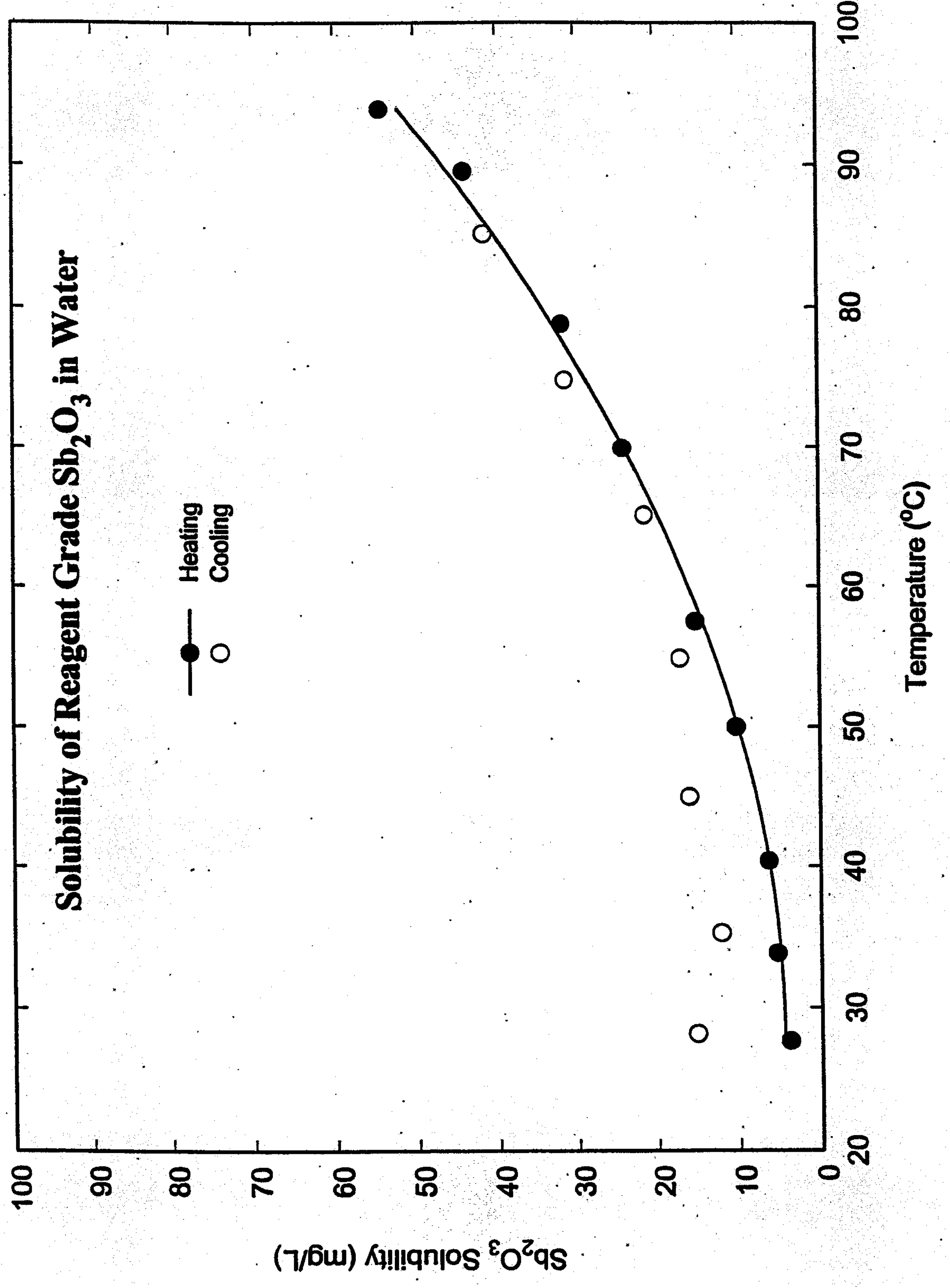


Fig. 25 - Experimentally determined solubility of Sb_2O_3 over reagent grade Sb_2O_3.

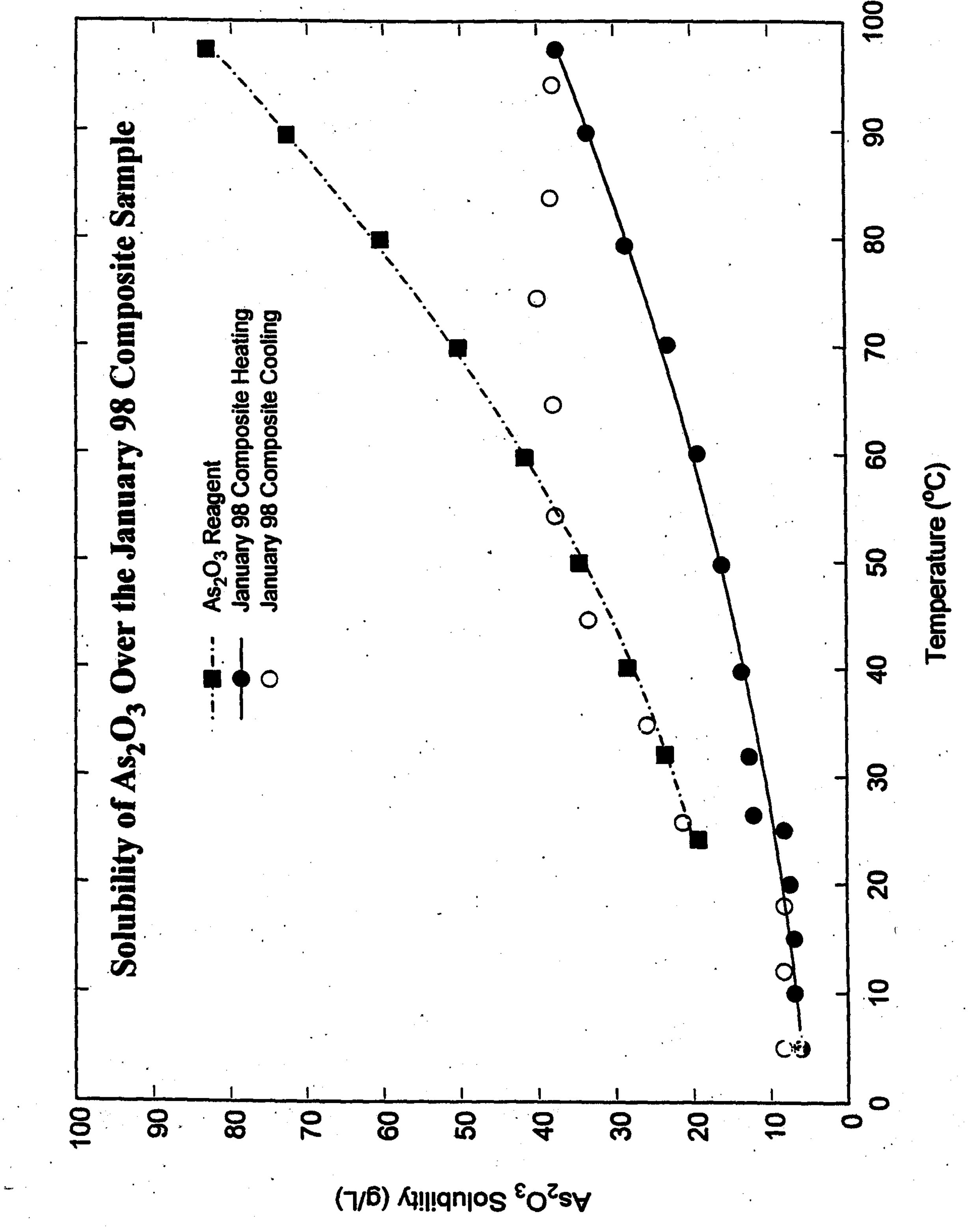


Fig. 26 - Experimentally determined solubility of As_2O_3 over the January 98 Composite sample.

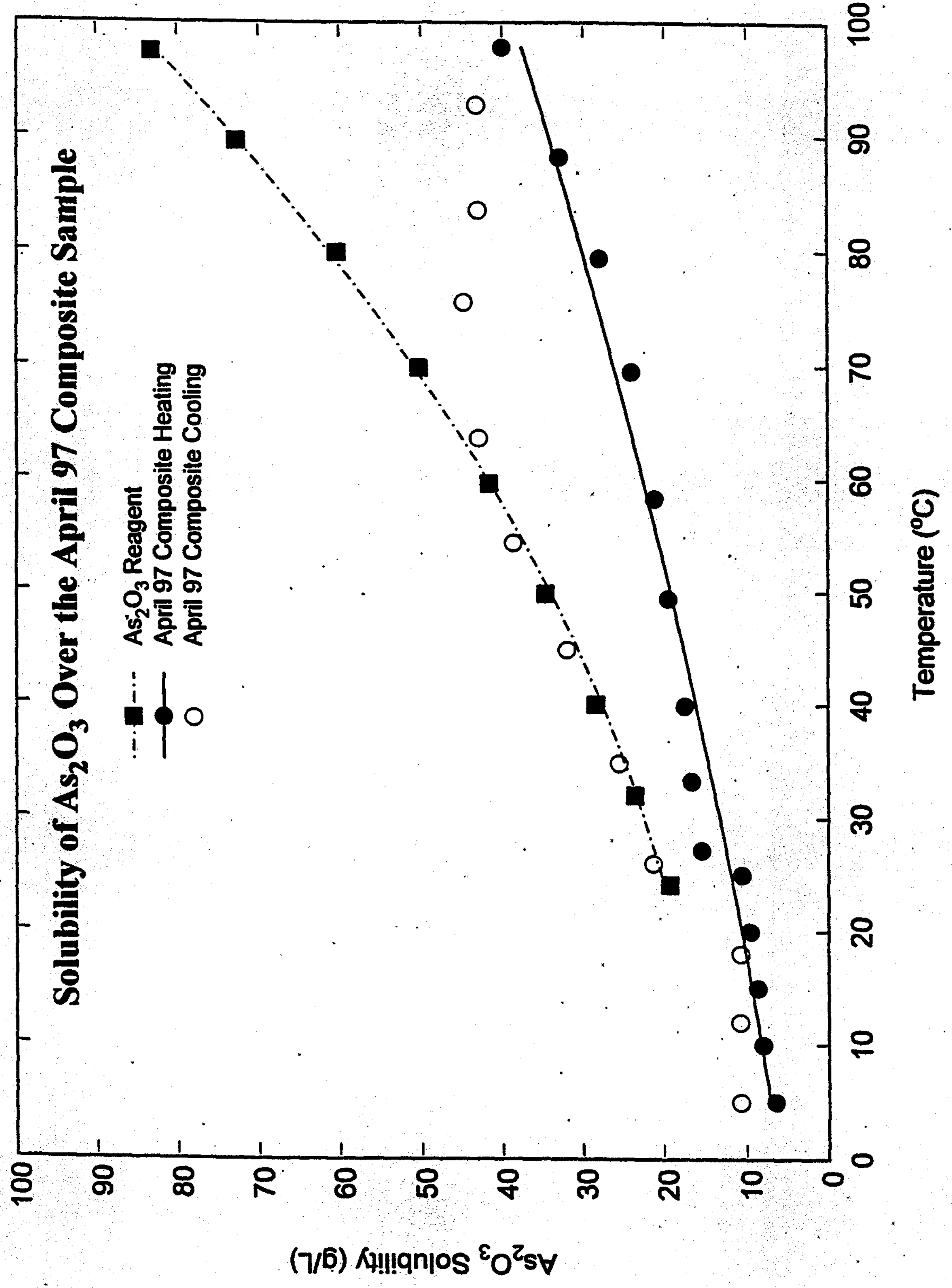


Fig. 27 - Experimentally determined solubility of As_2O_3 over the April 97 Composite sample.

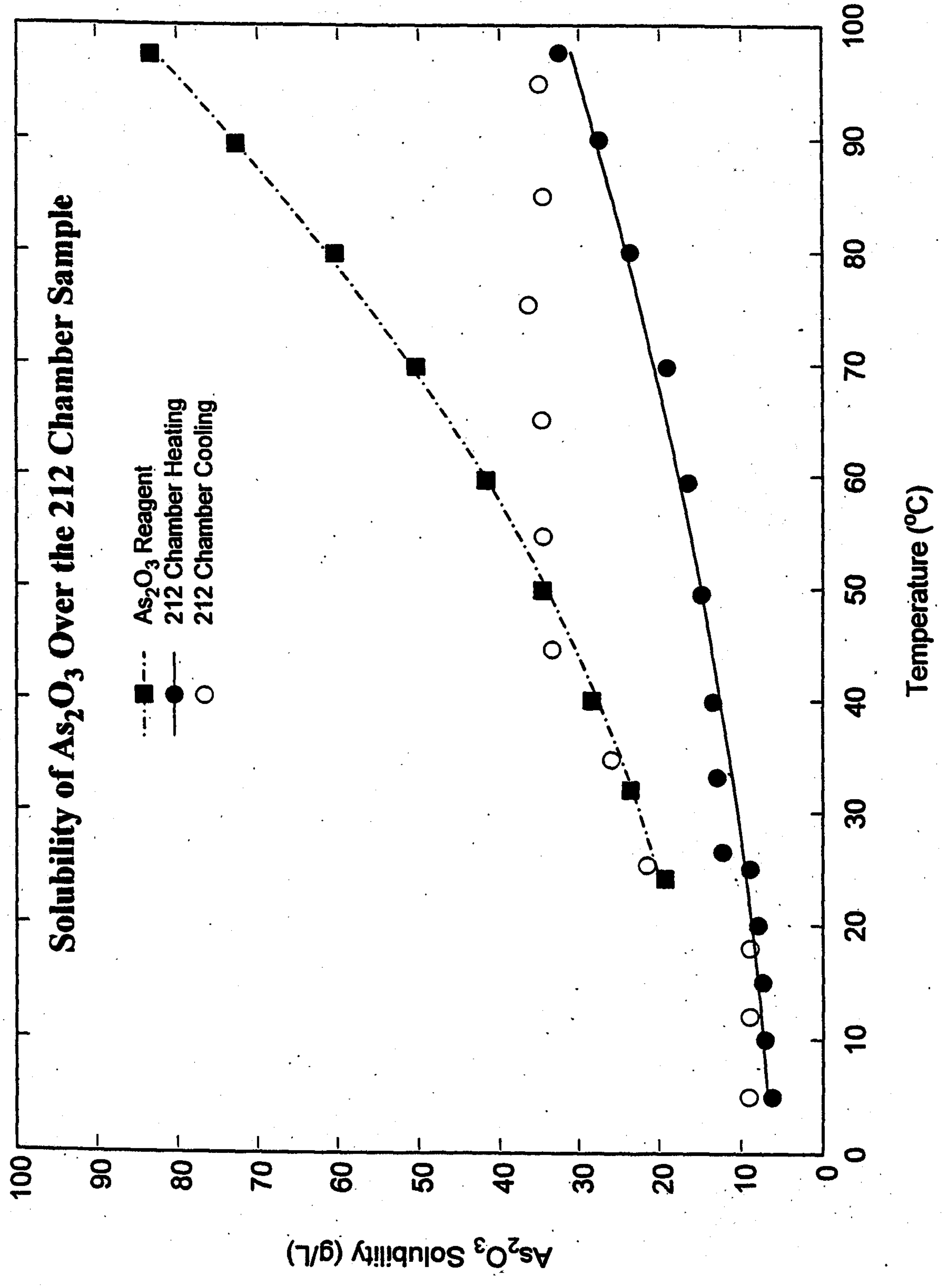


Fig. 28 - Experimentally determined solubility of As_2O_3 over the 212 Chamber sample.

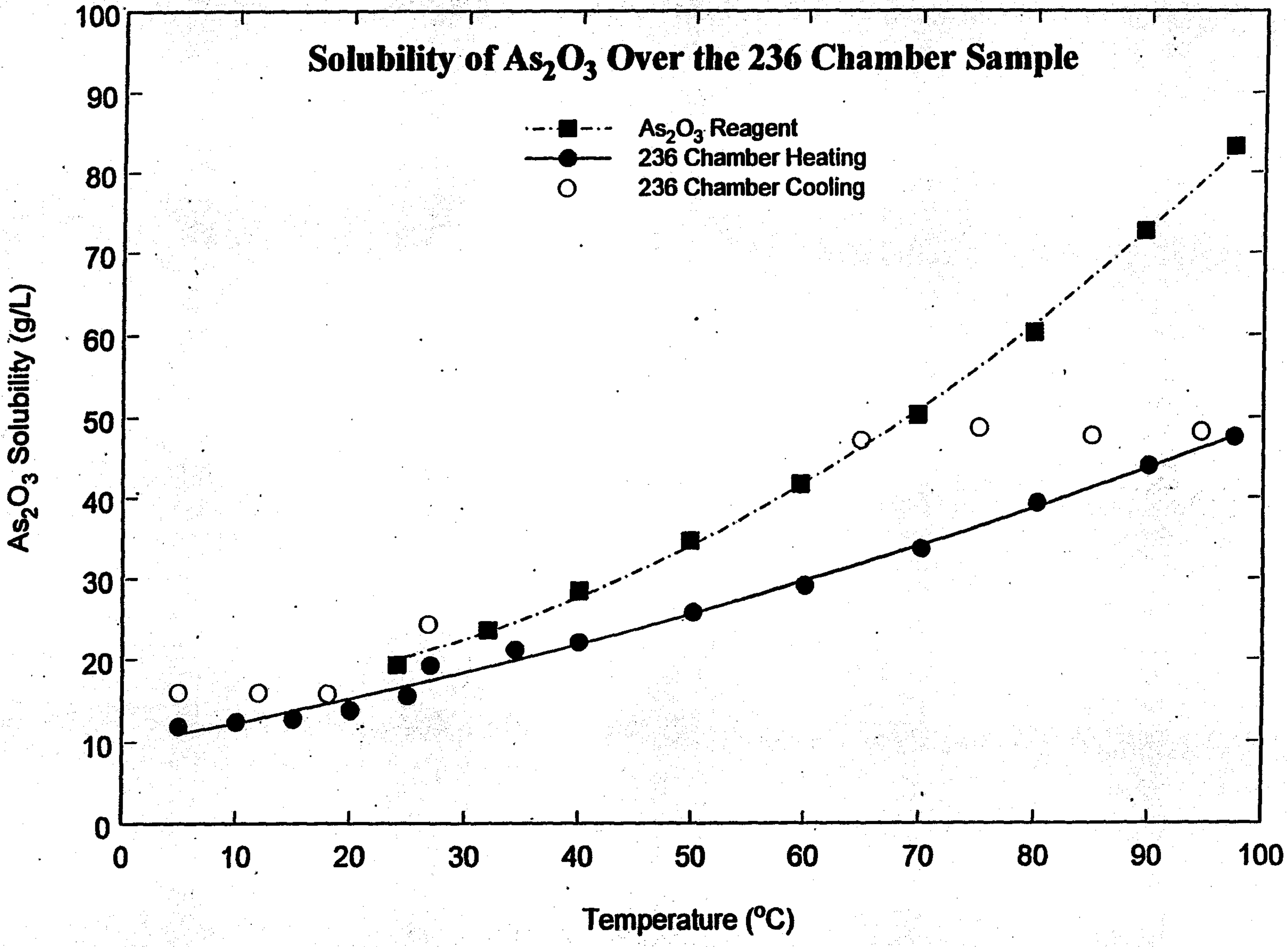


Fig. 29 - Experimentally determined solubility of As_2O_3 over the 236 Chamber sample.

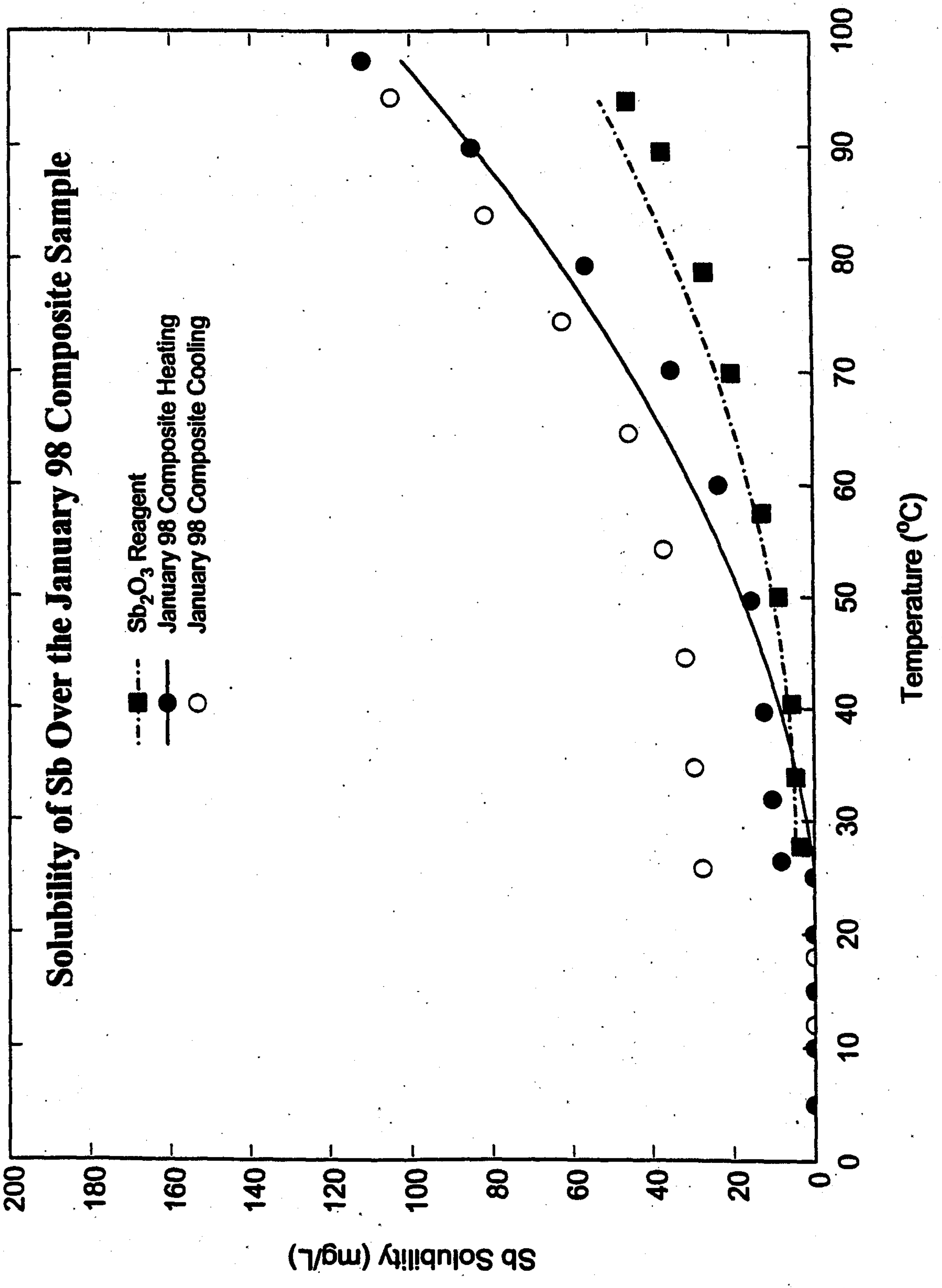


Fig. 30 - Experimentally determined solubility of Sb over the January 98 Composite sample.

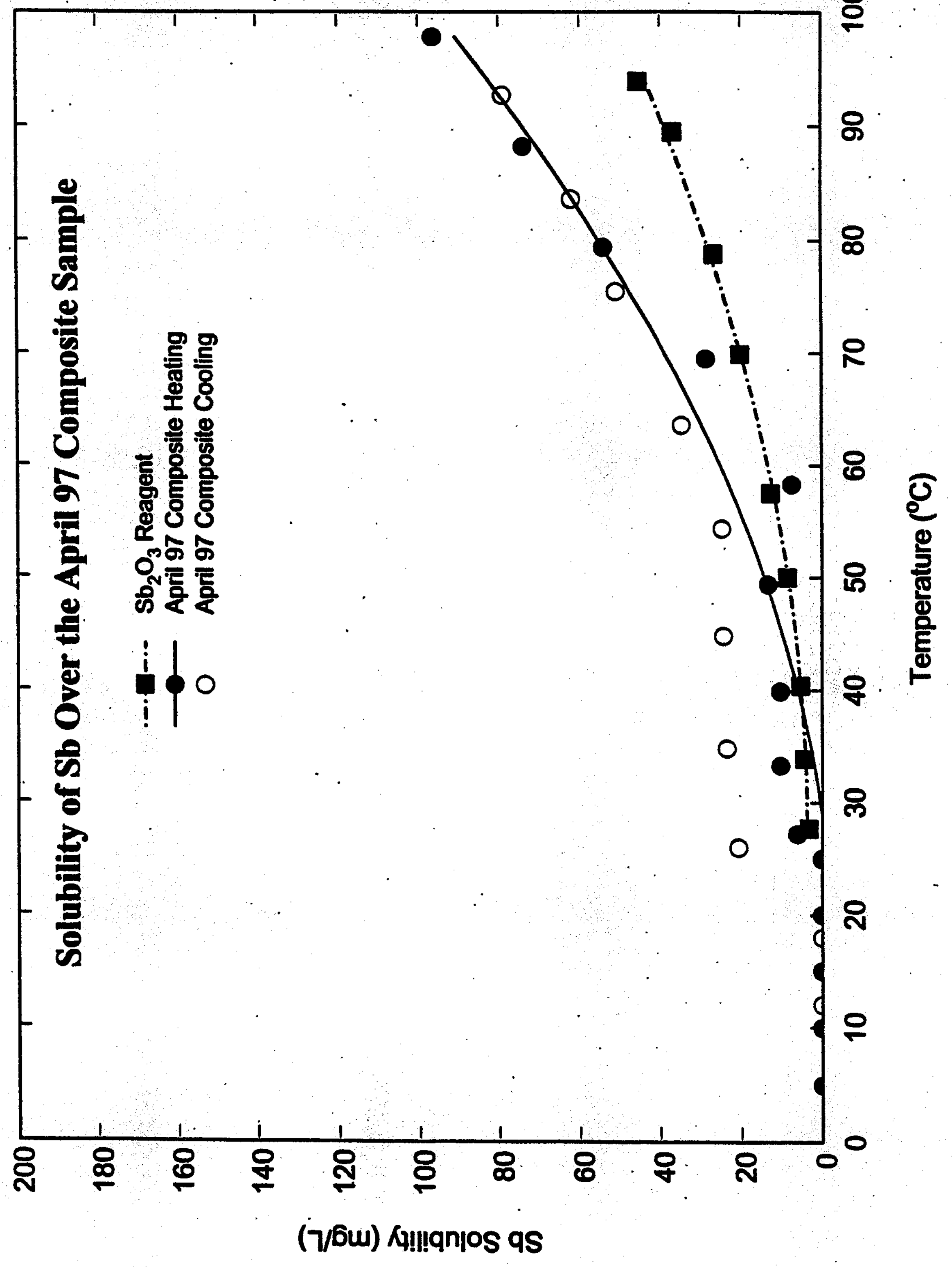


Fig. 31 - Experimentally determined solubility of Sb over the April 97 Composite sample.

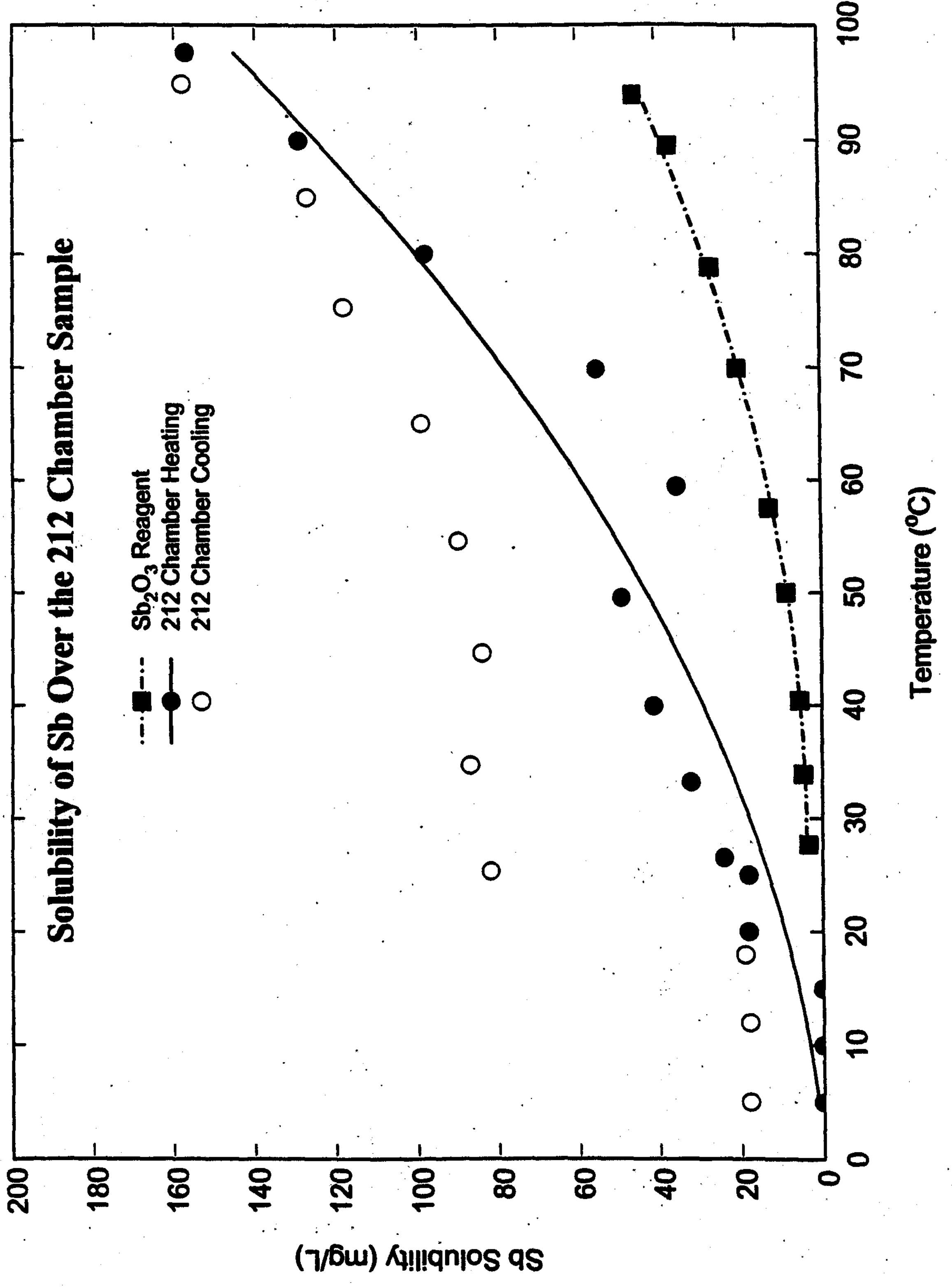


Fig. 32 - Experimentally determined solubility of Sb over the 212 Chamber sample.

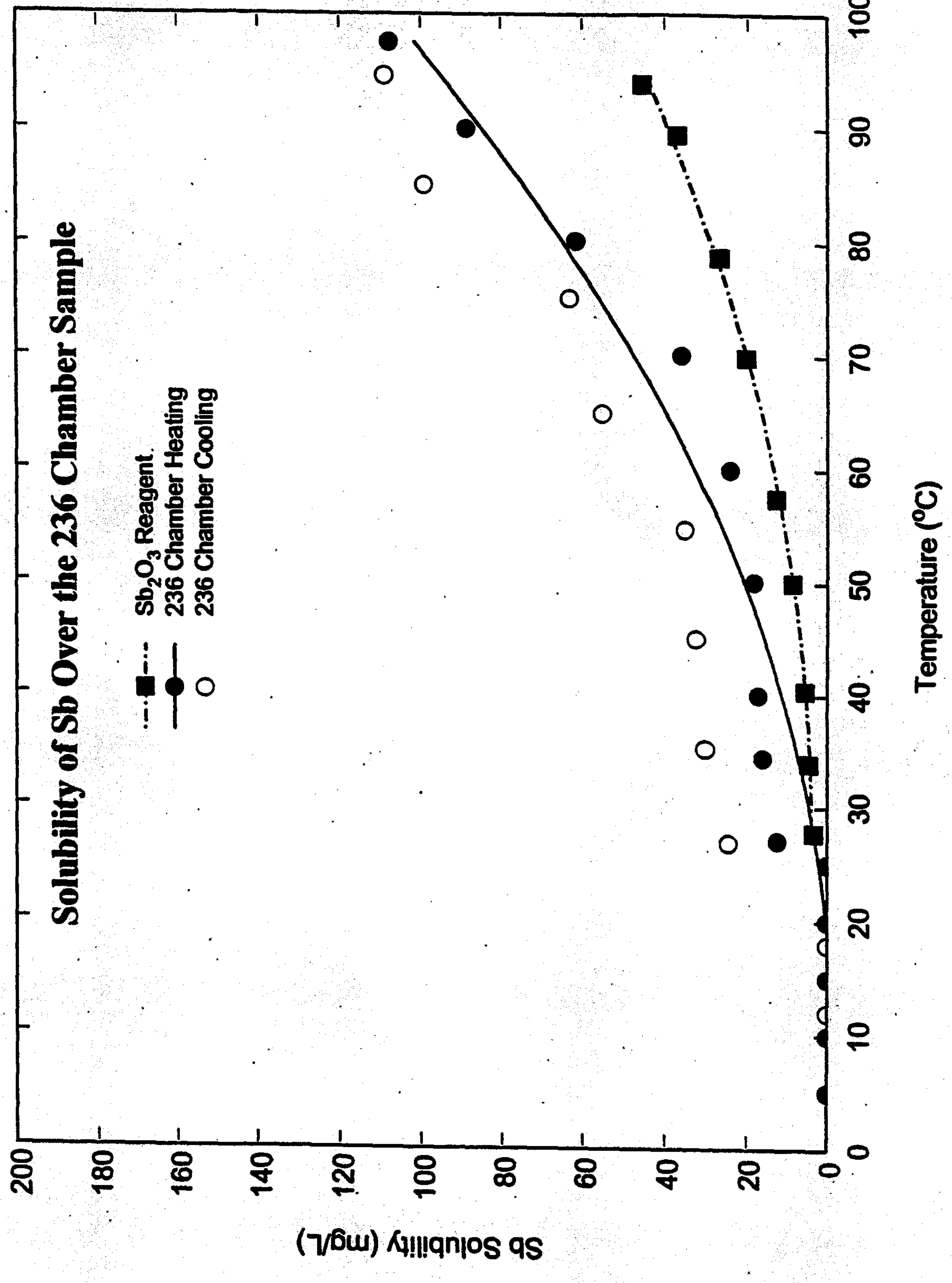


Fig. 33 - Experimentally determined solubility of Sb over the 236 Chamber sample.

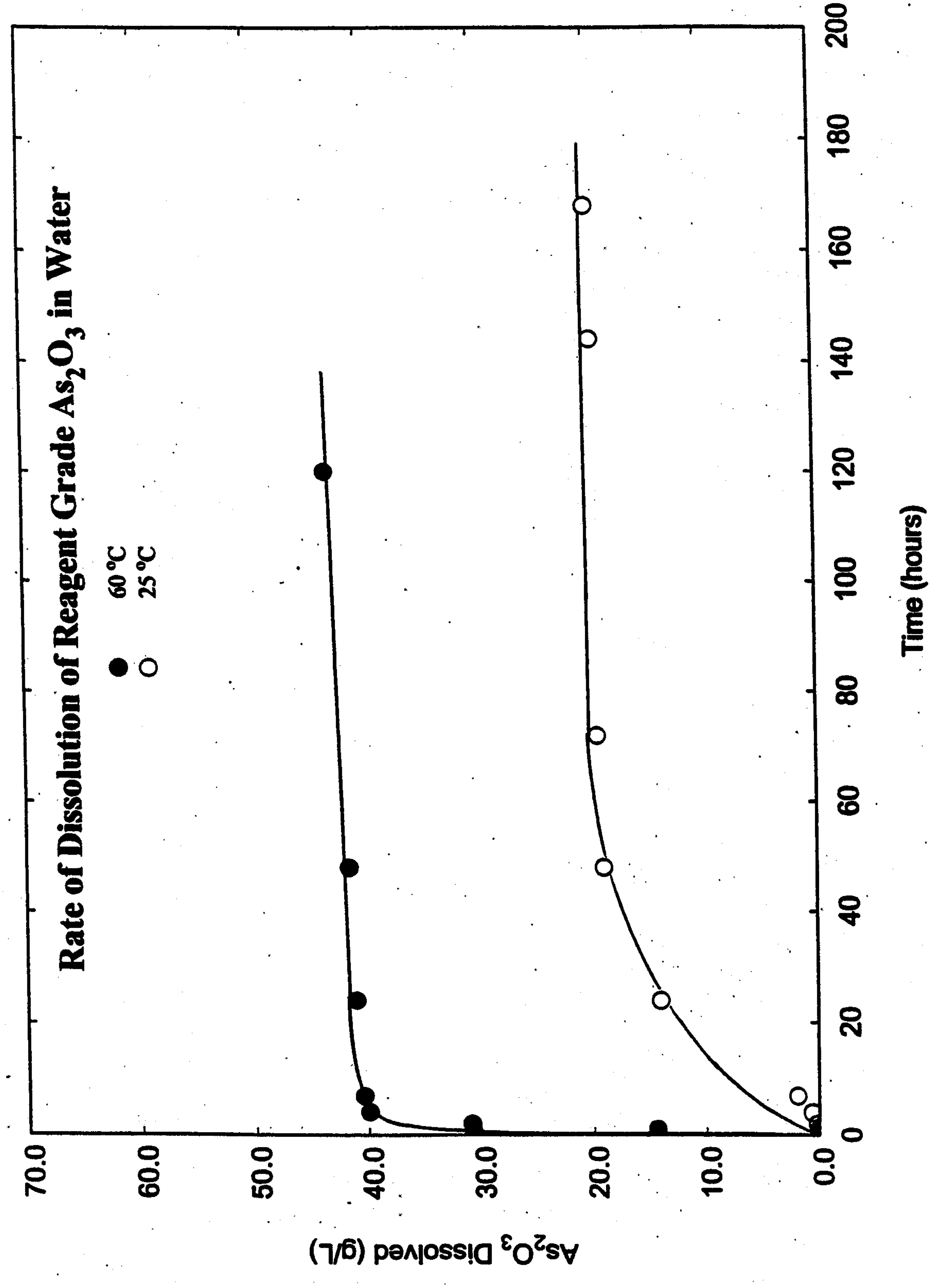


Fig. 34 - The solubility of As_2O_3, from reagent grade As_2O_3, in water as a function of time at 25°C and 60°C.

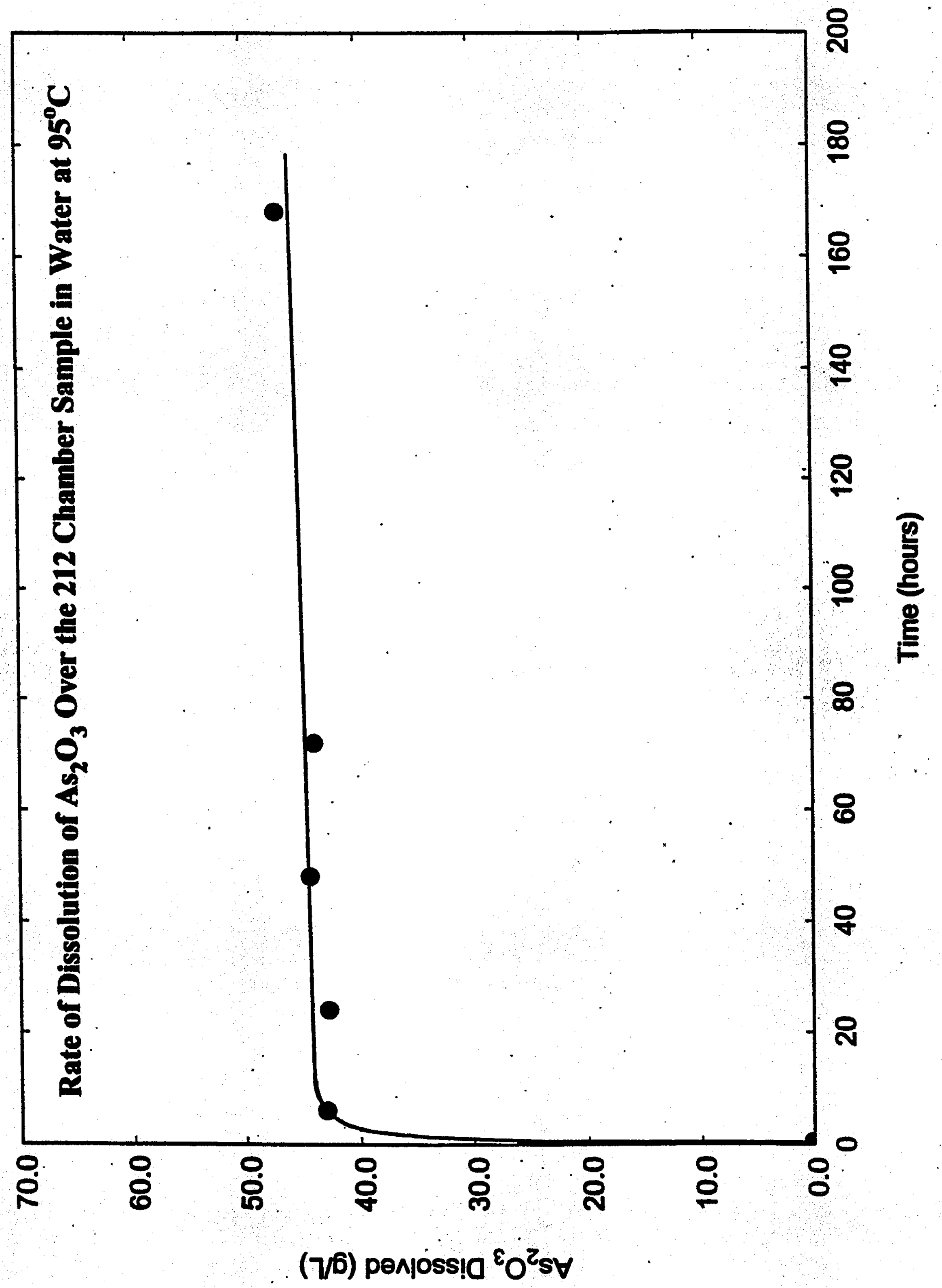


Fig. 35 - The solubility of As_2O_3, from the 212 Chamber sample, in water as a function of time at 95°C.

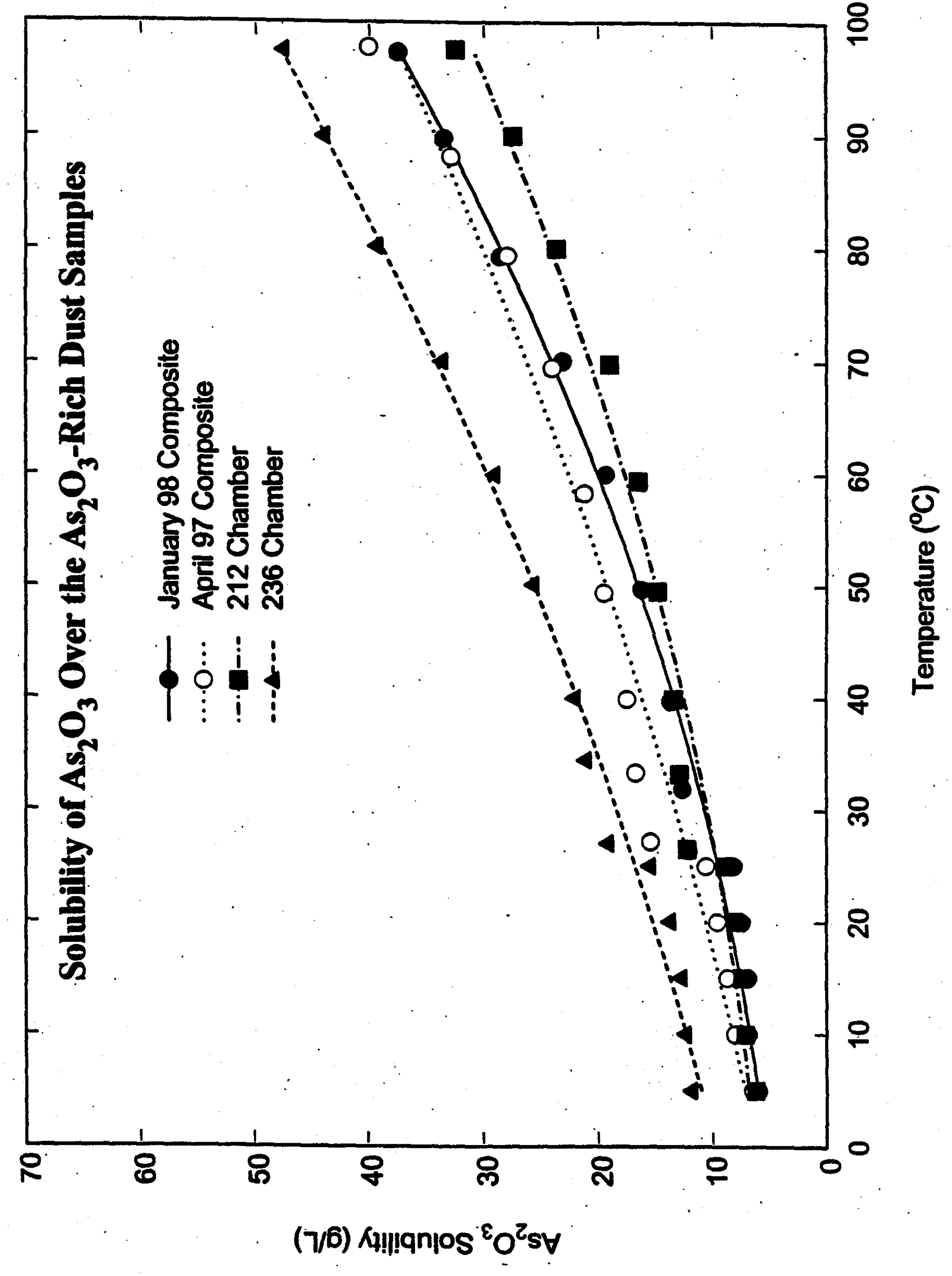


Fig. 36 - Comparison of the solubilities of As_2O_3 over the four As_2O_3-rich dust samples as a function of temperature, as obtained on heating only.

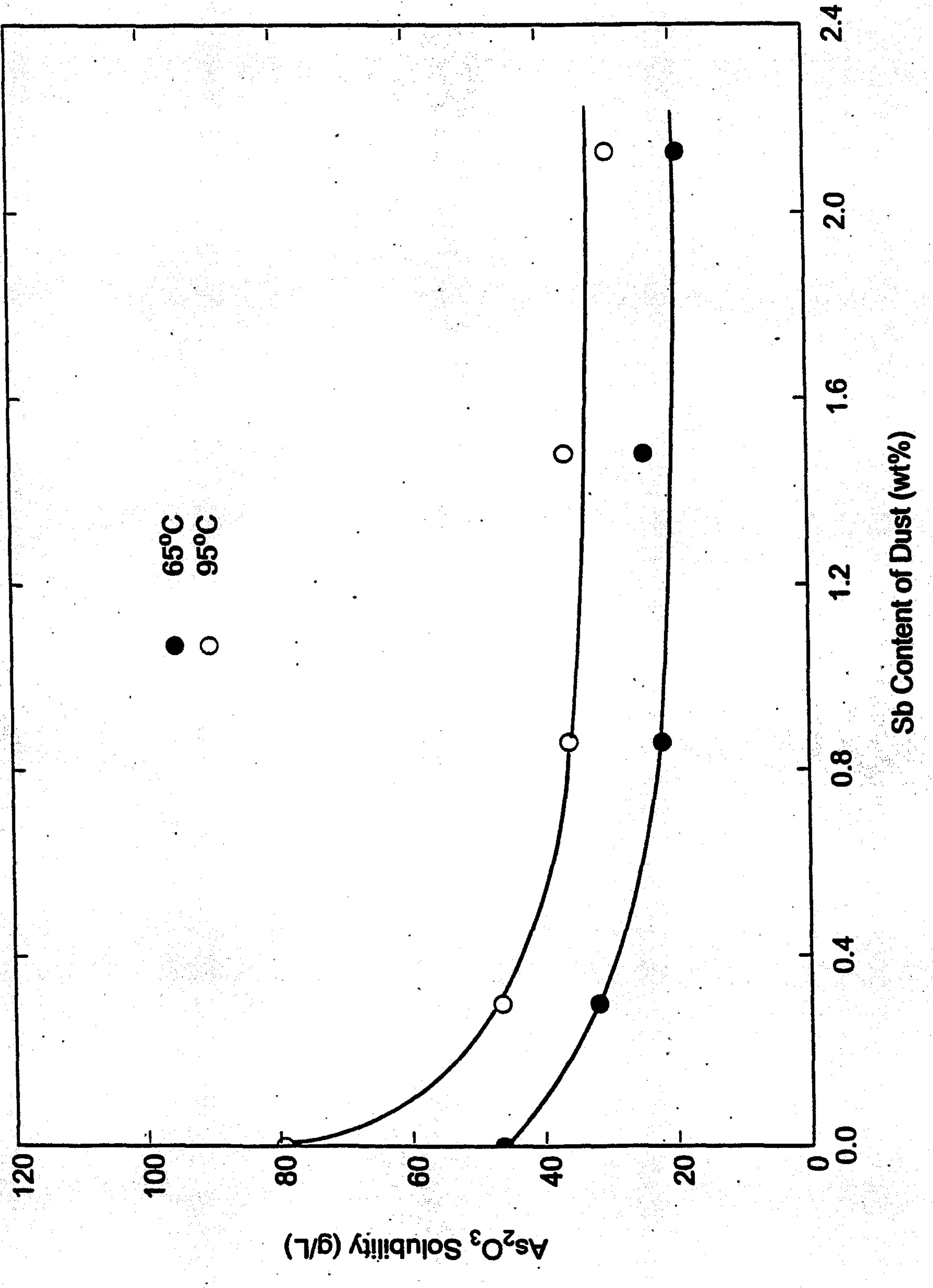


Fig. 37 - Solubility of As_2O_3 over the four As_2O_3-rich dust samples as a function of the Sb content of the dust.

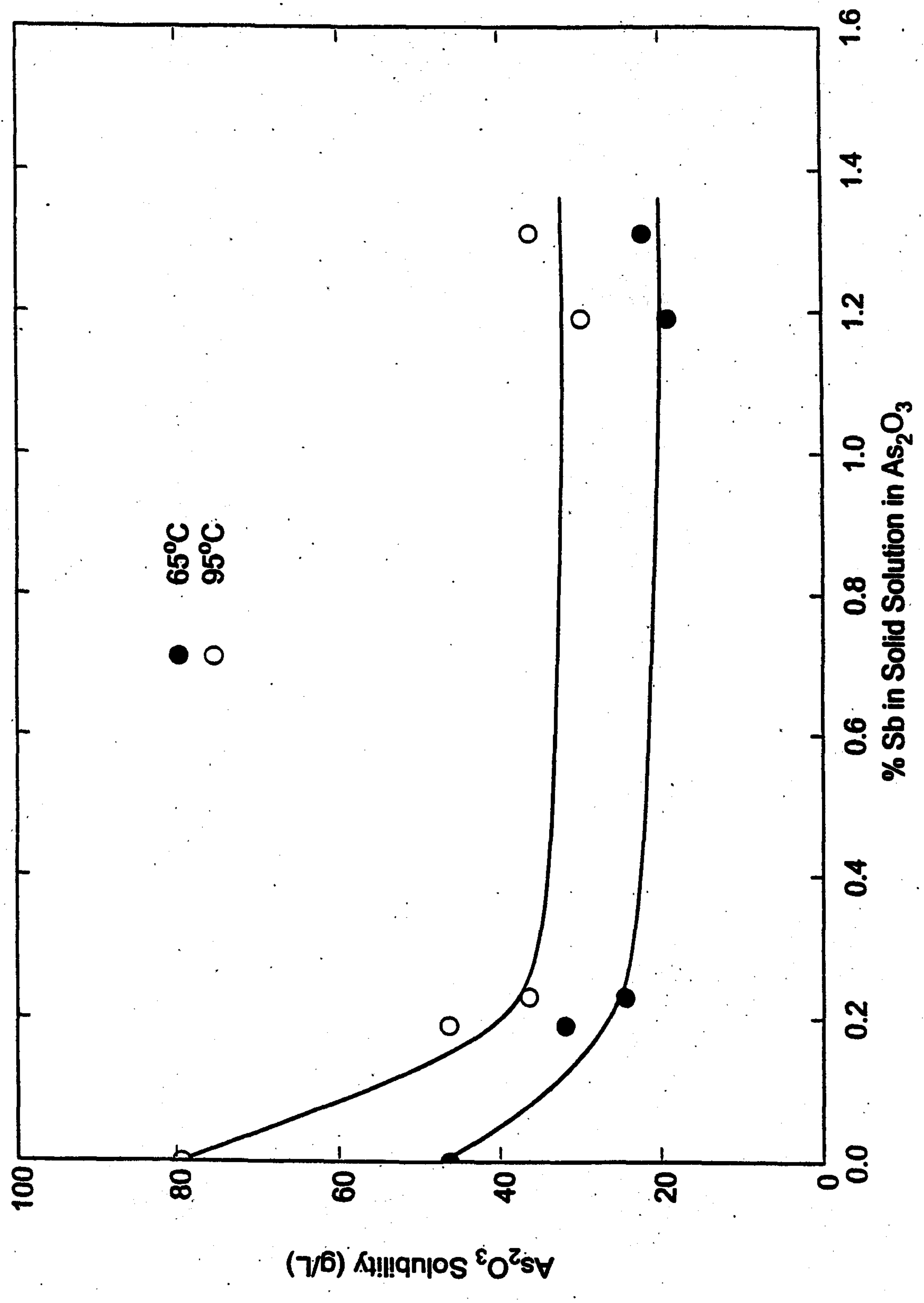


Fig. 38 - Solubility of As_2O_3 over the four As_2O_3-rich dust samples as a function of the solid solution Sb content of the As_2O_3 crystals in the dust.

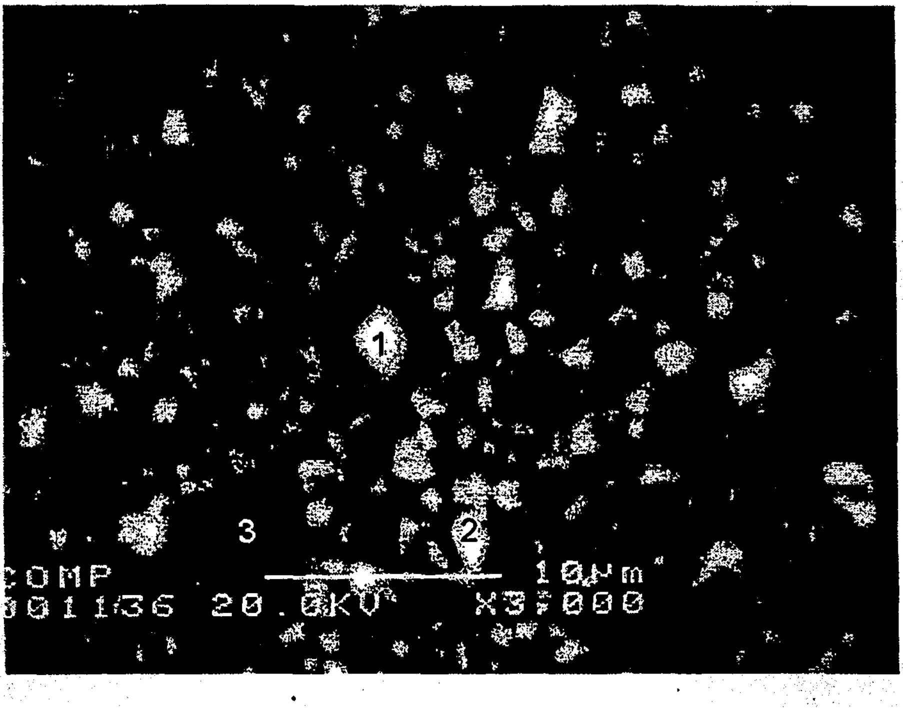


Fig. 39 – Backscattered electron micrograph showing the general morphology of the April 97 Composite sample after water leaching at 70 °C at a pulp density of 75 g/L solids. 1- As_2O_3, 2- $(Sb,As)_2O_3$, 3- silicates

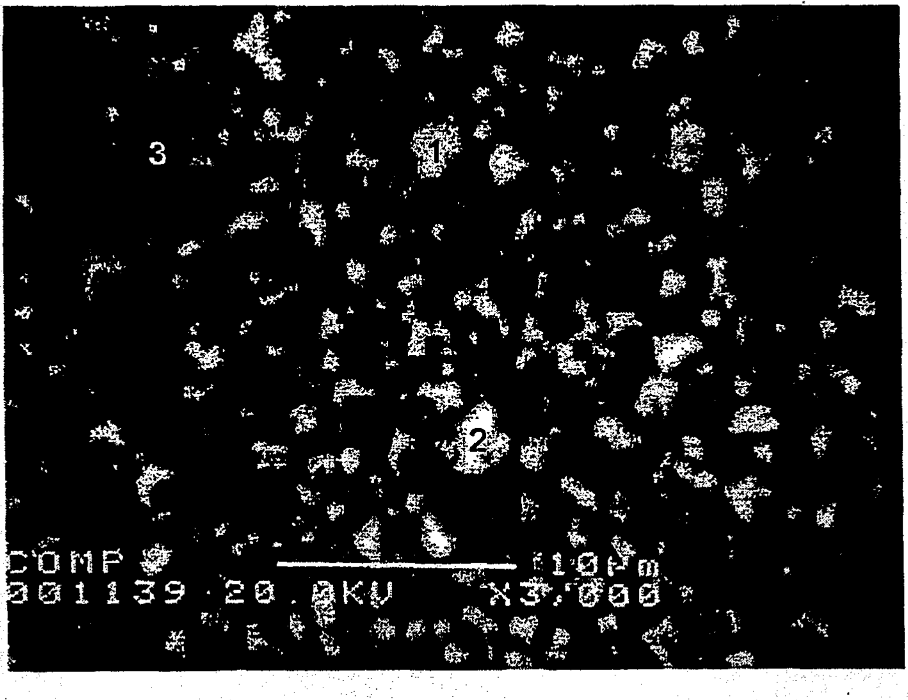


Fig. 40 - Backscattered electron micrograph showing the general morphology of the April 97 Composite sample after water leaching at 70 °C at a pulp density of 150 g/L solids. 1- As_2O_3, 2- $(Sb,As)_2O_3$, 3- silicates

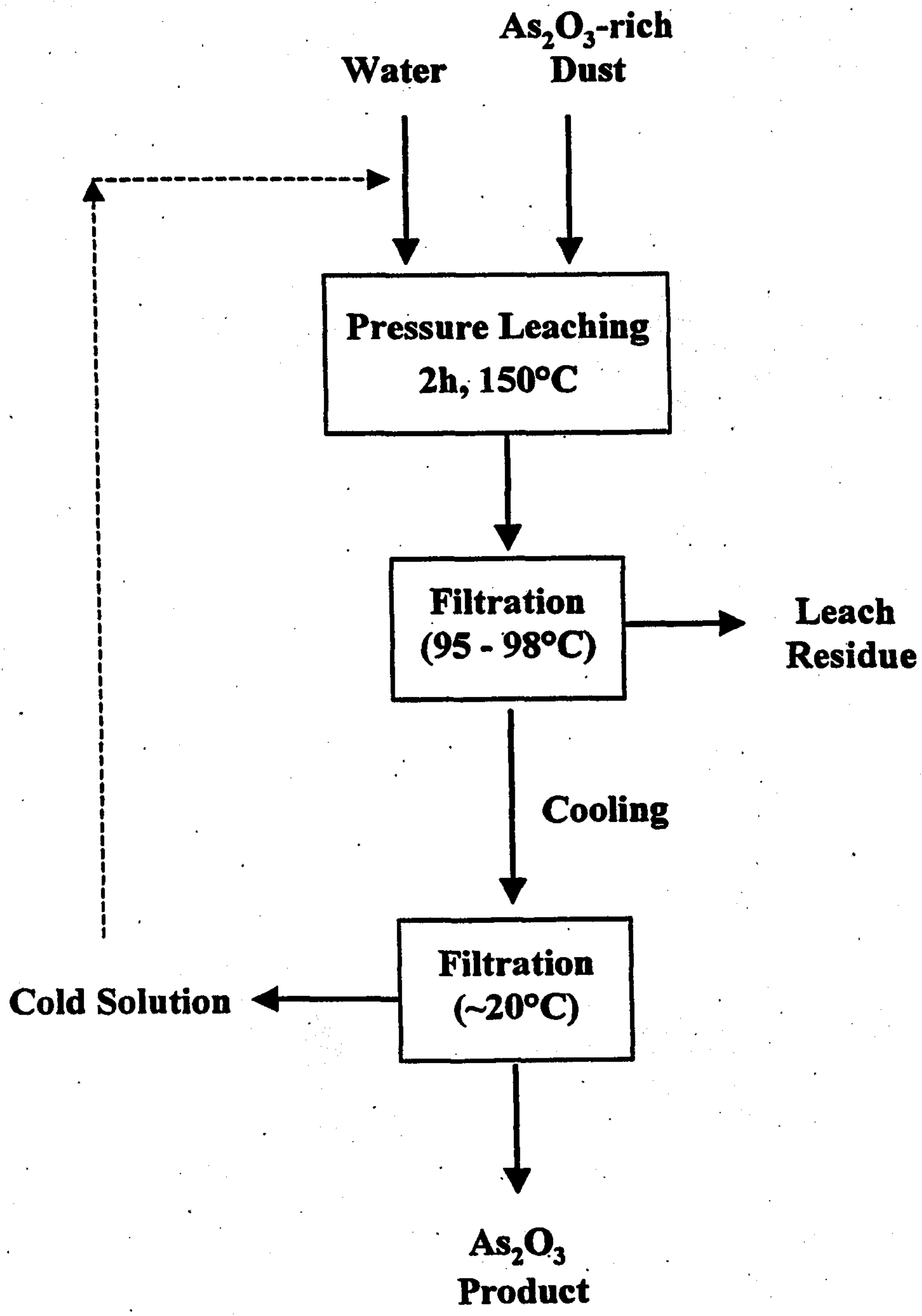


Fig. 41 - Schematic representation of the hot water leaching procedure used to produce an As_2O_3-saturated solution at 95°C, from which pure As_2O_3 can be crystallized.

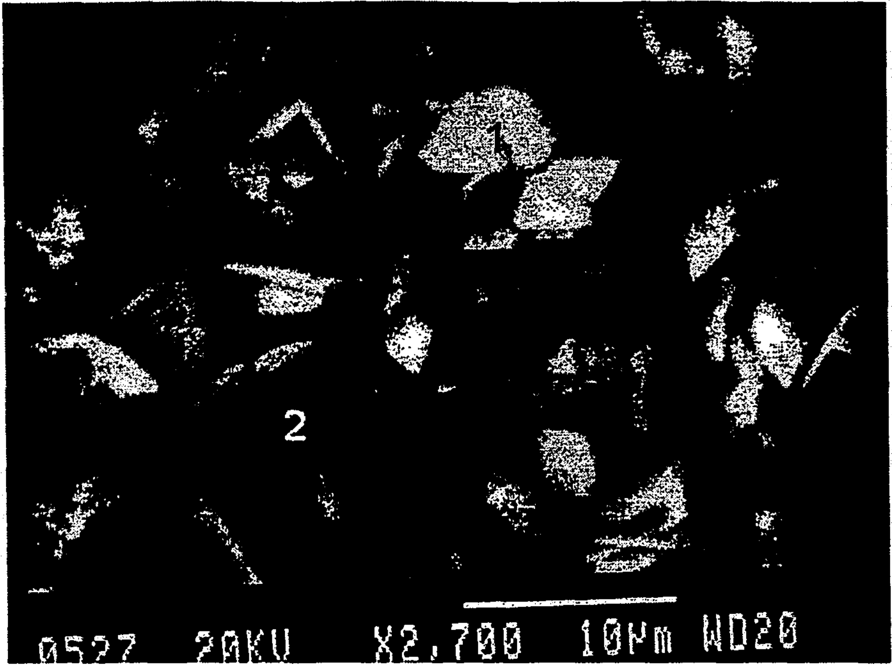


Fig. 42 - Backscattered electron micrograph of the residue from the leaching of 77 g/L of the April 97 Composite sample for 2 h at 150°C. 1- recrystallized $(Sb,As)_2O_3$, 2- chlorite and muscovite

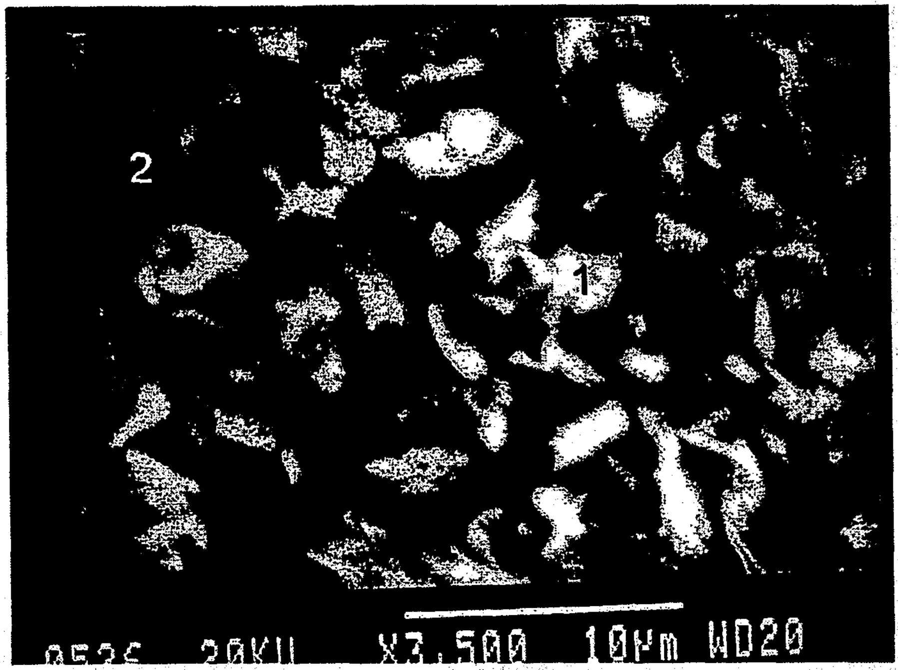


Fig. 43 - Backscattered electron micrograph of the residue from the leaching of 85 g/L of the April 97 Composite sample for 2 h at 150°C. 1- recrystallized $(Sb,As)_2O_3$, 2- chlorite and muscovite

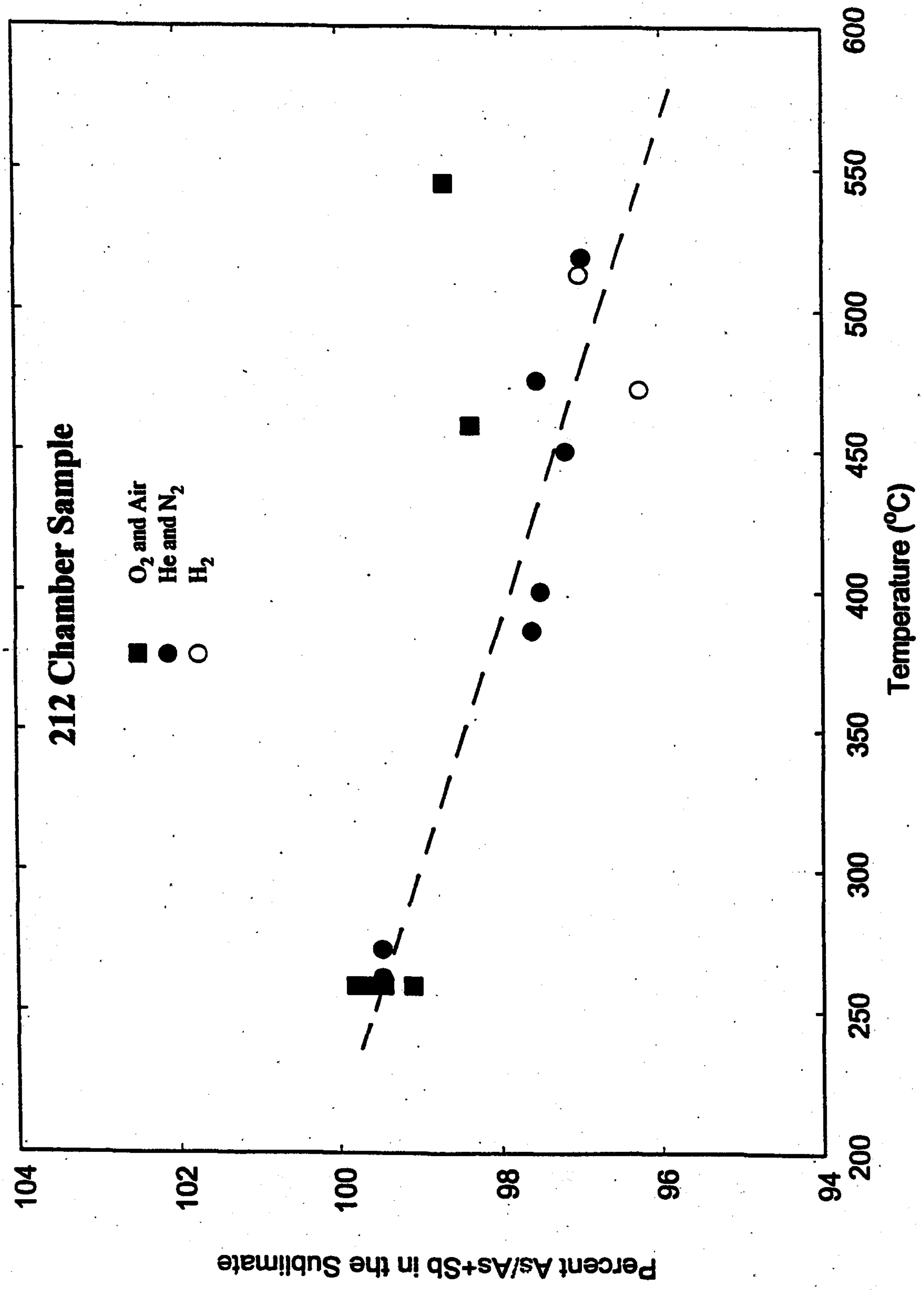


Fig. 44 - Effect of temperature and the sublimation atmosphere on the As/As+Sb ratio of the re-sublimed 212 Chamber sample.

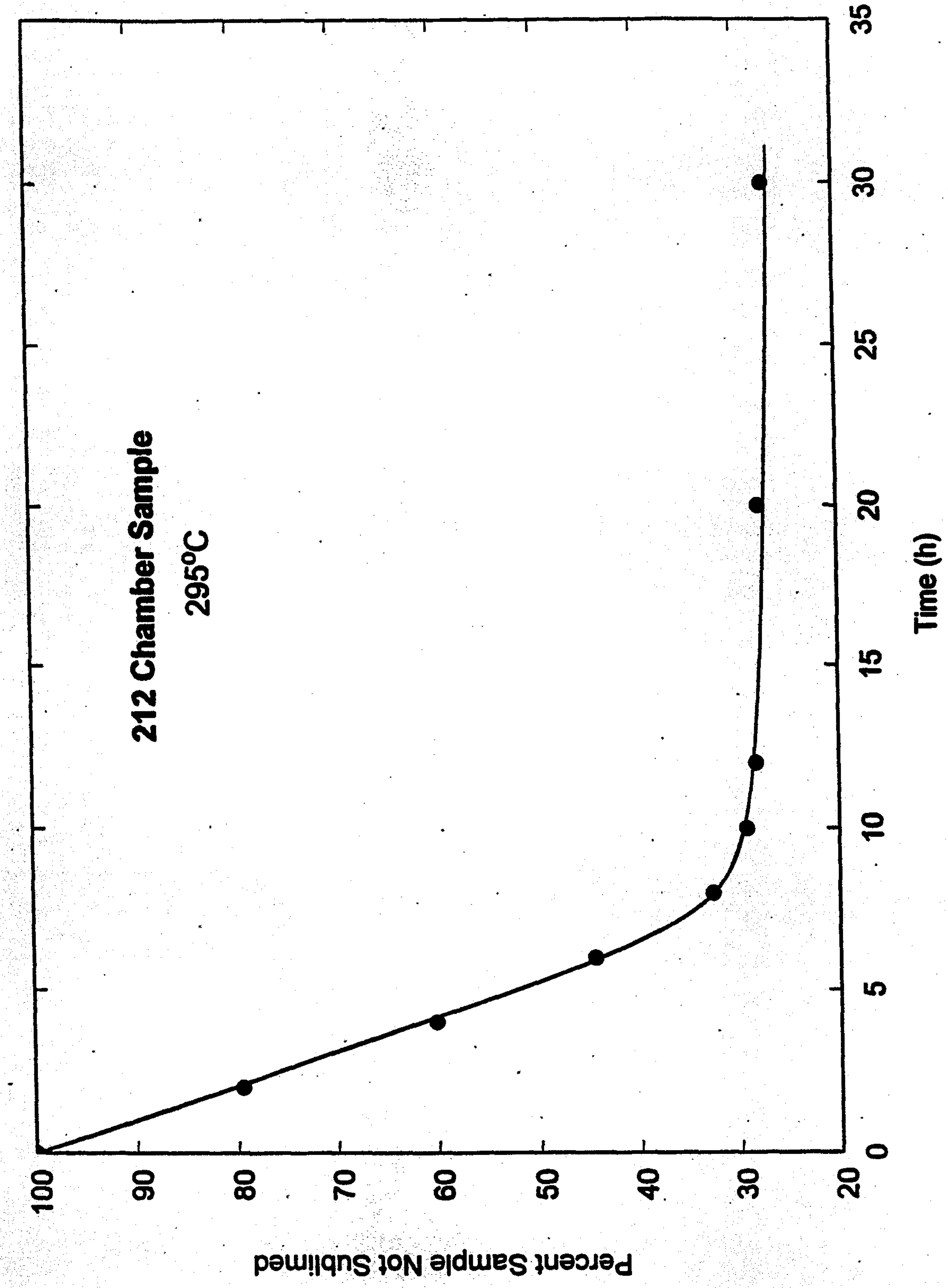


Fig. 45 - Extent of re-sublimation of the 212 Chamber sample as a function of heating time at 259°C.

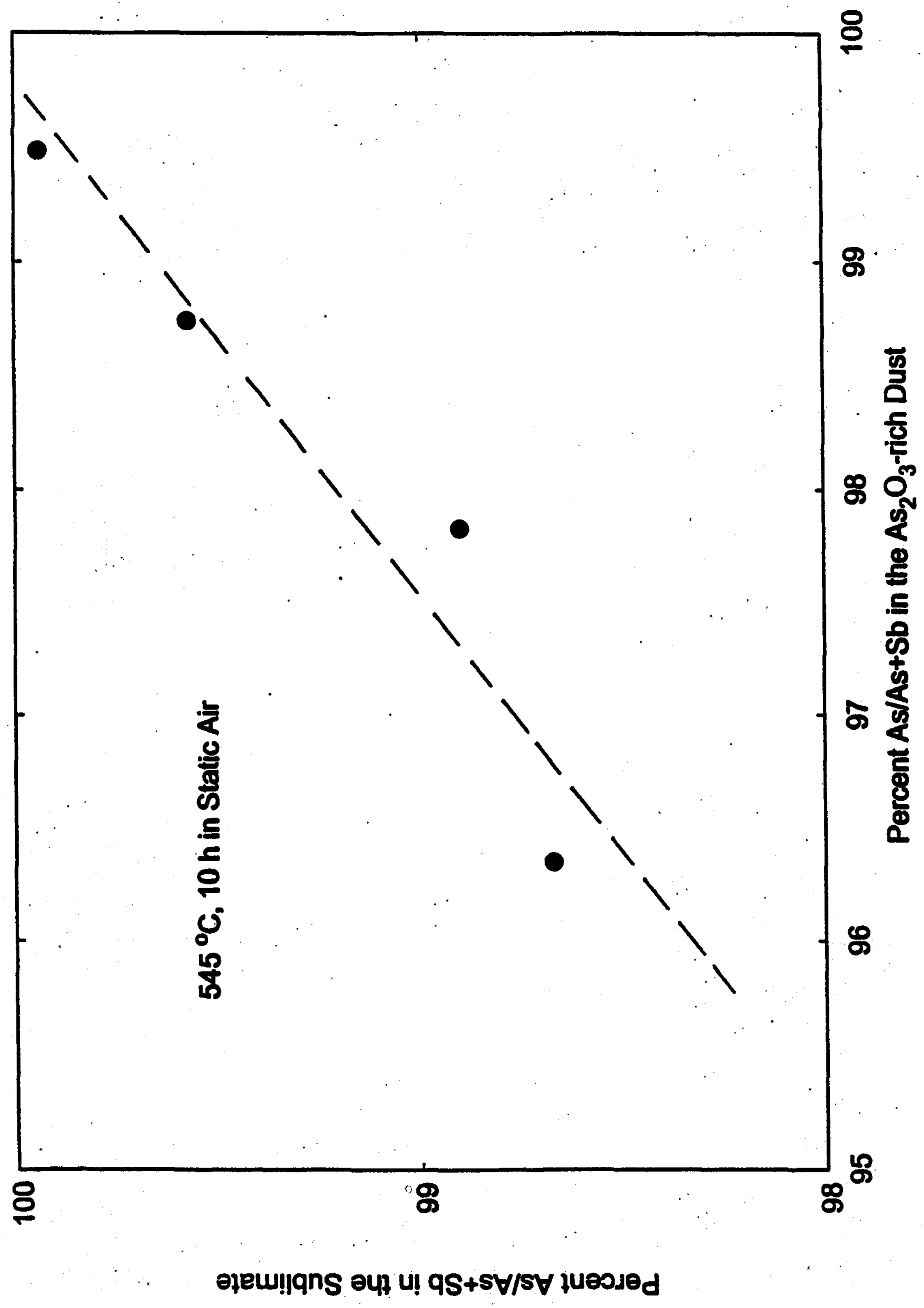


Fig. 46 - Relationship between the As/As+Sb percentage of the As_2O_3-rich dust and the As/As+Sb percentage of the re-sublimation product made at 545°C in air.

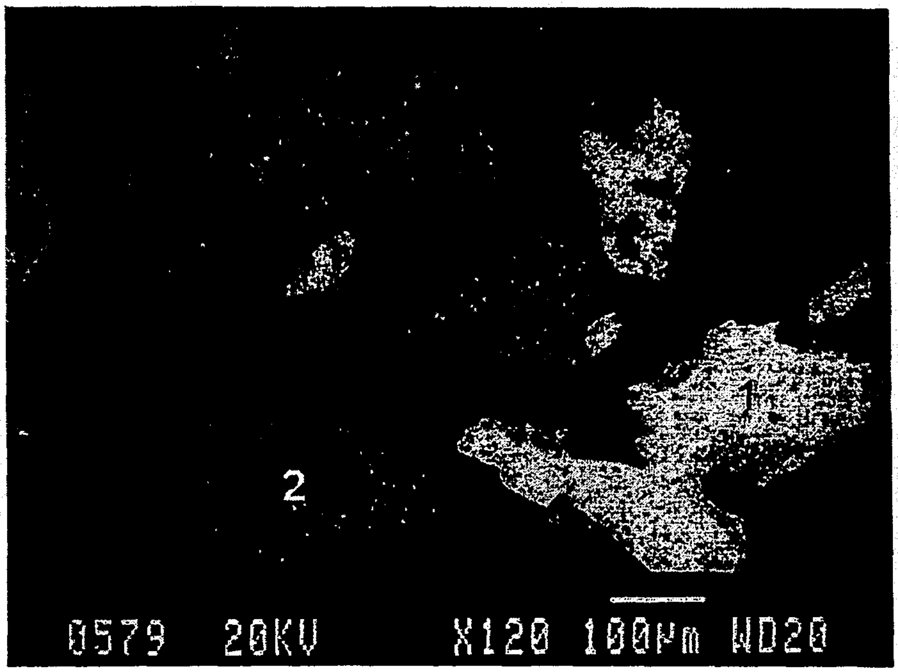


Fig. 47 - Backscattered electron micrograph showing the sublimation residue after heating the January 98 Composite sample at 545°C. 1- $(As,Sb)_2O_3$, 2- clusters of silicates and iron arsenate

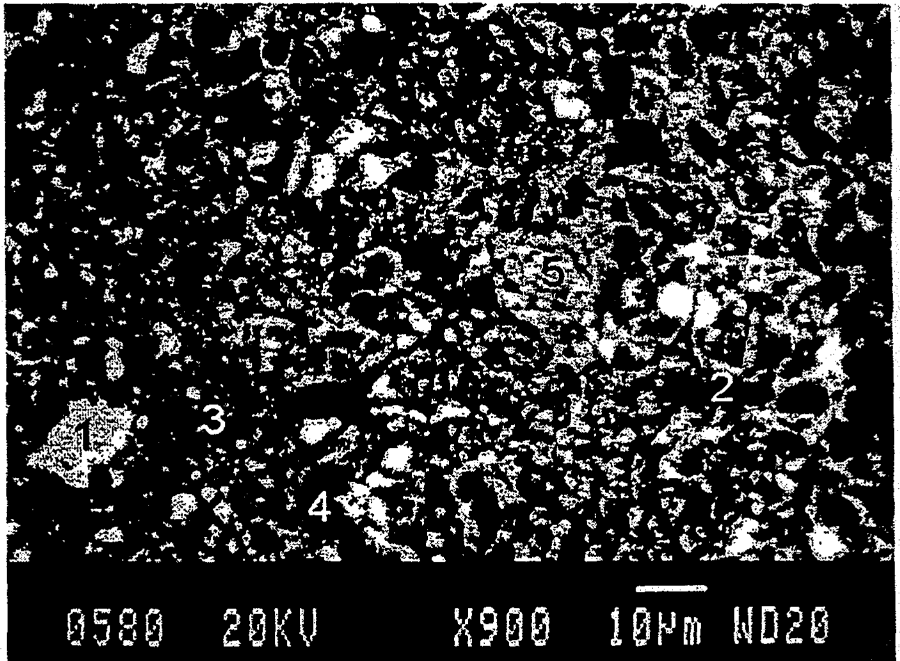


Fig. 48 - Backscattered electron micrograph showing the detailed texture of the agglomerates present in the sublimation residue from the January 98 Composite sample. 1- iron arsenate, 2- $CaSO_4$, 3- muscovite, 4- quartz, 5- mixture of iron arsenates and silicates, 6- $CaSO_4$

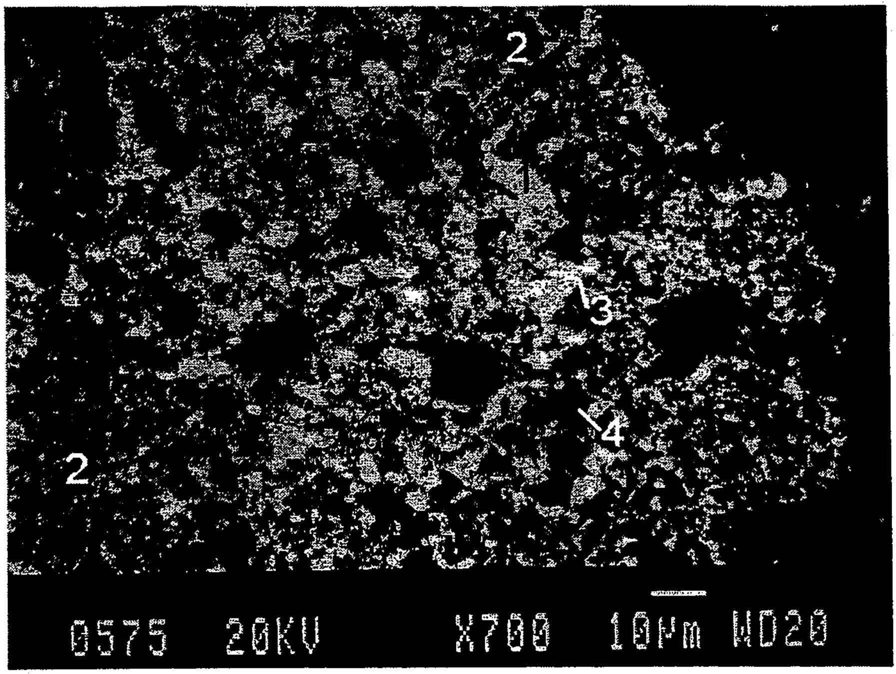


Fig. 49 - Backscattered electron micrograph of the sublimation residue from heating the April 97 Composite sample at 545°C. 1- iron arsenate, 2- muscovite, 3- iron arsenate-antimonate (bright rim), 4- quartz

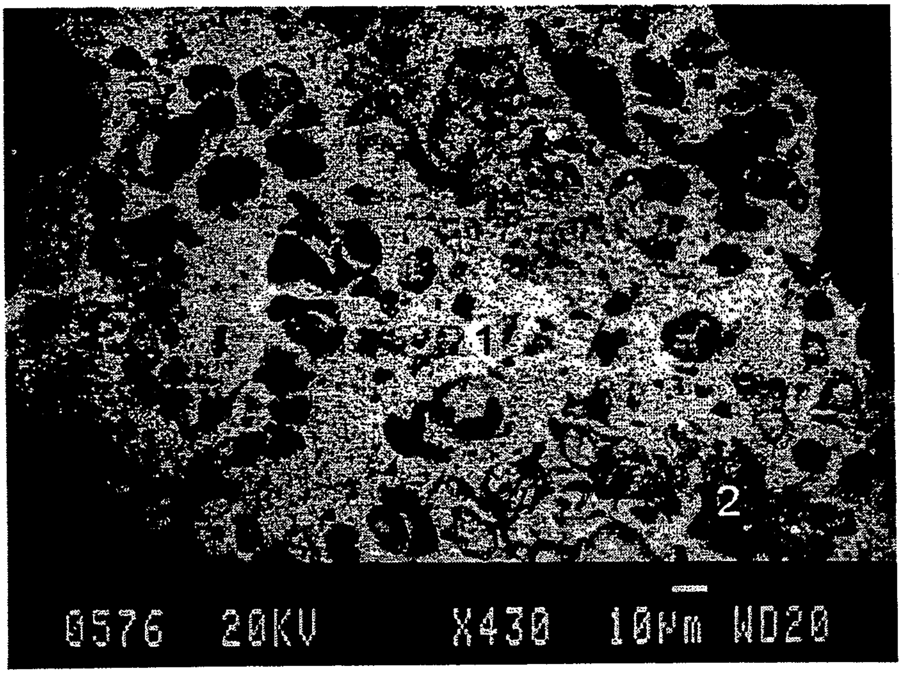


Fig. 50 - Backscattered electron micrograph illustrating the morphology of As_2O_3 in the sublimation residue from the heating of the April 97 Composite sample. 1- As_2O_3, 2- muscovite (grey)

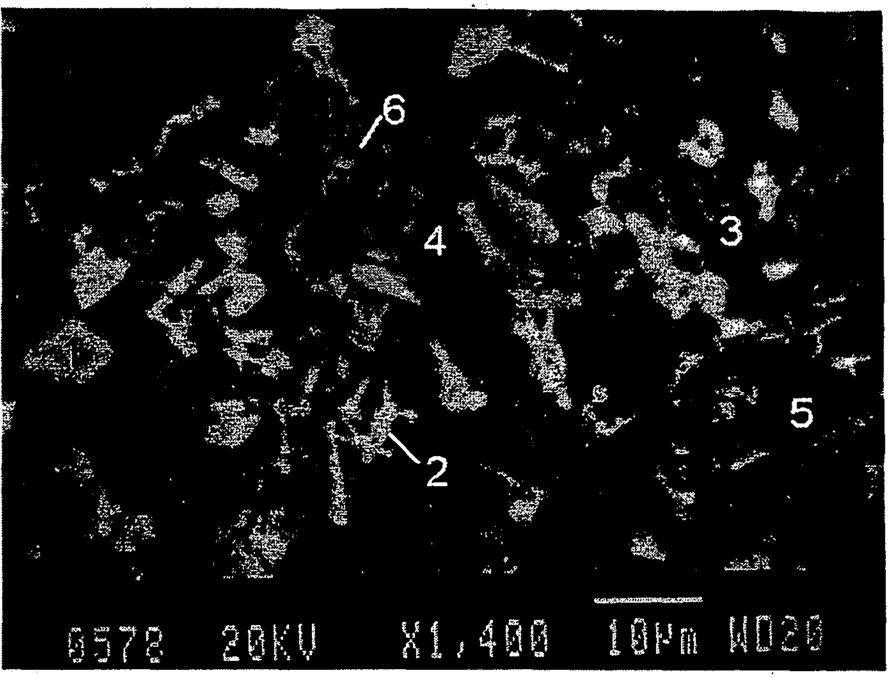


Fig. 51 - Backscattered electron micrograph of the sublimation residue from heating the 236 Chamber sample to 545 °C. 1- iron arsenate, 2-As_2O_3, 3- $CaSO_4$, 4- quartz, 5- chlorite, 6- muscovite

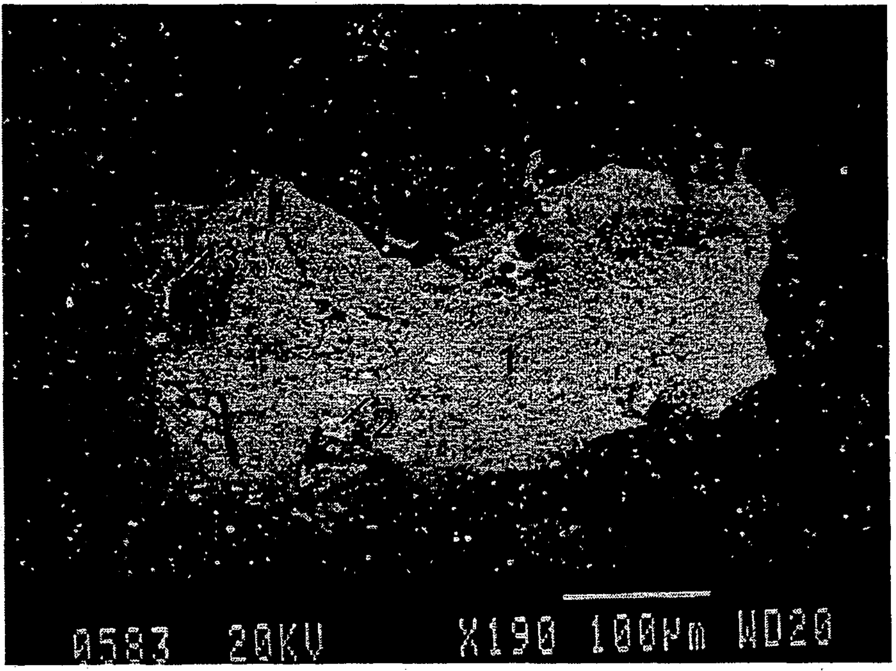


Fig. 52 - Backscattered electron micrograph of a large mass of arsenic oxide in the sublimation residue from heating the 212 Chamber sample to 610°C. 1- arsenic oxide, 2- iron arsenate, 3- silicates

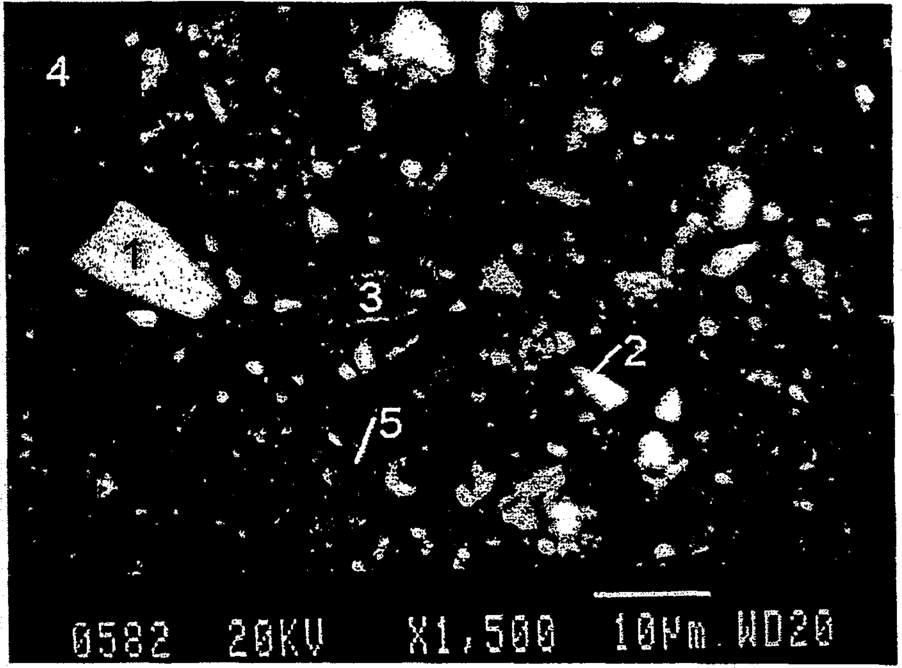


Fig. 53 - Backscattered electron micrograph showing a number of tiny particles in the sublimation residue from the heating of the 212 Chamber sample. 1- iron oxide, 2- iron arsenate, 3- Ca arsenate, 4- chlorite, 5- muscovite

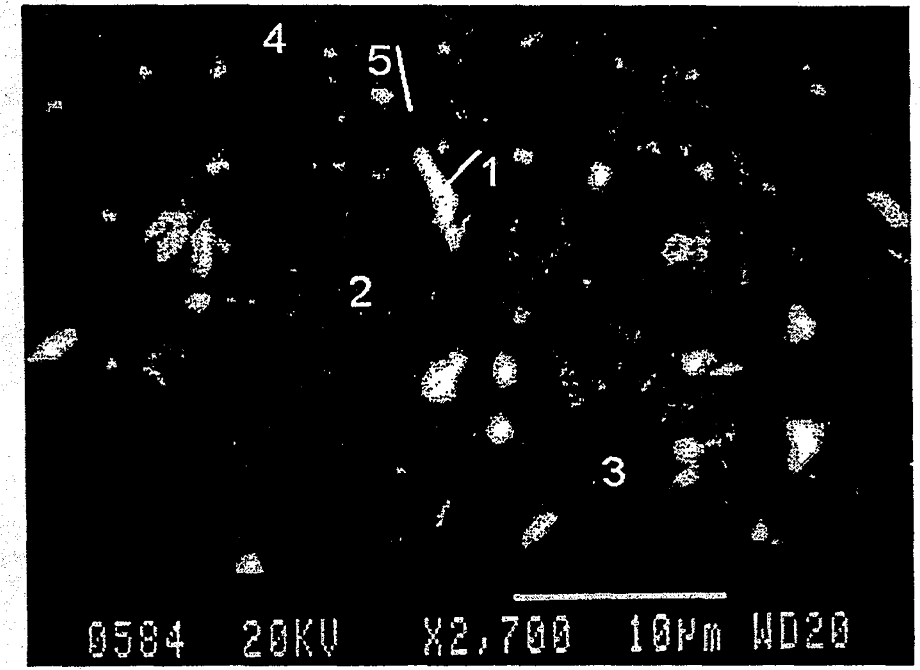
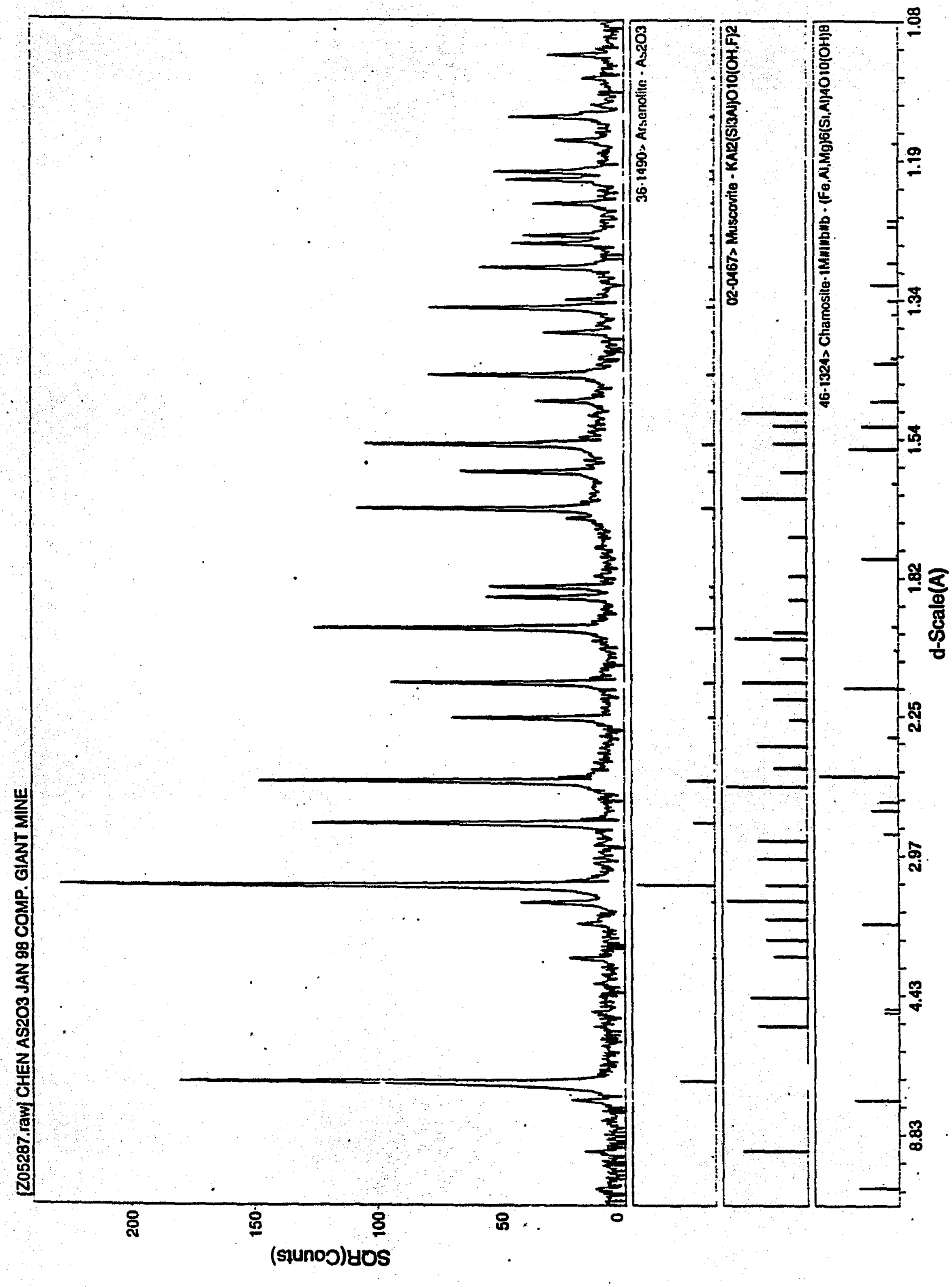


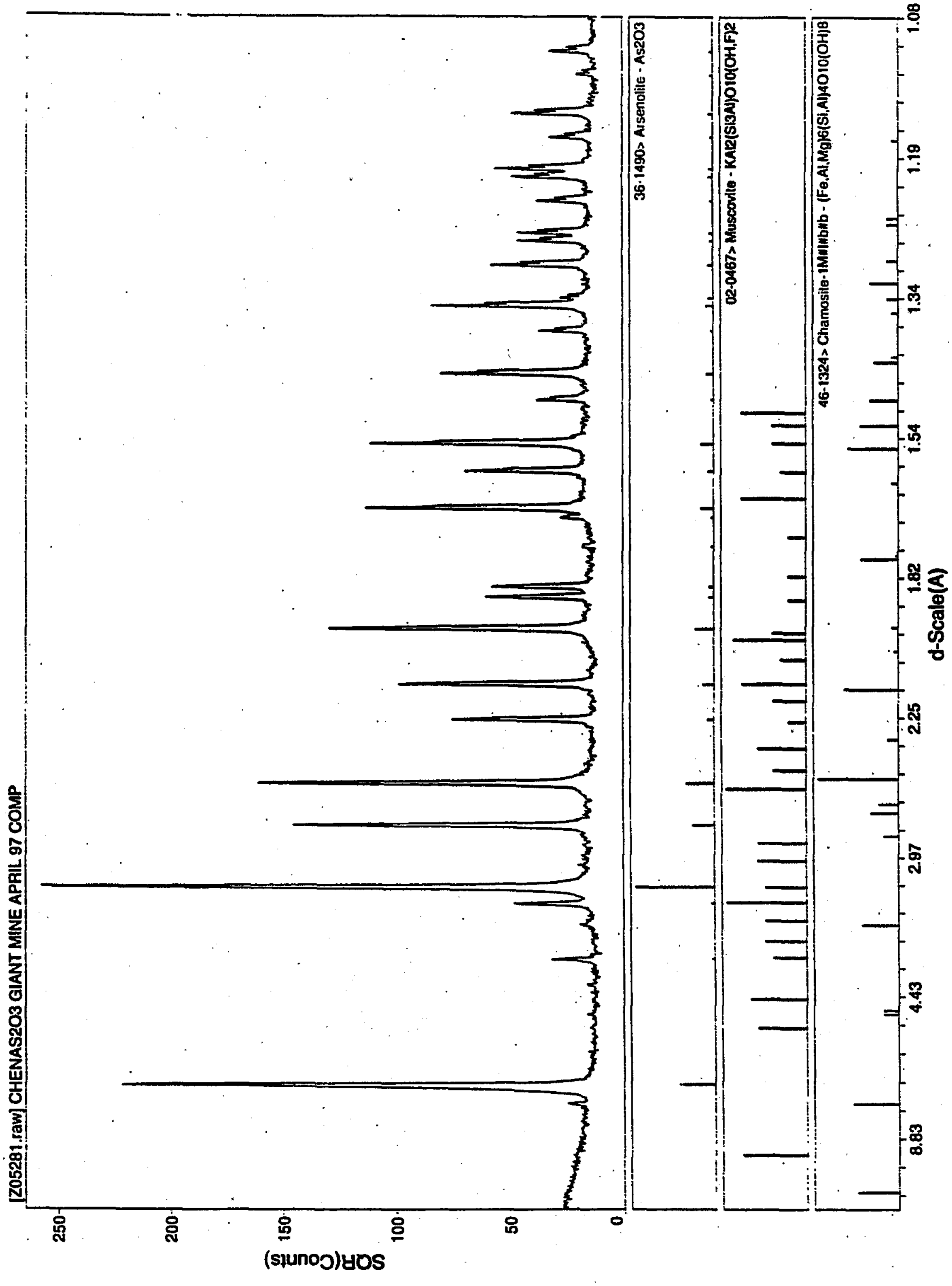
Fig. 54 - Backscattered electron micrograph showing the fine particles present in the sublimation residue from the heating of the 212 Chamber sample. 1- iron arsenate, 2-$CaSO_4$, 3- quartz, 4- chlorite, 5- muscovite

APPENDIX 1

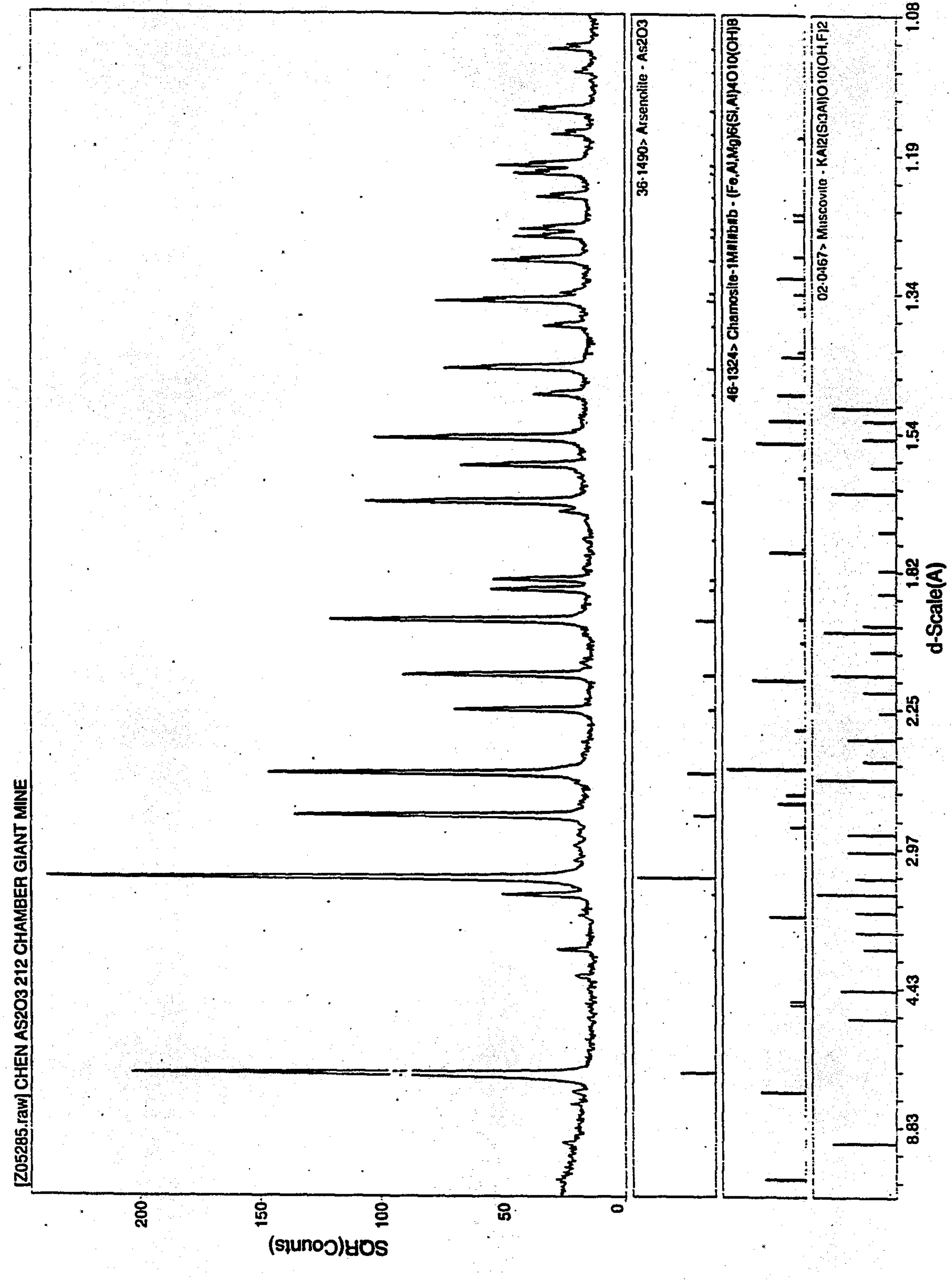
X-ray Diffraction Patterns of the Four Dust Samples

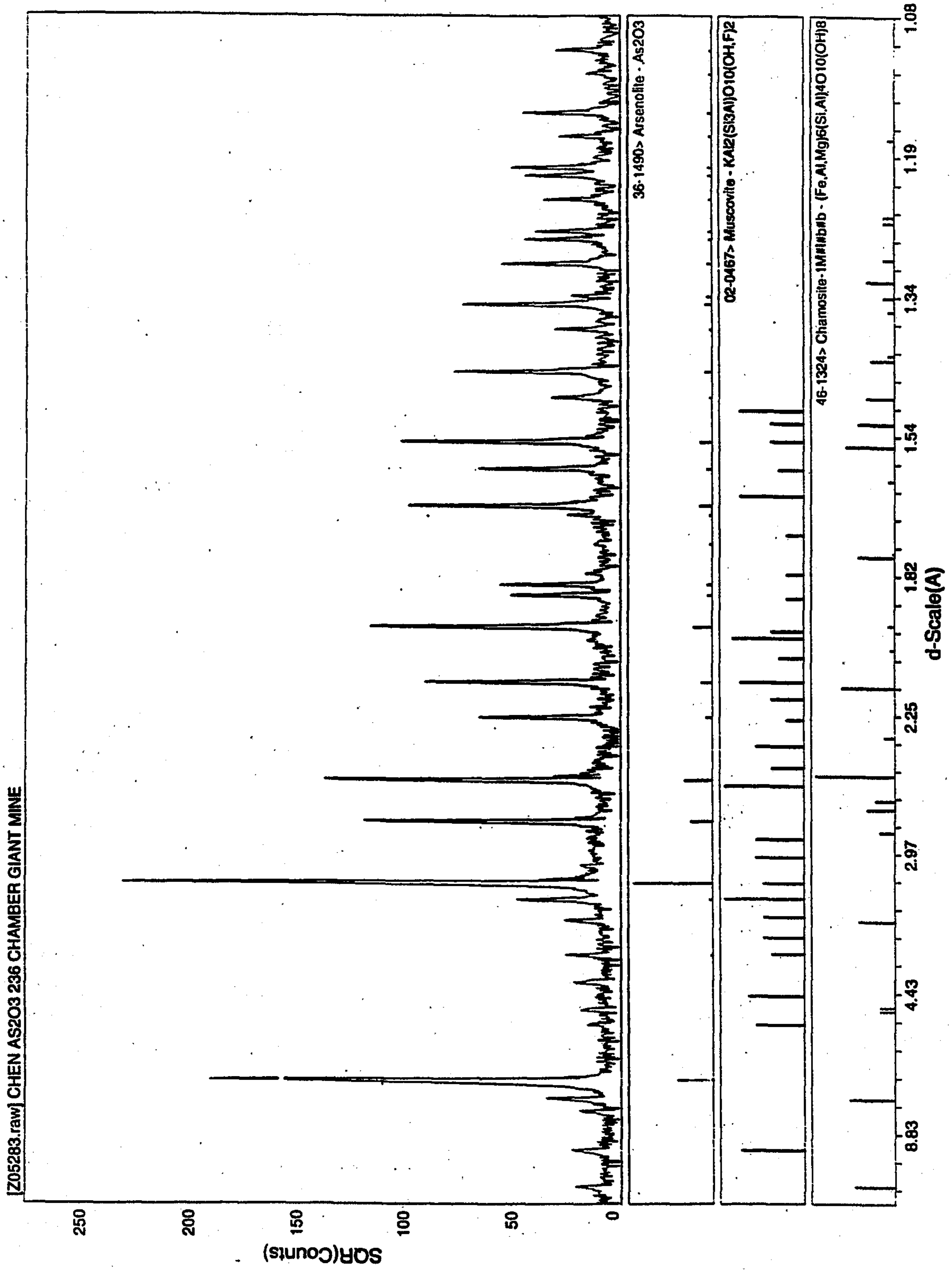

[Z05287.raw] CHEN AS2O3 JAN 98 COMP. GIANT MINE
SQR(Counts)
0
50
100
150
200
36-1490> Arsenolite - As2O3
02-0467> Muscovite - KAl2(Si3Al)O10(OH,F)2
46-1324> Chamosite-1M#Ib#b - (Fe,Al,Mg)6(Si,Al)4O10(OH)8
d-Scale(A)
8.83
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.08

PROTECTED BUSINESS INFORMATION



CANMET


[Z05285.raw] CHEN AS2O3 212 CHAMBER GIANT MINE
SQR(Counts)
0
50
100
150
200
36-1490> Arsenolite - As2O3
46-1324> Chamosite-1M#IIb#b - (Fe,Al,Mg)6(Si,Al)4O10(OH)8
02-0467> Muscovite - KAl2(Si3Al)O10(OH,F)2
8.83
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.08
d-Scale(A)


[Z05283.raw] CHEN AS2O3 236 CHAMBER GIANT MINE
36-1490> Arsenolite - As2O3
02-0467> Muscovite - KAl2(Si3Al)O10(OH,F)2
46-1324> Chamosite-1M#I#b#b - (Fe,Al,Mg)6(Si,Al)4O10(OH)8
SQR(Counts)
0
50
100
150
200
250
d-Scale(A)
8.83
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.08

APPENDIX 2

Detailed Electron Microprobe Analyses of the Arsenic Carriers in the January 98 Composite Sample

As_2O_3 Phase

```
Nov 17 14:59 1998  /tmp/x_text.pri Page 1


Weight percent        Group : CHEN            Sample : As2O3-Giant      Page 1

Element    64        65        66        67        68        73        74        77
Sb        0.565     0.473     0.749     0.391     0.252     0.824       -         -
As       78.306    81.706    77.828    77.738    71.230    70.437    76.266    78.963
Fe        0.148     0.087     0.154     0.233     0.066     0.459     0.135     0.136
Pb          -         -       0.072     0.072     0.066     0.020     0.021     0.012
S           -         -         -         -         -         -         -         -
Cr          -         -         -         -         -         -         -         -
O        20.981    17.734    21.197    21.566    28.386    28.260    23.578    20.889
Ca          -         -         -         -         -         -         -         -
Bi          -         -         -         -         -         -         -         -
Si          -         -         -         -         -         -         -         -
-------------------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent        Group : CHEN            Sample : As2O3-Giant

Element    79        80        81        82        93        94        95        96
Sb        0.219     1.236       -       0.249     0.068     0.185     0.096     0.137
As       74.593    78.837    74.456    74.419    71.324    76.143    80.717    72.961
Fe        0.079     0.063     0.058     0.040     0.592     0.083     0.096     0.129
Pb          -       0.049       -         -         -         -         -         -
S           -         -         -         -         -         -         -         -
Cr          -         -         -         -         -         -         -         -
O        25.109    19.815    25.486    25.292    28.016    23.589    19.091    26.773
Ca          -         -         -         -         -         -         -         -
Bi          -         -         -         -         -         -         -         -
Si          -         -         -         -         -         -         -         -
-------------------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent        Group : CHEN            Sample : As2O3-Giant

Element    98        99        100       101       103       104       106       107
Sb        1.890     2.189     1.708     4.028     0.142     0.485     0.358     0.004
As       74.045    67.162    69.288    63.048    79.110    78.778    80.137    81.485
Fe        0.104     0.076     0.118     0.295     0.010     0.096     0.091     0.016
Pb          -         -       0.109     0.076     0.076       -       0.016     0.003
S           -         -         -         -         -         -         -         -
Cr          -         -         -         -         -         -         -         -
O        23.961    30.573    28.777    32.553    20.662    20.641    19.398    18.492
Ca          -         -         -         -         -         -         -         -
Bi          -         -         -         -         -         -         -         -
Si          -         -         -         -         -         -         -         -
-------------------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
```

```
Nov 17 14:59 1998  /tmp/x_text.pri Page 2


Weight percent      Group : CHEN            Sample : As2O3-Giant      Page 2

Element  108       109       110       111       112       113       114       115
Sb        5.244     4.470     4.815     4.700     4.220     5.010     5.383     0.093
As       70.591    74.667    66.640    73.101    76.093    68.165    75.553    73.885
Fe        0.321     0.113     2.015     0.103     0.075     0.078     0.164     0.051
Pb        1.886     0.040     0.080      -         -         -        0.022      -
S          -         -         -         -         -         -         -         -
Cr         -         -         -         -         -         -         -         -
O        21.958    20.710    26.450    22.096    19.612    26.747    18.878    25.971
Ca         -         -         -         -         -         -         -         -
Bi         -         -         -         -         -         -         -         -
Si         -         -         -         -         -         -         -         -
-------------------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent      Group : CHEN            Sample : As2O3-Giant

Element  116       117       118       119       120       121       122
Sb        0.125     0.190     0.204     0.098     0.086     0.229     0.109
As       77.097    82.115    79.724    75.853    75.723    74.496    73.427
Fe        0.057     0.065     0.069     0.018     0.066     0.263     0.066
Pb         -         -         -        0.026     0.026      -         -
S          -         -         -         -         -         -         -
Cr         -         -         -         -         -         -         -
O        22.721    17.630    20.003    24.005    24.099    25.012    26.398
Ca         -         -         -         -         -         -         -
Bi         -         -         -         -         -         -         -
Si         -         -         -         -         -         -         -
---------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent      Group : CHEN            Sample : As2O3-Giant

Element| Minimum  Maximum  Average    Sigma
Sb     |    -       5.383    1.313    1.843
As     |  63.048   82.115   75.028    4.449
Fe     |   0.010    2.015    0.177    0.324
Pb     |    -       1.886    0.069    0.300
S      |    -        -        -        -
Cr     |    -        -        -        -
O      |  17.630   32.553   23.413    3.7[illegible]
Ca          -        -        -        -
Bi     |    -        -        -        -
Si     |    -        -        -        -
--------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 39
```

$(Sb,As)_2O_3$ Phase

```
Nov 17 15:05 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN            Sample : As2O3-Giant       Page 1

Element   83       84       85       86       87       88       89       90
Sb       43.796   43.086   45.125   46.538   44.369   47.773   45.406   45.197
As       31.385   32.624   35.882   38.956   36.116   37.141   37.692   35.961
Fe        0.039    0.019    0.042    0.088    0.043    0.070    0.049    0.022
Pb        0.066      -        -        -        -        -        -        -
S           -        -        -        -        -        -        -        -
Cr          -        -        -        -        -        -        -        -
O        24.714   24.271   18.951   14.418   19.472   15.016   16.853   18.820
Ca          -        -        -        -        -        -        -        -
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
-------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN            Sample : As2O3-Giant

Element   91       92     | Minimum  Maximum  Average    Sigma
Sb       44.779   40.505  |  40.505   47.773   44.657    1.968
As       36.910   28.946  |  28.946   38.956   35.161    3.148
Fe        0.076    0.029  |   0.019    0.088    0.048    0.023
Pb          -        -    |     -      0.066    0.007    0.021
S           -        -    |     -        -        -        -
Cr          -        -    |     -        -        -        -
O        18.235   30.520  |  14.418   30.520   20.127    4.975
Ca          -        -    |     -        -        -        -
Bi          -        -    |     -        -        -        -
Si          -        -    |     -        -        -        -
-------------------------------------------------------------
Total   100.000  100.000  | 100.000  100.000  100.000    0.000
No. of data 10
```

As-bearing Iron Arsenate

```
Nov 17 15:02 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN              Sample : As2O3-Giant       Page 1

Element   70       71       72       211      212      213      214      215
Sb        1.154    1.244    1.217    2.103    2.065    1.623    1.912    1.831
As        3.721    3.266    3.159    5.417    5.522    5.184    5.871    4.972
Fe       61.043   60.595   61.119   57.519   58.305   58.833   58.428   57.798
Pb        0.097    0.068    0.070    0.148    0.073    0.152    0.056    0.097
S           -        -        -      0.047    0.051    0.075    0.057    0.070
Cr          -        -        -        -        -        -        -        -
O        33.985   34.827   34.435   34.766   33.984   34.133   33.676   35.232
Ca          -        -        -        -        -        -        -        -
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element  216    | Minimum  Maximum  Average    Sigma
Sb        1.889 |  1.154    2.103    1.671    0.376
As        5.005 |  3.159    5.871    4.680    1.022
Fe       58.385 | 57.519   61.119   59.114    1.412
Pb        0.179 |  0.056    0.179    0.104    0.044
S         0.047 |    -      0.075    0.039    0.030
Cr          -   |    -        -        -        -
O        34.495 | 33.676   35.232   34.393    0.495
Ca          -   |    -        -        -        -
Bi          -   |    -        -        -        -
Si          -   |    -        -        -        -
-------------------------------------------------------
Total   100.000 | 100.000  100.000  100.000      -
No. of data 9   |
```

Iron Arsenate Phase

```
Nov 17 15:10 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN             Sample : As2O3-Giant       Page 1

Element  218       219       220       221       222       223       224       225
Sb         0.065     0.146     0.332     0.239     0.224     0.382     0.215     0.173
As        17.388    17.115    12.752    15.636    17.843    12.973    15.710    16.825
Fe         9.849    10.061     6.943    14.154     7.959     6.307     9.540    10.100
Pb         0.057     0.137     0.098     0.130     0.081     0.066     0.165     0.190
S          4.824     7.413     2.976     4.226     4.195     2.652     3.545     5.126
Cr         -         -         -         -         -         -         -         -
O         67.752    60.667    76.774    65.460    69.639    77.425    70.558    65.299
Ca         0.065     4.392     0.125     0.082     0.059     0.195     0.260     2.233
Bi         -         0.069     -         0.073     -         -         0.007     0.054
Si         -         -         -         -         -         -         -         -
---------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
Weight percent       Group : CHEN             Sample : As2O3-Giant

Element  226       227       228       229       230       231       232       233
Sb         0.271     0.406     0.114     0.317     0.215     0.209     0.231     0.876
As        16.656    20.243    18.526    21.637    14.585    12.066    17.371     7.924
Fe        10.111     9.686     8.624     2.193     8.167     8.706     1.781    38.332
Pb         0.101     0.099     0.076     0.090     0.042     0.066     0.108     0.133
S          4.689     4.857     4.692     0.997     3.423     2.919     0.439     0.236
Cr         -         -         -         -         -         -         -         -
O         68.080    64.606    66.763    74.566    73.347    75.803    77.456    52.441
Ca         0.045     0.052     1.152     0.142     0.176     0.204     2.581     0.058
Bi         0.047     0.051     0.053     0.058     0.045     0.027     0.033     -
Si         -         -         -         -         -         -         -         -
---------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000


Weight percent       Group : CHEN             Sample : As2O3-Giant

Element| Minimum   Maximum   Average     Sigma
Sb     |   0.065     0.876     0.276     0.184
As     |   7.924    21.637    15.953     3.350
Fe     |   1.781    38.332    10.157     8.093
Pb     |   0.042     0.190     0.102     0.040
S      |   0.236     7.413     3.576     1.878
Cr     |   -         -         -         -
O      |  52.441    77.456    69.165     6.822
Ca     |   0.045     4.392     0.739     1.259
Bi     |   -         0.073     0.032     0.027
Si     |   -         -         -         -
---------------------------------------------
Total  | 100.000   100.000   100.000     0.000
```

APPENDIX 3

Detailed Electron Microprobe Analyses of the Arsenic Carriers in the April 97 Composite Sample

As_2O_3 Phase

```
Nov 17 15:15 1998  /tmp/x_text.pri Page 1

Weight percent       Group : CHEN              Sample : As2O3-Giant       Page 1

Element  124      128      132      135      138      181      183      184
Sb         0.314    0.283    0.043      -        -        0.432    0.545    0.288
As        71.451   76.482   78.023   78.387   79.112   78.019   77.481   78.598
Fe         0.056    0.093    0.353    0.051    0.069    0.122    0.221    0.320
Pb           -        -        -      0.066      -      0.041    0.076    0.064
S            -      0.039    0.021    0.014    0.017    0.015    0.057    0.086
Cr           -        -        -        -        -        -        -        -
O         28.151   23.089   21.560   21.474   20.802   21.371   21.620   20.554
Ca         0.028    0.014      -      0.008      -        -        -      0.090
Bi           -        -        -        -        -        -        -        -
Si           -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total    100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element  185      186      187      188      190      191      192      194
Sb         0.257    0.323    0.523    0.366    0.287    0.410    0.531      -
As        73.244   72.670   73.804   78.201   82.705   80.481   74.779   73.096
Fe         0.526    0.426    0.317    0.190    0.030    0.028    0.313    0.184
Pb         0.070    0.170    0.088    0.114      -      0.042    0.084    0.016
S          0.040    0.114    0.112    0.005    0.003    0.009    0.025    0.069
Cr           -        -        -        -        -        -        -        -
O         25.776   26.127   25.055   21.086   16.975   19.030   24.229   26.442
Ca         0.087    0.170    0.101    0.038      -        -      0.039    0.193
Bi           -        -        -        -        -        -        -        -
Si           -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total    100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element  195      196      197      204      205      207      209      210
Sb           -      0.006    0.292    0.110      -      0.345    0.013    0.333
As        76.555   78.131   75.405   78.008   71.834   73.841   77.855   72.840
Fe         0.351    0.037    0.091    0.033    0.526    0.075    0.033    0.075
Pb         0.004    0.066    0.029    0.027      -      0.012      -      0.043
S          0.069    0.018      -        -      0.181    0.019    0.016    0.002
Cr           -        -        -        -        -        -        -        -
O         22.861   21.695   24.178   21.822   27.329   25.708   22.070   26.692
Ca         0.160    0.047    0.005      -      0.130      -      0.013    0.015
Bi           -        -        -        -        -        -        -        -
Si           -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total    100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000
```

```
Nov 17 15:15 1998  /tmp/x_text.pri Page 2


Weight percent       Group : CHEN             Sample : As2O3-Giant       Page 2

Element| Minimum  Maximum  Average    Sigma
Sb     |    -       0.545    0.238    0.190
As     |  71.451   82.705   76.292    2.944
Fe     |   0.028    0.526    0.188    0.163
Pb     |    -       0.170    0.042    0.044
S      |    -       0.181    0.039    0.046
Cr     |    -        -        -        -
O      |  16.975   28.151   23.154    2.810
Ca     |    -       0.193    0.047    0.062
Bi     |    -        -        -        -
Si     |    -        -        -        -
-----------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 24
```

```
Nov 17 15:18 1998  /tmp/x_text.pri Page 1
```

Sb-Rich As_2O_3 Phase

```
Weight percent       Group : CHEN             Sample : As2O3-Giant       Page 1

Element  126      127      130      131      198      199      200      201
Sb       12.145   15.091   14.693   14.919   13.316   12.794   13.121   12.318
As       60.555   60.291   57.803   50.848   59.585   54.435   68.707   64.521
Fe        0.885    0.107    0.075    1.624    0.117    0.336    0.107    0.181
Pb        0.027     -        -       0.158    0.029    0.114    0.063    0.021
S         0.063    0.025    0.018    0.217     -       0.067    0.009    0.008
Cr         -        -        -        -        -        -        -        -
O        26.299   24.472   27.411   31.628   26.936   32.166   17.993   22.610
Ca        0.026    0.014     -       0.606    0.017    0.088     -       0.304
Bi         -        -        -        -        -        -        -       0.037
Si         -        -        -        -        -        -        -        -
-------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN             Sample : As2O3-Giant

Element| Minimum  Maximum  Average    Sigma
Sb     |  12.145   15.091   13.550    1.187
As     |  50.848   68.707   59.593    5.543
Fe     |   0.075    1.624    0.429    0.552
Pb     |    -       0.158    0.052    0.057
S      |    -       0.217    0.051    0.072
Cr     |    -        -        -        -
O      |  17.993   32.166   26.189    4.634
Ca     |    -       0.606    0.132    0.217
Bi     |    -       0.037    0.005    0.013
Si     |    -        -        -        -
-----------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 8
```

$(Sb,As)_2O_3$

```
Nov 17 15:26 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN            Sample : As2O3-Giant      Page 1

Element  140      141      142      143      144      145      146      147
Sb       45.633   43.482   43.907   45.878   42.855   45.013   43.809   44.892
As       37.987   36.043   32.523   35.877   36.761   39.460   39.234   39.160
Fe        0.221    0.207    0.625    0.232    0.154    0.141    0.132    0.153
Pb        0.304    0.312    0.285    0.344    0.058    0.022    0.077    0.022
S         0.879    0.967    0.875    0.623    0.727    0.798    0.801    0.898
Cr         -        -        -        -        -        -        -        -
O        14.866   18.931   21.714   16.942   19.445   14.566   15.947   14.875
Ca        0.110    0.058    0.071    0.104     -        -        -        -
Bi         -        -        -        -        -        -        -        -
Si         -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN            Sample : As2O3-Giant

Element  148      149      150      151      152      153      154      155
Sb       44.593   46.242   45.309   43.101   45.296   46.099   44.308   43.363
As       36.261   34.370   37.696   35.448   42.452   41.041   35.134   35.569
Fe        0.186    0.843    0.158    0.081    0.090    0.079    0.128    0.075
Pb        0.041    0.004    0.021    0.008    0.028    0.028    0.015    0.013
S         0.918    0.747    1.011    0.925    0.728    0.807    1.023    0.868
Cr         -        -        -        -        -        -        -        -
O        18.001   17.794   15.805   20.437   11.406   11.946   19.392   20.112
Ca         -        -        -        -        -        -        -        -
Bi         -        -        -        -        -        -        -        -
Si         -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN            Sample : As2O3-Giant

Element  156      157      158      159      160      161      162      163
Sb       42.547   42.430   44.359   44.224   46.634   45.104   43.136   44.154
As       35.744   36.355   36.134   32.764   37.442   34.918   33.076   33.840
Fe        0.073    0.084    0.040    0.131    0.135    0.068    0.046    0.052
Pb        0.013    0.005    0.018    0.051    0.015    0.087    0.074    0.142
S         0.785    0.709    0.872    0.851    0.589    1.239    0.947    0.962
Cr         -        -        -        -        -        -        -        -
O        20.838   20.417   18.577   21.979   15.185   18.584   22.721   20.850
Ca         -        -        -        -        -        -        -        -
Bi         -        -        -        -        -        -        -        -
Si         -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000
```

```
Nov 17 15:26 1998  /tmp/x_text.pri Page 2


Weight percent       Group : CHEN             Sample : As2O3-Giant       Page 2

Element  164      165      166      167      168      169      170      171
Sb       44.315   43.796   43.124   45.819   46.776   44.387   44.277   46.770
As       36.273   33.075   30.711   41.406   35.104   35.265   32.131   30.944
Fe        0.046    0.072    0.057    0.079    0.067     -       0.020    0.055
Pb         -       0.035    0.018    0.063    0.016     -        -       0.080
S         0.984    0.706    0.838    0.780    0.502    0.962    1.048    0.618
Cr         -        -        -        -        -        -        -        -
O        18.382   22.316   25.252   11.853   17.535   19.386   22.524   21.533
Ca         -        -        -        -        -        -        -        -
Bi         -        -        -        -        -        -        -        -
Si         -        -        -        -        -        -        -        -
-------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000


Weight percent       Group : CHEN             Sample : As2O3-Giant

Element| Minimum  Maximum  Average    Sigma
Sb     |  42.430   46.776   44.551    1.243
As     |  30.711   42.452   35.944    2.883
Fe     |    -       0.843    0.142    0.168
Pb     |    -       0.344    0.069    0.099
S      |   0.502    1.239    0.843    0.152
Cr     |    -        -        -         -
O      |  11.406   25.252   18.441    3.396
Ca     |    -       0.110    0.011    0.030
Bi     |    -        -        -         -
Si     |    -        -        -         -
-------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 32
```

```
Nov 17 15:23 1998  /tmp/x_text.pri Page 1
```

As-, Sb-bearing Iron Oxide.

```
Weight percent      Group : CHEN          Sample : As2O3-Giant      Page 1

Element  133      206      240      241    | Minimum  Maximum  Average    Sigma
Sb        2.075    0.588    9.285    8.889 |   0.588    9.285    5.209    4.521
As        7.984    6.690   10.017   11.481 |   6.690   11.481    9.043    2.125
Fe       49.972   55.313   29.040   18.359 |  18.359   55.313   38.171   17.407
Pb        0.054      -      0.176    0.254 |     -      0.254    0.121    0.115
S         0.043    0.316    1.554    1.518 |   0.043    1.554    0.858    0.791
Cr          -        -        -        -   |     -        -        -        -
O        39.872   37.093   49.031   57.089 |  37.093   57.089   45.771    9.107
Ca          -        -      0.897    2.405 |     -      2.405    0.826    1.135
Bi          -        -        -      0.005 |     -      0.005    0.001    0.002
Si          -        -        -        -   |     -        -        -        -
---------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000 | 100.000  100.000  100.000    0.000
No. of data 4
```

```
Nov 17 15:36 1998  /tmp/x_text.pri Page 1
```

Ca Arsenate-Sulphate Phase

```
Weight percent      Group : CHEN              Sample : As2O3-Giant     Page 1

Element  178      179      180      239     | Minimum  Maximum  Average   Sigma
Sb      17.191   13.102   20.287   11.158   |  11.158   20.287   15.434   4.097
As       8.350    8.188    9.579    7.731   |   7.731    9.579    8.462   0.789
Fe       1.918    2.465    2.062    2.550   |   1.918    2.550    2.249   0.306
Pb       0.160    0.144    0.158    0.127   |   0.127    0.160    0.147   0.015
S        8.780    9.642    7.416    9.895   |   7.416    9.895    8.933   1.118
Cr         -        -        -        -     |     -        -        -       -
O       52.304   54.351   50.274   56.274   |  50.274   56.274   53.301   2.588
Ca      11.297   12.108   10.224   12.265   |  10.224   12.265   11.474   0.935
Bi         -        -        -        -     |     -        -        -       -
Si         -        -        -        -     |     -        -        -       -
-------------------------------------------------------------------------------
Total  100.000  100.000  100.000  100.000   | 100.000  100.000  100.000     -
No. of data 4
```

```
Nov 17 15:40 1998  /tmp/x_text.pri Page 1
```

Calcium Oxide Phase

```
Weight percent      Group : CHEN              Sample : As2O3-Giant     Page 1

Element  176      177      235      236     | Minimum  Maximum  Average   Sigma
Sb       0.575    0.565    0.256    0.264   |   0.256    0.575    0.415   0.179
As       1.263    1.854    0.242    0.375   |   0.242    1.854    0.933   0.763
Fe       5.290    5.363    6.051    5.734   |   5.290    6.051    5.609   0.353
Pb         -        -        -      0.002   |     -      0.002    0.001   0.001
S        0.650    0.803    0.437    0.205   |   0.205    0.803    0.524   0.260
Cr         -        -        -        -     |     -        -        -       -
O       74.541   73.147   72.678   73.356   |  72.678   74.541   73.431   0.793
Ca      17.681   18.268   20.330   20.064   |  17.681   20.330   19.086   1.310
Bi         -        -      0.006      -     |     -      0.006    0.002   0.003
Si         -        -        -        -     |     -        -        -       -
-------------------------------------------------------------------------------
Total  100.000  100.000  100.000  100.000   | 100.000  100.000  100.000     -
No. of data 4
```

APPENDIX 4

Detailed Electron Microprobe Analyses of the Arsenic Carriers in the 212 Chamber Sample

As_2O_3 Phase

```
Nov 17 14:26 1998  /tmp/x_text.pri Page 1


Weight percent        Group : CHEN               Sample : As2O3-Giant       Page 1

Element  265       271       272       273       274       276       277       278
Sb         0.979     1.411     2.360     0.544     0.313     0.844     2.998     0.157
As        70.242    70.853    70.287    75.898    77.990    73.076    78.202    79.328
Fe         0.935     0.924     0.527     0.602     0.500     1.723     0.603     0.822
Pb         0.014       -         -       0.005       -       0.088     0.128     0.084
S          0.094     0.044       -       0.053     0.020     0.083     0.051     0.036
Cr           -         -         -         -         -         -         -         -
O         27.554    26.742    26.807    22.865    21.173    23.886    17.962    19.531
Ca         0.182     0.026     0.019     0.033     0.004     0.300     0.056     0.042
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent        Group : CHEN               Sample : As2O3-Giant

Element  280       292       293       295       302       305       306       307
Sb         0.080     3.524     0.863     1.022     0.682     1.609     0.378     2.845
As        70.319    75.295    79.063    80.226    73.812    79.775    76.108    76.990
Fe         0.484     0.343     0.636     0.257     0.754     0.395     0.317     0.377
Pb           -       0.033     0.225     0.124     0.021     0.029       -         -
S          0.027     0.057     0.075     0.031     0.068     0.038     0.017     0.031
Cr           -         -         -         -         -         -         -         -
O         29.058    20.670    19.016    18.288    24.663    18.154    23.167    19.726
Ca         0.032     0.078     0.122     0.052       -         -       0.013     0.031
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent        Group : CHEN               Sample : As2O3-Giant

Element  310       311       312       313       333       334       336       337
Sb         1.340     1.079     1.309     0.831     2.396     2.159     0.841     0.329
As        70.349    73.523    77.994    82.427    71.014    71.878    72.676    80.878
Fe         0.497     0.268     0.408     0.324     0.570     0.360     0.449     0.339
Pb         0.051       -         -       0.003       -       0.013     0.028       -
S          0.039     0.025     0.017     0.004     0.024     0.006     0.034     0.158
Cr           -         -         -         -         -         -         -         -
O         27.688    25.105    20.270    16.395    25.953    25.584    25.966    18.087
Ca         0.036       -       0.002     0.016     0.043       -       0.006     0.209
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
```

```
Nov 17 14:26 1998  /tmp/x_text.pri Page 2


Weight percent      Group : CHEN              Sample : As2O3-Giant       Page 2

Element  338       342       345       346       347       348       351
Sb        0.539     2.395     1.155     0.385     0.577     0.631     0.534
As       74.644    75.411    75.283    78.806    81.081    81.522    81.534
Fe        0.556     1.498     0.386     0.409     0.516     0.373     0.479
Pb        0.059       -       0.050     0.022       -         -         -
S         0.097     0.035     0.028     0.049     0.009     0.010     0.073
Cr          -         -         -         -         -         -         -
O        23.991    20.270    22.926    20.126    17.598    17.352    16.802
Ca        0.114       -       0.029     0.040     0.037     0.012     0.053
Bi          -         -         -         -         -         -         -
Si          -       0.391     0.143     0.163     0.182     0.100     0.525
--------------------------------------------------------------------------
Total   100.000   100.000   100.000   100.000   100.000   100.000   100.000


Weight percent      Group : CHEN              Sample : As2O3-Giant

Element| Minimum  Maximum   Average    Sigma
Sb     |   0.080    3.524     1.197    0.910
As     |  70.242   82.427    76.016    3.909
Fe     |   0.257    1.723     0.569    0.329
Pb     |     -      0.225     0.032    0.051
S      |     -      0.158     0.043    0.034
Cr     |     -        -         -        -
O      |  16.395   29.058    22.044    3.749
Ca     |     -      0.300     0.051    0.069
Bi     |     -        -         -        -
Si     |     -      0.525     0.049    0.122
--------------------------------------------
Total  | 100.000  100.000   100.000    0.000
No. of data 31
```

As_2O_3 Phase

```
Nov 17 14:37 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN            Sample : As2O3-Giant      Page 1

Element  275       279       288       289       296       301       303       304
Sb         1.021     1.620     2.513     3.400     1.806     6.599     3.140     4.956
As        58.067    58.341    65.540    54.565    59.154    65.030    60.973    67.111
Fe         1.062     0.673     0.708     1.208     0.063     0.614     0.620     0.789
Pb           -       0.025       -         -         -       0.011     0.049     0.060
S          0.049     0.094     0.019     0.107     0.016     0.027     0.058     0.029
Cr           -         -         -         -         -         -         -         -
O         39.708    39.134    31.162    40.470    38.952    27.697    34.555    26.990
Ca         0.093     0.113     0.058     0.250     0.009     0.022     0.605     0.065
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
-------------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
Weight percent       Group : CHEN            Sample : As2O3-Giant

Element  309       335       339       341       343       350
Sb         3.822     1.836     1.114     1.625     1.319     1.828
As        62.170    69.817    62.117    68.103    65.600    66.392
Fe         0.766     0.617     0.345     0.238     0.160     0.352
Pb           -       0.038       -       0.066       -       0.091
S          0.066     0.065     0.098     0.157     0.030     0.040
Cr           -         -         -         -         -         -
O         33.045    27.505    35.372    29.564    31.879    31.003
Ca         0.131     0.122     0.059     0.013     0.012     0.012
Bi           -         -         -         -         -         -
Si           -         -       0.895     0.234     1.000     0.282
-----------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000


Weight percent       Group : CHEN            Sample : As2O3-Giant

Element | Minimum   Maximum   Average     Sigma
Sb      |    1.021     6.599     2.614     1.618
As      |   54.565    69.817    63.070     4.435
Fe      |    0.063     1.208     0.587     0.328
Pb      |      -       0.091     0.024     0.031
S       |    0.016     0.157     0.061     0.041
Cr      |      -         -         -         -
O       |   26.990    40.470    33.360     4.763
Ca      |    0.009     0.605     0.112     0.157
Bi      |      -         -         -         -
Si      |      -       1.000     0.172     0.342
-----------------------------------------------------
Total   | 100.000   100.000   100.000     0.000
```

$(As,Sb)_2O_3$ Phase

```
Nov 17 14:48 1998  /tmp/x_text.pri Page 1

Weight percent       Group : CHEN             Sample : As2O3-Giant      Page 1

Element  314     315     316     317     318     320     321
Sb      24.603  24.612  22.194  23.718  31.108  20.938  23.966
As      47.398  56.720  52.440  54.573  42.577  51.417  48.142
Fe       0.170   1.495   0.121   0.129   0.171   0.129   0.142
Pb        -       -      0.003    -       -      0.114   0.071
S         -      0.025   0.006   0.009    -      0.010    -
Cr        -       -       -       -       -       -       -
O       27.829  17.148  25.236  21.571  26.144  27.392  27.679
Ca        -       -       -       -       -       -       -
Bi        -       -       -       -       -       -       -
Si        -       -       -       -       -       -       -
-----------------------------------------------------------------
Total  100.000 100.000 100.000 100.000 100.000 100.000 100.000

Weight percent       Group : CHEN             Sample : As2O3-Giant

Element| Minimum  Maximum  Average    Sigma
Sb     |  20.938   31.108   24.448    3.229
As     |  42.577   56.720   50.467    4.793
Fe     |   0.121    1.495    0.337    0.511
Pb     |    -       0.114    0.027    0.047
S      |    -       0.025    0.007    0.009
Cr     |    -        -        -        -
O      |  17.148   27.829   24.714    3.981
Ca     |    -        -        -        -
Bi     |    -        -        -        -
Si     |    -        -        -        -
--------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 7
```

As-bearing Iron Oxide

```
Nov 17 14:30 1998  /tmp/x_text.pri Page 1


Weight percent      Group : CHEN           Sample : As2O3-Giant      Page 1

Element  267       268       281       282       283       284       286       287
Sb         2.603     2.228     9.899     7.119     7.244     7.262     1.228     1.336
As         9.505     9.744     3.820     3.513     9.188     7.645    10.200     5.790
Fe        52.541    51.492    54.219    56.888    47.949    50.239    44.902    57.538
Pb         0.674     0.529     0.169     0.255     0.418     0.340     0.275     0.676
S          0.187     0.197     0.038     0.023     0.051     0.045     3.027     0.077
Cr           -         -         -         -         -         -         -         -
O         33.936    35.145    31.855    32.202    35.007    34.364    40.274    34.415
Ca         0.554     0.665       -         -       0.143     0.105     0.094     0.168
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
-----------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000

Weight percent      Group : CHEN           Sample : As2O3-Giant

Element  294       297       298       299       324       325       326       331
Sb         1.697     0.777     0.918     1.755     1.566     1.478     1.503     0.853
As        10.005     6.857    10.100    14.886     8.747     9.579     9.370     7.774
Fe        55.489    53.219    47.717    45.202    54.921    56.178    55.977    54.132
Pb         0.782     0.290     0.227     0.178     0.371     0.361     0.310     0.371
S          0.041     0.427     0.792     0.240     0.070     0.052     0.066     0.066
Cr           -         -         -         -         -         -         -         -
O         30.987    38.108    39.816    37.673    34.163    32.178    32.596    36.571
Ca         0.999     0.322     0.430     0.066     0.162     0.174     0.178     0.233
Bi           -         -         -         -         -         -         -         -
Si           -         -         -         -         -         -         -         -
-----------------------------------------------------------------------------------
Total    100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000


Weight percent      Group : CHEN           Sample : As2O3-Giant

Element| Minimum  Maximum  Average    Sigma
Sb     |   0.777    9.899    3.092    2.955
As     |   3.513   14.886    8.545    2.727
Fe     |  44.902   57.538   52.413    4.097
Pb     |   0.169    0.782    0.389    0.184
S      |   0.023    3.027    0.337    0.744
Cr     |     -        -        -        -
O      |  30.987   40.274   34.956    2.833
Ca     |     -      0.999    0.268    0.271
Bi     |     -        -        -        -
Si     |     -        -        -        -
-------------------------------------------
Total  | 100.000  100.000  100.000    0.000
```

Iron Arsenate

```
Nov 17 14:45 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN             Sample : As2O3-Giant      Page 1

Element  291      395      396      398      399      400      401      402
Sb        0.739    0.468    0.538    0.535    0.539    0.441    0.475    0.444
As       26.195   29.858   36.551   31.050   30.207   27.167   26.769   27.823
Fe       12.286   12.912   13.187   13.156   13.218   12.978   12.341   12.864
Pb        1.106    0.599    0.797    0.727    0.778    0.687    0.750    0.716
S         1.380    1.499    1.517    1.443    1.231    1.128    1.432    1.542
Cr          -        -        -        -        -        -        -        -
O        54.829   53.915   46.565   52.325   53.276   56.887   57.466   55.851
Ca        3.465    0.739    0.766    0.724    0.725    0.703    0.760    0.745
Bi          -        -        -        -        -        -        -        -
Si          -      0.010    0.079    0.040    0.026    0.009    0.007    0.015
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN             Sample : As2O3-Giant

Element  403      404      405      406      407      408      409      410
Sb        0.526    0.472    0.478    0.552    0.439    0.483    0.430    0.421
As       37.339   34.839   30.144   33.352   28.275   32.681   29.246   29.950
Fe       13.034   11.686   13.122   13.085   12.184   12.987   12.164   12.662
Pb        0.739    0.732    0.785    0.838    0.724    0.819    0.728    0.654
S         1.632    1.810    1.494    1.621    1.270    1.531    1.721    1.492
Cr          -        -        -        -        -        -        -        -
O        45.847   49.521   53.230   49.779   56.436   50.674   54.965   54.111
Ca        0.764    0.807    0.716    0.742    0.646    0.766    0.717    0.690
Bi          -        -        -        -        -        -        -        -
Si        0.119    0.133    0.031    0.031    0.026    0.059    0.029    0.020
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN             Sample : As2O3-Giant

Element  411      412      413      414      415
Sb        0.503    0.476    0.531    0.552    0.389
As       36.250   35.715   34.865   31.363   35.566
Fe       12.413   12.008   12.496   12.523   11.344
Pb        0.664    0.504    0.645    0.689    0.595
S         1.969    2.181    1.635    1.457    2.210
Cr          -        -        -        -        -
O        47.430   48.241   48.951   52.593   49.076
Ca        0.708    0.753    0.783    0.796    0.728
Bi          -        -        -        -        -
Si        0.063    0.122    0.094    0.027    0.092
--------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000
```

```
Nov 17 14:45 1998  /tmp/x_text.pri Page 2


Weight percent       Group : CHEN            Sample : As2O3-Giant       Page 2

Element| Minimum  Maximum  Average    Sigma
Sb     |   0.389    0.739    0.497    0.073
As     |  26.195   37.339   31.676    3.537
Fe     |  11.344   13.218   12.602    0.526
Pb     |   0.504    1.106    0.727    0.118
S      |   1.128    2.210    1.581    0.277
Cr     |     -        -        -        -
O      |  45.847   57.466   51.998    3.535
Ca     |   0.646    3.465    0.869    0.596
Bi     |     -        -        -        -
Si     |     -      0.133    0.049    0.041
-------------------------------------------
Total  | 100.000  100.000  100.000    0.000
No. of data 21
```

```
Nov 17 14:39 1998  /tmp/x_text.pri Page 1
```

Fe-bearing As_2O_3 Phase

```
Weight percent       Group : CHEN              Sample : As2O3-Giant      Page 1

Element  327      328      330     | Minimum  Maximum  Average    Sigma
Sb         2.058    1.758    1.896 |   1.758    2.058    1.904    0.150
As        29.934   41.343   34.366 |  29.934   41.343   35.214    5.752
Fe         9.599    5.080    5.206 |   5.080    9.599    6.628    2.573
Pb         3.000    2.309    2.346 |   2.309    3.000    2.552    0.389
S          0.081    0.081    1.301 |   0.081    1.301    0.488    0.704
Cr           -        -        -   |     -        -        -        -
O         52.371   47.392   50.764 |  47.392   52.371   50.176    2.541
Ca         2.957    2.037    4.121 |   2.037    4.121    3.038    1.044
Bi           -        -        -   |     -        -        -        -
Si           -        -        -   |     -        -        -        -
-----------------------------------------------------------------------
Total    100.000  100.000  100.000 | 100.000  100.000  100.000      -
No. of data 3
```

Calcium-Iron Arsenate

```
Nov 17 14:16 1998  /tmp/x_text.pri Page 1


Weight percent        Group : CHEN             Sample : As2O3-Giant      Page 1

Element   264       266       269    | Minimum   Maximum   Average    Sigma
Sb          0.062     0.702     0.827|   0.062     0.827     0.530    0.410
As          1.384    10.119    20.764|   1.384    20.764    10.756    9.706
Fe          9.931     8.038     8.296|   8.038     9.931     8.755    1.027
Pb          0.066     0.335     0.345|   0.066     0.345     0.249    0.158
S           0.048     0.381     1.084|   0.048     1.084     0.504    0.529
Cr          -         -         -    |   -         -         -        -
O          69.852    65.666    60.290|  60.290    69.852    65.269    4.793
Ca         18.657    14.759     8.394|   8.394    18.657    13.937    5.181
Bi          -         -         -    |   -         -         -        -
Si          -         -         -    |   -         -         -        -
---------------------------------------------------------------------------
Total     100.000   100.000   100.000| 100.000   100.000   100.000    0.000
No. of data 3
```

APPENDIX 5

Detailed Electron Microprobe Analyses of the Arsenic Carriers in the 236 Chamber Sample

As_2O_3 Phase

```
Nov 17 14:04 1998  /tmp/x_text.pri Page 2


Weight percent       Group : CHEN            Sample : As2O3-Giant       Page 2

Element    49       50       51       53       57       58       59       243
Sb        0.534    0.314    0.614    0.232    0.335    0.370      -      0.166
As       77.000   78.211   78.880   75.289   72.403   78.069   75.750   74.988
Fe        0.188    0.174    0.140    0.354    0.195    1.134    0.672    0.182
Pb          -        -      0.017    0.026      -        -        -      0.081
S           -        -        -        -        -        -        -      0.009
Cr          -        -        -        -        -        -        -        -
O        22.278   21.301   20.349   24.099   27.067   20.427   23.578   24.540
Ca          -        -        -        -        -        -        -      0.034
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN            Sample : As2O3-Giant

Element   244      245      250      251      254      255      259      352
Sb          -      0.066      -      0.402    0.063    0.418      -        -
As       75.243   78.860   78.134   77.139   78.528   76.776   78.927   78.866
Fe        0.230    0.226    0.168    0.381    0.125    0.205    0.189    0.205
Pb        0.139    0.092    0.052      -        -      0.011      -      0.053
S         0.008      -      0.001    0.020    0.016      -      0.010    0.004
Cr          -        -        -        -        -        -        -        -
O        24.341   20.734   21.621   22.035   21.268   22.582   20.874   20.762
Ca        0.039    0.022    0.024    0.023      -      0.008      -      0.010
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -      0.100
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN            Sample : As2O3-Giant

Element   354      356      358      359      360      362      365      366
Sb        0.042    0.270    0.765    0.281    0.992    0.052    0.437    0.885
As       77.077   73.469   71.413   76.127   75.802   76.455   78.141   79.656
Fe        0.845    0.160    0.261    0.398    0.481    0.198    0.163    0.488
Pb          -      0.025      -        -        -        -      0.029    0.004
S         0.011      -      0.114    0.039    0.060    0.027    0.005    0.029
Cr          -        -        -        -        -        -        -        -
O        22.025   25.981   27.142   22.653   22.455   23.204   21.216   18.734
Ca          -      0.017    0.092    0.016    0.023      -      0.009    0.016
Bi          -        -        -        -        -        -        -        -
Si          -      0.078    0.213    0.486    0.187    0.064      -      0.188
------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000
```

```
Nov 17 14:04 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN              Sample : As2O3-Giant       Page 1

Element     1        3        12       21       22       23       24       25
Sb          -      0.200    0.292      -        -        -        -      0.079
As       77.198   76.000   75.906   76.555   73.349   78.201   75.431   73.491
Fe        0.105    0.190    0.487    0.251    0.225    0.262    0.349    0.219
Pb          -      0.001    0.075    0.011      -        -        -        -
S           -        -        -        -        -        -        -        -
Cr          -        -        -        -        -        -        -        -
O        22.697   23.609   23.240   23.183   26.426   21.537   24.220   26.211
Ca          -        -        -        -        -        -        -        -
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element    26       27       28       29       30       34       35       36
Sb        0.155      -        -      0.077    0.315    0.154    0.066    0.395
As       73.142   71.447   73.011   76.710   78.581   76.675   75.166   77.462
Fe        0.231    0.161    0.223    0.193    0.256    0.212    0.320    0.539
Pb          -        -        -      0.013    0.031    0.048    0.082    0.073
S           -        -        -        -        -        -        -        -
Cr          -        -        -        -        -        -        -        -
O        26.472   28.392   26.766   23.007   20.817   22.911   24.366   21.531
Ca          -        -        -        -        -        -        -        -
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element    37       38       39       41       42       43       44       48
Sb        0.097      -        -        -        -        -        -      0.380
As       79.877   78.183   75.430   79.193   78.728   77.544   76.380   79.390
Fe        0.303    0.737    0.242    0.181    0.384    0.229    0.422    0.187
Pb        0.058      -      0.014    0.019    0.029    0.045    0.037      -
S           -        -        -        -        -        -        -        -
Cr          -        -        -        -        -        -        -        -
O        19.665   21.080   24.314   20.607   20.859   22.182   23.161   20.043
Ca          -        -        -        -        -        -        -        -
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000
```

```
Nov 17 14:04 1998  /tmp/x_text.pri Page 4


Weight percent       Group : CHEN              Sample : As2O3-Giant      Page 3

Element   367      368      372      373      377      379      380      382
Sb        0.307    0.408    -        0.634    -        0.008    -        0.601
As       78.799   76.277   78.897   76.546   78.947   78.610   76.003   75.375
Fe        0.356    0.151    0.102    0.186    0.172    0.199    0.217    0.144
Pb        0.041    0.001    0.050    -        -        -        -        -
S         0.013    0.015    0.017    0.021    0.019    0.007    0.033    0.016
Cr        -        -        -        -        -        -        -        -
O        20.125   23.010   20.934   22.274   20.849   21.164   23.103   23.864
Ca        0.013    0.008    -        -        0.013    0.006    0.017    -
Bi        -        -        -        -        -        -        -        -
Si        0.346    0.130    -        0.339    -        0.006    0.627    -
----------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element   387      389      390      393    | Minimum  Maximum  Average    Sigma
Sb        0.121    -        0.182    0.090  |  -        0.992    0.197    0.243
As       78.843   78.886   76.698   79.115  | 71.413   79.877   76.787    2.101
Fe        0.106    0.122    0.086    0.229  |  0.086    1.134    0.279    0.190
Pb        0.017    0.017    0.045    0.010  |  -        0.139    0.021    0.030
S         -        0.014    0.011    0.012  |  -        0.114    0.009    0.018
Cr        -        -        -        -      |  -        -        -        -
O        20.902   20.882   22.818   20.278  | 18.734   28.392   22.646    2.124
Ca        -        -        -        0.027  |  -        0.092    0.007    0.015
Bi        -        -        -        -      |  -        -        -        -
Si        0.011    0.079    0.160    0.239  |  -        0.627    0.054    0.126
----------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  | 100.000  100.000  100.000    0.000
No. of data 60
```

As-bearing Iron Oxide

```
Nov 17 14:12 1998  /tmp/x_text.pri Page 1


Weight percent       Group : CHEN              Sample : As2O3-Giant       Page 1

Element     8        9        10       16       17       31       32       242
Sb        0.717    0.662    0.810    0.902    0.787    0.537    0.654    0.711
As       14.312   14.901    9.401    9.257    6.046    8.221    9.029   10.614
Fe       40.905   40.888   43.648   54.657   57.983   57.121   55.698   52.567
Pb        0.554    0.577    0.254    0.268    0.249    0.036    0.104    0.308
S           -        -        -        -        -        -        -      0.021
Cr          -        -      6.185      -        -        -        -        -
O        43.512   42.972   39.702   34.916   34.935   34.085   34.515   35.281
Ca          -        -        -        -        -        -        -      0.498
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
-------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Weight percent       Group : CHEN              Sample : As2O3-Giant

Element  248      249      256      257      258      261      355      363
Sb        0.248    0.241    0.518    0.856    0.671    0.496    0.184    0.247
As        5.813    5.620    6.449    9.314    5.461    7.541    1.947    3.342
Fe       45.771   43.665   55.930   54.822   55.575   55.111   66.342   62.327
Pb        0.115    0.147    0.143    0.275    0.188    0.132    0.028    0.225
S         0.040    0.030    0.029    0.008    0.035    0.037    0.029    0.014
Cr          -        -        -        -        -        -        -        -
O        47.680   49.955   36.684   34.376   37.844   36.431   31.455   33.679
Ca        0.333    0.342    0.247    0.349    0.226    0.252    0.015    0.166
Bi          -        -        -        -        -        -        -        -
Si          -        -        -        -        -        -        -        -
-------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000


Weight percent       Group : CHEN              Sample : As2O3-Giant

Element  364     | Minimum  Maximum  Average     Sigma
Sb        0.361  |  0.184    0.902    0.565     0.235
As        3.126  |  1.947   14.901    7.670     3.573
Fe       62.063  | 40.888   66.342   53.240     7.669
Pb        0.169  |  0.028    0.577    0.222     0.152
S         0.021  |    -      0.040    0.016     0.015
Cr          -    |    -      6.185    0.364     1.500
O        34.063  | 31.455   49.955   37.770     5.255
Ca        0.197  |    -      0.498    0.154     0.165
Bi          -    |    -        -        -         -
Si          -    |    -        -        -         -
-----------------------------------------------------
Total   100.000  | 100.000  100.000  100.000    0.000
```

Various Silicate Species

```
Nov 17 13:54 1998  /tmp/x_text.pri Page 1



Weight percent       Group : CHEN            Sample : Silicate-Giant    Page 1

   No.        Fe       Mg       Al       Si        K        O        Ca      Total
    1      0.840    0.535   14.224   16.467    4.691   63.243       -     100.000
    2      0.102    0.012    0.111   39.967    0.031   59.777       -     100.000
    3      0.258    0.025    0.396   43.919    0.215   55.187       -     100.000
    4     13.136   11.166   11.223   10.725    0.110   52.571    1.069   100.000
    5      1.172    0.447   17.346   21.235    7.104   52.661    0.035   100.000
    6      0.464    0.175    0.269   40.525    0.033   58.412    0.122   100.000
    7      4.587    1.140    3.667    4.912    0.897   84.230    0.567   100.000
    8      9.241    3.003    3.368    4.948    0.187   78.782    0.471   100.000
    9     14.217    8.564    9.542    8.552    0.049   58.964    0.112   100.000
   10     16.893    8.655   10.838    9.790    0.083   53.178    0.563   100.000
   11      1.893    1.081   13.505   18.193    7.288   57.913    0.127   100.000
   12      4.703    4.065   10.708   12.705    3.448   63.814    0.557   100.000
   13     14.816   10.738   10.760   11.334    0.231   51.869    0.252   100.000
   14     13.369    7.556    8.338    8.030    0.234   61.877    0.596   100.000
   15     11.607    7.245    6.861    6.579    0.222   66.708    0.778   100.000
   16     18.194    6.881   11.136   10.009    0.148   53.440    0.192   100.000
   17     17.539    8.979   10.863   10.206    0.022   52.334    0.057   100.000
   18     14.226    9.345   10.604    9.829    0.019   55.892    0.085   100.000
   19      3.383    1.998   15.390   16.338    4.968   57.849    0.074   100.000
  ------------------------------------------------------------------------------
Minimum    0.102    0.012    0.111    4.912    0.019   51.869       -     100.000
Maximum   18.194   11.166   17.346   43.919    7.288   84.230    1.069   100.000
Average    8.455    4.822    8.903   16.014    1.578   59.932    0.298   100.000
Sigma      6.757    4.109    5.151   12.127    2.538    8.786    0.312     0.000

No. of data 19
```

APPENDIX 6

Detailed Solubility Data for Reagent Grade As_2O_3 and Sb_2O_3, as well as for the Four As_2O_3-rich Dust Samples

Vessel 1: **100 g/L reagent grade As_2O_3** **Test 1**

Sample No.	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (g/L)	Total As Conc. (mg/L)
601903-1113-1-1	24.1	4.9058	718	14.64	19.32	< 10	< 0.2	728
601903-1116-1-2	32.0	4.9087	878	17.89	23.62	< 10	< 0.2	900
601903-1117-1-3	40.0	4.9116	1057	21.52	28.41	< 10	< 0.2	1039
601903-1118-1-4	49.8	4.9151	1290	26.25	34.65	< 5	< 0.1	1301
601903-1119-1-5	59.6	4.9187	1552	31.55	41.66	< 10	< 0.2	1575
601903-1120-1-6	69.8	4.9224	1873	38.05	50.24	< 10	< 0.2	1892
601903-1123-1-7	79.9	4.9261	2250	45.68	60.31	< 10	< 0.2	2236
601903-1124-1-8	89.6	4.9296	2712	55.01	72.64	< 10	< 0.2	2674
601903-1125-1-9	97.4	4.9325	3105	62.95	83.12	< 10	< 0.2	3031
601903-1126-1-10	94.3	4.9313	2965	60.13	79.39	< 50	< 1	2910
601903-1127-1-11	84.8	4.9279	2483	50.39	66.53	< 50	< 1	2464
601903-1130-1-12	74.7	4.9242	2079	42.22	55.74	5	0.10	2107
601903-1201-1-13	64.6	4.9205	1720	34.96	46.15	4	0.08	1740
601903-1201-1-14	54.3	4.9168	1393	28.33	37.41	5	0.10	1437
601903-1201-1-15	44.5	4.9132	1162	23.65	31.23	3	0.06	1178
601903-1204-1-16	34.7	4.9096	930	18.94	25.01	4	0.08	936
601903-1207-1-17	23.3	4.9055	735	14.98	19.78	4	0.08	737

Vessel 1: Reagent Grade As_2O_3 Test 2

Sample No.	Temperature (deg. C)	Weighing Dish Initial Wt. (g)	Weighing Dish Final Wt. (g)	Sample Net Weight (g)	Volume of Liquid (ml)	Density of Solution (g/ml)	Sample Dilution	Total As Conc.of Diluted Sample (mg/L)	Total As Conc. Corrected for dilution (g/L)	Conc. of As_2O_3 (g/L)
As-1-1	27.5	88.0382	93.0484	5.0102	4.9070	1.0210	0.0098	159	16.20	21.39
As-1-2	32.9	72.5726	77.5898	5.0172	4.9090	1.0220	0.0098	175	17.82	23.53
As-1-3	40.4	72.5694	77.5888	5.0194	4.9117	1.0219	0.0098	206	20.97	27.69
As-1-4	49.7	72.5713	77.6330	5.0617	4.9151	1.0298	0.0098	251	25.53	33.71
As-1-5	60.0	72.5696	77.6363	5.0667	4.9188	1.0301	0.0098	329	33.44	44.16
As-1-6	69.5	72.5708	77.6245	5.0537	4.9223	1.0267	0.0098	418	42.46	56.06
As-1-7	80.0	72.5719	77.6345	5.0626	4.9261	1.0277	0.0099	488	49.53	65.40
As-1-8	89.0	72.5706	77.6392	5.0686	4.9294	1.0282	0.0099	581	58.93	77.81
As-1-9	94.8	72.5729	77.6494	5.0765	4.9315	1.0294	0.0099	650	65.90	87.01
As-1-10	85.1	72.5698	77.6323	5.0625	4.9280	1.0273	0.0099	535	54.28	71.67
As-1-11	75.3	72.5706	77.6186	5.0480	4.9244	1.0251	0.0098	460	46.71	61.67
As-1-12	64.7	72.5707	77.6037	5.0330	4.9206	1.0229	0.0098	384	39.02	51.52
As-1-13	55.1	72.5685	77.5911	5.0226	4.9171	1.0215	0.0098	297	30.20	39.88
As-1-14	45.1	72.5721	77.5920	5.0199	4.9134	1.0217	0.0098	257	26.15	34.53
As-1-15	34.9	56.3292	61.3408	5.0116	4.9097	1.0208	0.0098	206	20.98	27.70
As-1-16	28.0	56.3291	61.3405	5.0114	4.9072	1.0212	0.0098	195	19.87	26.23

Vessel 2: Reagent Grade Sb_2O_3

Sample No.	Temperature (deg. C)	Weighing Dish Initial Wt. (g)	Weighing Dish Final Wt. (g)	Sample Net Weight (g)	Volume of Liquid (ml)	Density of Solution (g/ml)	Sample dilution	Total Sb Conc.of Diluted Sample (mg/L)	Total Sb Conc. Corrected for dilution (mg/L)	Conc. of Sb_2O_3 (mg/L)	Compsition by XRD
Sb-2-1	27.7	88.0350	92.9683	4.9333	4.9212	1.0025	0.0492	0.160	3.25	3.89	
Sb-2-2	33.9	88.0345	92.9624	4.9279	4.9239	1.0008	0.4924	2.200	4.47	5.35	
Sb-2-3	40.4	88.0362	92.9545	4.9183	4.9267	0.9983	0.4927	2.600	5.28	6.32	
Sb-2-4	50.0	88.0343	92.9426	4.9083	4.9310	0.9954	0.4931	4.170	8.46	10.12	
Sb-2-5	57.5	88.0386	92.9265	4.8879	4.9342	0.9906	0.4934	6.180	12.52	14.99	
Sb-2-6	69.9	88.0396	92.9100	4.8704	4.9397	0.9860	0.1976	3.970	20.09	24.05	
Sb-2-7	78.8	88.0362	92.8778	4.8416	4.9436	0.9794	0.1977	5.240	26.50	31.72	
Sb-2-8	89.5	88.0382	92.8485	4.8103	4.9483	0.9721	0.1979	7.270	36.73	43.97	
Sb-2-9	93.9	88.0367	92.8335	4.7968	4.9502	0.9690	0.1980	8.980	45.35	54.29	Sb_2O_3
Sb-2-10	85.1	88.0365	92.8773	4.8408	4.9464	0.9787	0.1979	6.860	34.67	41.51	
Sb-2-11	74.8	88.0364	92.8890	4.8526	4.9418	0.9819	0.1977	5.170	26.15	31.31	
Sb-2-12	65.1	88.0341	92.9134	4.8793	4.9376	0.9882	0.1975	3.520	17.82	21.34	
Sb-2-13	54.9	88.0390	92.9497	4.9107	4.9331	0.9955	0.1973	2.790	14.14	16.93	
Sb-2-14	45.0	80.1539	85.0654	4.9115	4.9288	0.9965	0.4929	6.540	13.27	15.88	
Sb-2-15	35.3	80.1547	85.0806	4.9259	4.9245	1.0003	0.4924	4.950	10.05	12.03	
Sb-2-16	28.2	88.0335	92.9565	4.9230	4.9214	1.0003	0.4921	6.200	12.60	15.08	

Vessel 5: **100 g/L Jan 98 Comp**

Sample No.	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (g/L)	Total As Conc. (mg/L)	Conc. Of Sb in diluted sample (mg/L)	Conc. Of Sb corrected for dilution (mg/L)	Conc. Of Fe in diluted sample (mg/L)	Conc. Of Fe corrected for dilution (mg/L)
H-JAN98-5	5.0	4.9313	225	4.56	6.02	0.70	0.01	232	< 1.0	< 20	< 0.1	< 2
H-JAN98-10	10.0	4.9326	257	5.21	6.88	< 5	< 0.1	258	< 1.0	< 20	< 0.1	< 2
H-JAN98-15	15.0	4.9338	258	5.23	6.90	1.00	0.02	259	< 0.8	< 16	< 0.05	< 1
H-JAN98-20	20.0	4.9351	278	5.63	7.44	1.00	0.02	286	< 0.8	< 16	0.14	2.84
H-JAN98-25	25.0	4.9364	306	6.20	8.18	1.00	0.02	305	< 0.4	< 8	0.19	3.85
601903-1113-5-1	26.4	4.9296	452	9.17	12.11	< 10	< 0.2	454	0.40	8.11	0.09	1.83
601903-1116-5-2	31.9	4.9316	472	9.57	12.64	< 10	< 0.2	481	0.50	10.14	< 0.06	< 1.2
601903-1117-5-3	39.7	4.9350	509	10.31	13.62	< 10	< 0.2	496	0.60	12.16	< 0.04	< 0.8
601903-1118-5-4	49.7	4.9390	605	12.25	16.17	< 10	< 0.2	603	0.75	15.19	0.11	2.23
601903-1119-5-5	60.0	4.9431	723	14.63	19.31	< 10	< 0.2	755	1.14	23.06	0.10	2.02
601903-1120-5-6	70.1	4.9472	865	17.48	23.09	< 10	< 0.2	915	1.72	34.77	< 0.09	< 1.8
601903-1123-5-7	79.3	4.9509	1070	21.61	28.54	< 10	< 0.2	1088	2.77	55.95	< 0.07	< 1.4
601903-1124-5-8	89.8	4.9551	1256	25.35	33.47	< 10	< 0.2	1279	4.18	84.36	< 0.07	< 1.4
601903-1125-5-9	97.4	4.9582	1407	28.38	37.47	< 10	< 0.2	1422	5.54	111.74	< 0.07	< 1.4
601903-1126-5-10	94.2	4.9569	1426	28.77	37.98	< 50	< 1	1418	5.19	104.70	< 0.07	< 1.4
601903-1127-5-11	83.8	4.9527	1434	28.95	38.23	< 50	< 1	1416	4.02	81.17	< 0.06	< 1.2
601903-1130-5-12	74.4	4.9489	1496	30.23	39.91	13.00	0.26	1509	3.06	61.83	< 0.06	< 1.2
601903-1201-5-13	64.5	4.9449	1422	28.76	37.97	12.00	0.24	1481	2.24	45.30	< 0.06	< 1.2
601903-1201-5-14	54.2	4.9408	1412	28.58	37.73	13.00	0.26	1464	1.82	36.84	< 0.07	< 1.4
601903-1201-5-15	44.5	4.9369	1250	25.32	33.43	9.00	0.18	1305	1.56	31.60	< 0.07	< 1.4
601903-1204-5-16	34.7	4.9329	969	19.64	25.94	12.00	0.24	1010	1.45	29.39	< 0.07	< 1.4
601903-1207-5-17	25.7	4.9293	796	16.15	21.32	13.00	0.26	804	1.36	27.59	< 0.09	< 1.8
C-JAN98-18	18.0	4.9346	307	6.22	8.21	1.60	0.03	313	< 0.9	< 18	0.28	5.67
C-JAN98-12	12.0	4.9331	310	6.28	8.30	1.60	0.03	313	< 0.9	< 18	0.32	6.49
C-JAN98-5	5.0	4.9313	312	6.33	8.35	2.20	0.04	311	< 0.9	< 18	0.29	5.88

Vessel 4: **100 g/L April 97 Comp**

Sample No.	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (g/L)	Total As Conc. (mg/L)	Conc. Of Sb in diluted sample (mg/L)	Conc. Of Sb corrected for dilution (mg/L)	Conc. Of Fe in diluted sample (mg/L)	Conc. Of Fe corrected for dilution (mg/L)
H-APR97-5	5.0	4.8988	240	4.90	6.47	< 0.5	< 10	240	< 1.0	< 20	< 0.1	< 2
H-APR97-10	10.0	4.9006	298	6.08	8.03	< 0.5	< 10	299	< 1.0	< 20	< 0.1	< 2
H-APR97-15	15.0	4.9025	322	6.57	8.67	1.00	0.02	326	< 0.8	< 16	< 0.05	< 1
H-APR97-20	20.0	4.9043	356	7.26	9.58	1.00	0.02	363	< 0.8	< 16	< 0.05	< 1
H-APR97-25	25.0	4.9061	393	8.01	10.58	1.00	0.02	387	< 0.4	< 8	< 0.02	< 0.4
601903-1113-4-1	27.2	4.9207	574	11.66	15.40	9.00	0.18	589	0.30	6.10	< 0.03	< 0.6
601903-1116-4-2	33.3	4.9236	622	12.63	16.68	< 10	< 0.2	626	0.50	10.16	< 0.06	< 1.2
601903-1117-4-3	39.9	4.9266	651	13.21	17.45	< 10	< 0.2	636	0.50	10.15	< 0.04	< 0.8
601903-1118-4-4	49.4	4.9311	728	14.76	19.49	< 10	< 0.2	719	0.65	13.18	< 0.04	< 0.8
601903-1119-4-5	58.3	4.9352	792	16.05	21.19	< 10	< 0.2	828	0.36	7.29	< 0.09	< 1.8
601903-1120-4-6	69.5	4.9405	898	18.18	24.00	< 10	< 0.2	949	1.41	28.54	< 0.09	< 1.8
601903-1123-4-7	79.4	4.9451	1045	21.13	27.90	< 10	< 0.2	1112	2.66	53.79	< 0.07	< 1.4
601903-1124-4-8	88.2	4.9492	1232	24.89	32.87	< 10	< 0.2	1275	3.65	73.75	< 0.07	< 1.4
601903-1125-4-9	97.8	4.9537	1502	30.32	40.03	< 10	< 0.2	1476	4.77	96.29	< 0.07	< 1.4
601903-1126-4-10	92.7	4.9513	1620	32.72	43.20	< 50	< 1	1629	3.91	78.97	< 0.07	< 1.4
601903-1127-4-11	83.6	4.9471	1611	32.56	43.00	< 50	< 1	1622	3.06	61.85	< 0.06	< 1.2
601903-1130-4-12	75.5	4.9433	1675	33.88	44.74	11.00	0.22	1698	2.51	50.78	< 0.06	< 1.2
601903-1201-4-13	63.6	4.9377	1605	32.50	42.92	11.00	0.22	1675	1.71	34.63	< 0.06	< 1.2
601903-1201-4-14	54.3	4.9334	1445	29.29	38.67	11.00	0.22	1481	1.22	24.73	< 0.07	< 1.4
601903-1201-4-15	44.8	4.9289	1195	24.24	32.01	8.00	0.16	1219	1.20	24.35	< 0.07	< 1.4
601903-1204-4-16	34.8	4.9243	953	19.35	25.55	10.00	0.20	973	1.16	23.56	< 0.07	< 1.4
601903-1207-4-17	26.0	4.9202	795	16.16	21.33	10.00	0.20	810	1.02	20.73	< 0.09	< 1.8
C-APR97-18	18.0	4.9035538	399	8.14	10.74	1.20	0.02	398	< 0.9	< 18	0.06	1.22
C-APR97-12	12.0	4.9013692	401	8.18	10.80	1.30	0.03	401	< 0.9	< 18	0.06	1.22
C-APR97-5	5.0	4.8968205	398	8.12	10.73	1.60	0.03	397	< 0.9	< 18	0.06	1.22

Vessel 2: **100 g/L 212 Chamber**

Sample No.	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (g/L)	Total As Conc. (mg/L)	Conc. Of Sb in diluted sample (mg/L)	Conc. Of Sb corrected for dilution (mg/L)	Conc. Of Fe in diluted sample (mg/L)	Conc. Of Fe corrected for dilution (mg/L)
H-212-5	5.0	4.9112	231	4.70	6.21	8.00	0.16	240	< 1.0	< 20	< 0.1	< 2
H-212-10	10.0	4.9134	265	5.39	7.12	7.00	0.14	271	< 1.0	< 20	< 0.1	< 2
H-212-15	15.0	4.9156	275	5.59	7.39	7.00	0.14	279	< 0.8	< 16	< 0.05	< 1
H-212-20	20.0	4.9178	297	6.04	7.97	8.00	0.16	308	0.89	18	< 0.05	< 1
H-212-25	25.0	4.9200	334	6.79	8.96	9.00	0.18	338	0.88	18	< 0.02	< 0.4
601903-1113-2-1	26.5	4.9208	455	9.25	12.21	6.00	0.12	471	1.20	24	0.03	0.6
601903-1116-2-2	33.2	4.9236	481	9.77	12.90	< 10	< 0.2	497	1.60	32	< 0.06	< 1.2
601903-1117-2-3	39.9	4.9265	500	10.15	13.40	9.00	0.18	497	2.00	41	< 0.04	< 0.8
601903-1118-2-4	49.5	4.9307	553	11.22	14.81	10.00	0.20	558	2.40	49	0.05	1.0
601903-1119-2-5	59.4	4.9351	616	12.48	16.48	11.00	0.22	645	1.74	35	< 0.09	< 1.8
601903-1120-2-6	69.8	4.9396	710	14.37	18.98	12.00	0.24	757	2.74	55	< 0.09	< 1.8
601903-1123-2-7	80.0	4.9441	885	17.90	23.63	18.00	0.36	920	4.83	98	< 0.07	< 1.4
601903-1124-2-8	90.0	4.9485	1028	20.77	27.43	20.00	0.40	1037	6.39	129	< 0.07	< 1.4
601903-1125-2-9	97.6	4.9518	1219	24.62	32.50	25.00	0.50	1259	7.75	157	< 0.07	< 1.4
601903-1126-2-10	94.9	4.9507	1312	26.50	34.99	27.00	0.55	1347	7.82	158	< 0.07	< 1.4
601903-1127-2-11	85.0	4.9463	1293	26.14	34.51	26.00	0.53	1345	6.27	127	< 0.06	< 1.2
601903-1130-2-12	75.3	4.9421	1360	27.52	36.33	28.00	0.57	1382	5.76	117	< 0.06	< 1.2
601903-1201-2-13	65.0	4.9375	1299	26.31	34.74	27.00	0.55	1388	4.87	99	< 0.06	< 1.2
601903-1201-2-14	54.6	4.9330	1290	26.15	34.53	28.00	0.57	1335	4.46	90	< 0.07	< 1.4
601903-1201-2-15	44.6	4.9286	1245	25.26	33.35	27.00	0.55	1280	4.15	84	< 0.07	< 1.4
601903-1204-2-16	34.7	4.9242	970	19.70	26.01	28.00	0.57	1030	4.26	87	< 0.07	< 1.4
601903-1207-2-17	25.3	4.9201	804	16.34	21.58	28.00	0.57	824	4.05	82	< 0.09	< 1.8
C-212-18	18.0	4.9169	335	6.81	9.00	9.00	0.18	343	0.92	19	< 0.04	< 0.8
C-212-12	12.0	4.9143	335	6.82	9.00	9.00	0.18	346	0.90	18	< 0.04	< 0.8
C-212-5	5.0	4.9112	338	6.88	9.09	9.00	0.18	346	0.90	18	< 0.04	< 0.8

Vessel 3: **100 g/L 236 Chamber**

Sample No.	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (g/L)	Total As Conc. (mg/L)	Conc. Of Sb in diluted sample (mg/L) :	Conc. Of Sb corrected for dilution (mg/L)	Conc. Of Fe in diluted sample (mg/L)	Conc. Of Fe corrected for dilution (mg/L)
H-236-5	5.0	4.9103	442	9.00	11.88	12.00	0.24	445	< 1.0	< 20	< 0.1	< 2
H-236-10	10.0	4.9127	462	9.40	12.42	13.00	0.26	465	< 1.0	< 20	< 0.1	< 2
H-236-15	15.0	4.9150	476	9.68	12.79	12.00	0.24	477	< 0.8	< 16	< 0.05	< 1
H-236-20	20.0	4.9173	513	10.43	13.77	12.00	0.24	527	< 0.8	< 16	< 0.05	< 1
H-236-25	25.0	4.9197	578	11.75	15.51	13.00	0.26	576	< 0.4	< 8	< 0.02	< 0.4
601903-1113-3-1	27.0	4.9206	639	12.99	17.15	8.00	0.16	648	0.60	12.19	0.06	1.22
601903-1116-3-2	34.4	4.3988	704	16.00	21.13	8.00	0.18	719	0.70	15.91	< 0.06	< 1.2
601903-1117-3-3	40.0	4.4003	737	16.75	22.11	10.00	0.23	721	0.75	17.04	< 0.04	< 0.8
601903-1118-3-4	50.1	4.4029	859	19.51	25.76	11.00	0.25	870	0.80	18.17	< 0.04	< 0.8
601903-1119-3-5	60.0	4.4054	971	22.04	29.10	15.00	0.34	1011	1.06	24.06	< 0.09	< 1.8
601903-1120-3-6	70.1	4.4060	1123	25.48	33.64	13.00	0.29	1168	1.58	35.84	< 0.09	< 1.8
601903-1123-3-7	80.2	4.4106	1313	29.77	39.31	15.00	0.34	1337	2.71	61.44	< 0.07	< 1.4
601903-1124-3-8	90.0	4.4131	1469	33.29	43.95	16.00	0.36	1520	3.90	88.37	< 0.07	< 1.4
601903-1125-3-9	97.5	4.4150	1592	36.06	47.61	19.00	0.43	1585	4.75	107.59	< 0.07	< 1.4
601903-1126-3-10	94.6	4.4143	1613	36.54	48.25	20.00	0.45	1623	4.80	108.74	< 0.07	< 1.4
601903-1127-3-11	85.0	4.4118	1593	36.11	47.67	21.00	0.48	1574	4.37	99.05	< 0.06	< 1.2
601903-1130-3-12	75.1	4.4093	1626	36.88	48.69	21.00	0.48	1697	2.78	63.05	< 0.06	< 1.2
601903-1201-3-13	64.9	4.4067	1573	35.70	47.13	20.00	0.45	1674	2.43	55.14	< 0.06	< 1.2
601903-1201-3-14	54.7	4.4040	1566	35.56	46.95	20.00	0.45	1608	1.54	34.97	< 0.07	< 1.4
601903-1201-3-15	45.0	4.4015	1589	36.10	47.67	20.00	0.45	1619	1.42	32.26	< 0.07	< 1.4
601903-1204-3-16	35.2	4.3990	1559	35.44	46.79	19.00	0.43	1584	1.33	30.23	< 0.07	< 1.4
601903-1207-3-17	26.8	4.3969	809	18.40	24.29	20.00	0.45	824	1.08	24.56	< 0.09	< 1.8
C-236-18	18.0	4.9164	588	11.96	15.79	13.00	0.26	584	< 0.9	< 18	0.05	1.02
C-236-12	12.0	4.9136	592	12.05	15.91	13.00	0.26	596	< 0.9	< 18	0.05	1.02
C-236-5	5.0	4.9103	591	12.04	15.89	13.00	0.26	587	< 0.9	< 18	0.05	1.02

Vessel 6: **50 g/L Reagent grade As_2O_3**

Sample No.	Time (hours)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)	Total As Conc. (mg/L)
	0.0	22.0		0.00	0.00	0.00	0.00	0.00	0.00
601903-EQ-1	0.5	22.0	4.9064	0.60	0.01	0.02	< 0.1	< 2	
601903-EQ-2	1.0	22.0	4.9064	1.90	0.04	0.05	< 0.1	< 2	
601903-EQ-3	2.0	22.5	4.9067	6.40	0.13	0.17	< 0.1	< 2	
601903-EQ-4	4.0	23.5	4.9074	22.00	0.45	0.59	< 5	< 100	22.00
601903-EQ-5	7.0	25.0	4.9083	71.00	1.45	1.91	< 5	< 100	69.40
601903-EQ-6	24.0	25.0	4.9083	519.00	10.57	13.96	< 10	< 200	521.00
601903-EQ-7	48.0	25.2	4.9084	703.00	14.32	18.91	< 10	< 200	727.00
601903-EQ-8	72.0	25.5	4.9086	721.00	14.69	19.39	< 10	< 200	763.00
601903-EQ-9	144.0	25.5	4.9086	730.00	14.87	19.64	< 10	< 200	739.00
601903-EQ-10	168.0	25.8	4.9088	743.00	15.14	19.98	< 10	< 200	736.00

Vessel 6: **75 g/L Reagent grade As_2O_3**

Sample No.	Time (hours)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)	Total As Conc. (mg/L)
					0.00	0.00		0.00	
601903-EQ60-1	1.0	59.5	4.9294	535	10.85	14.33	19	385.45	494
601903-EQ60-2	2.0	60.0	4.9297	1150	23.33	30.80	17	344.85	1125
601903-EQ60-3	4.1	60.4	4.9299	1489	30.20	39.88	24	486.82	1447
601903-EQ60-4	7.0	60.0	4.9297	1506	30.55	40.34	< 50	< 1000	1492
601903-EQ60-5	24.0	59.9	4.9296	1529	31.02	40.95	< 50	< 1000	1508
601903-EQ60-6	48.0	59.6	4.9294	1548	31.40	41.46	< 50	< 1000	1527
601903-EQ60-7	120.0	59.9	4.9296	1612	32.70	43.18		0.00	

Vessel 1: 100 g/L 212 Chamber Sample Saturation Test at 95°C

Sample No.	Time (hours)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)
	0.0	95.0	4.9316	0	0.00	0.00	0	0.00
601903-212-95-1	6.0	95.0	4.9316	1605	32.55	42.97	17	344.72
601903-212-95-2	24.0	95.4	4.9317	1595	32.34	42.70	22	446.09
601903-212-95-3	48.0	94.6	4.9314	1654	33.54	44.28	29	588.06
601903-212-95-4	72.0	94.8	4.9315	1639	33.24	43.88	36	730.00
601903-212-95-5	168.0	94.5	4.9314	1752	35.53	46.91	54	1095.02

Vessel 4: **100 g/L Jan 98 Sample**

Sample No.	Time (days)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)
601904-EQ4-1	7.0	26.2	4.9202	444	9.02	11.9	3.5	71.1
601904-EQ4-2	9.0	26.7	4.9205	446	9.06	12.0	3.5	71.1
601904-EQ4-3	21.0	26.0	4.9202	470	9.55	12.6	4.0	81.3

Vessel 3: **100 g/L Apr 97 Sample**

Sample No.	Time (days)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)
601903-EQ3-1	7.0	26.1	4.3967	604	13.7	18.1	3.4	77.3
601903-EQ3-2	9.0	26.8	4.3969	601	13.7	18.0	3.2	72.8
601903-EQ3-3	21.0	26.2	4.3967	608	13.8	18.3	4.0	91.0

Vessel 1: **100 g/L 212 Chamber Sample**

Sample No.	Time (days)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)
601903-EQ1-1	7.0	23.3	4.9055	448	9.13	12.1	15.0	306
601903-EQ1-2	9.0	23.8	4.9057	446	9.09	12.0	15.0	306
601903-EQ1-3	21.0	23.0	4.9054	465	9.48	12.5	16.0	326

Vessel 2: **100 g/L 236 Chamber Sample**

Sample No.	Time (days)	Temp. (°C)	Volume of Liquid (ml)	Conc. of As^{3+} in diluted sample (mg/L)	Conc. of As^{3+} Corrected for dilution (g/L)	As_2O_3 Concentration (g/L)	Conc. of As^{5+} in diluted sample (mg/L)	Conc. of As^{5+} Corrected for dilution (mg/L)
601903-EQ2-1	7.0	26.5	4.9206	684	13.9	18.4	16.3	331
601903-EQ2-2	9.0	26.9	4.9208	686	13.9	18.4	16.2	329
601903-EQ2-3	21.0	26.4	4.9206	706	14.3	18.9	17.0	345

As_2O_3 Solubility at Variable Pulp Densities at 70°C

Vessel: Sealed glass 2 L reaction kettle heated in oil bath
Solution: 1.0 L Water
Dust sample: Apr 97 Comp Dust
Temperature: 70°C
Sampling Time: 96 hours
Filtration: Millipore 0.45 micron pore size
Stirring: Magnetic stirring bar

Note: 5 drops of liquid detergent added to all slurries to reduce surface scum.

Sample No.	Pulp Density (g/L)	Total As in diluted sample (g/L)	[As] corrected for dilution (g/L)	[As_2O_3] (g/L)	Total Sb in diluted sample (mg/L)	[Sb] corrected for dilution (mg/L)	Weight of Solids after Filtration (g)	Solids Composition
APR97-75	75.0	1.539	31.47	41.55	2.03	41.51	38.2	
APR97-150	150.0	1.783	36.38	48.03	1.83	37.33	99.7	
APR97-225	225.0	1.823	37.01	48.87	1.68	34.11	168.6	
APR97-300	300.0	1.921	39.20	51.76	1.80	36.73	248.5	

APPENDIX 7

Detailed Electron Microprobe Analyses of the As_2O_3 Phase Remaining in the April 97 Composite Sample After Water Leaching at 70°C and Various Pulp Densities

April 97 Composite, 70°C, 75 g/L Solids

```
Weight percent        Group : CHEN             Sample : As2O3-Residue     Page 1

Element       1        2        6        12       15       17       18       21
As         81.826   78.599   75.992   75.499   71.261   72.131   73.781   80.177
Sb          0.609    0.374    0.692    0.637    1.013    7.445    1.289    1.460
Fe          0.093    0.196    0.132    0.157    0.155    0.134    0.247    0.159
Pb          0.095    0.131    0.369    0.277    0.167    0.127    0.118    0.056
Si          0.727      -        -        -        -        -      0.899      -
O          16.650   20.700   22.815   23.430   27.404   20.163   23.666   18.148
---------------------------------------------------------------------------------
Total     100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element      22       24       37       38       49
As         74.277   72.814   70.944   70.209   74.530
Sb          2.069    1.912    0.279    1.654    1.996
Fe          0.270    0.178    0.150    0.312    0.189
Pb          0.234    0.159    0.030      -      0.142
Si            -      0.022      -        -        -
O          23.150   24.915   28.597   27.825   23.143
-----------------------------------------------------
Total     100.000  100.000  100.000  100.000  100.000

Element| Minimum  Maximum  Average  Sigma
As     |  70.209   81.826   74.772   3.600
Sb     |   0.279    7.445    1.648   1.850
Fe     |   0.093    0.312    0.182   0.061
Pb     |     -      0.369    0.147   0.101
Si     |     -      0.899    0.127   0.307
O      |  16.650   28.597   23.124   3.598
------------------------------------------
Total  | 100.000  100.000  100.000   0.000
No. of data 13
```

April 97 Composite, 70°C, 150 g/L Solids

```
Weight percent          Group : CHEN            Sample : As2O3-Residue     Page 1

Element      50       51       52       56       57       59       62       64
As       77.884   83.331   77.177   72.840   76.611   74.083   71.983   72.474
Sb        0.334    0.548    0.621    0.469    0.579    0.408    1.580    0.569
Fe        0.444    0.487    0.413    0.206    0.148    0.080    0.329    0.182
Pb        0.010    0.092    0.159    0.171    0.157    0.295    0.354    0.330
Si          -        -      0.195    0.046    0.612    0.186    0.208    0.558
O        21.328   15.542   21.435   26.268   21.893   24.948   25.546   25.887
---------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element      67       68       69       71       81       82       88       96
As       74.889   77.129   72.399   75.007   73.137   75.008   73.238   73.702
Sb        0.655    0.716    1.074    0.625    0.948    0.566    4.254    0.629
Fe        0.268    0.231    0.435    0.184    0.088    0.119    0.208    0.102
Pb        0.708    0.901    1.279    0.101    0.179    0.157    0.058    0.201
Si        0.438    0.731    0.233      -        -        -        -        -
O        23.042   20.292   24.580   24.083   25.648   24.150   22.242   25.366
---------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element      98       99      100      103      105      106      107      121
As       73.573   74.842   76.408   72.892   75.354   75.734   76.574   78.217
Sb        0.128    0.122    0.153    1.001    1.151    0.432    0.534    0.823
Fe        0.114    0.120    0.089    0.107    0.430    0.141    0.087    0.212
Pb        0.075    0.170    0.407    0.007    0.245    0.346    0.376    0.133
Si          -        -        -        -        -        -        -        -
O        26.110   24.746   22.943   25.993   22.820   23.347   22.429   20.615
---------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element     122      125      126      132      137      138      147
As       73.198   75.280   72.282   74.901   70.734   70.482   72.353
Sb        1.114    0.796    0.829    1.017    0.677    0.774    1.278
Fe        0.494    0.651    0.520    0.243    0.236    0.281    0.267
Pb        0.308    0.244    0.243    0.066    0.136    0.123    0.428
Si          -        -        -        -        -        -        -
O        24.886   23.029   26.126   23.773   28.217   28.340   25.674
------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element| Minimum  Maximum  Average   Sigma
As     |  70.482   83.331   74.636   2.581
Sb     |   0.122    4.254    0.819   0.720
Fe     |   0.080    0.651    0.255   0.156
Pb     |   0.007    1.279    0.273   0.267
Si     |     -      0.731    0.103   0.204
O      |  15.542   28.340   23.913   2.554
-----------------------------------------
Total  | 100.000  100.000  100.000   0.000
No. of data 31
```

April 97 Composite, 70°C , 75 g/L Solids

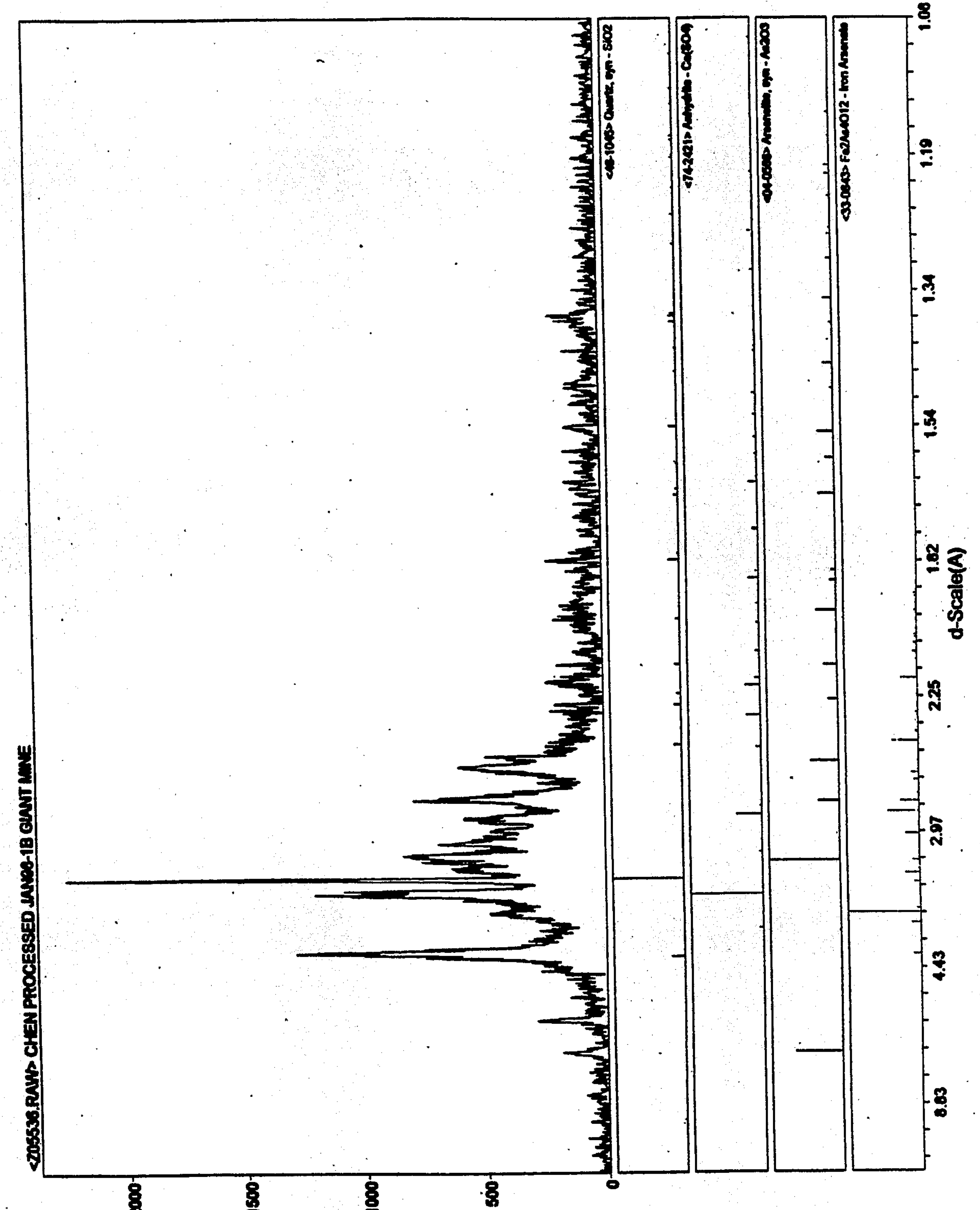
```
Weight percent        Group : CHEN              Sample : As2O3-Residue     Page 1

Element      13       20       34       36       40       41       42       45
As       58.280   62.449   40.916   48.939   33.805   45.710   46.559   48.021
Sb       15.677   12.045   28.279   21.496   18.192   19.093   18.218   24.980
Fe        0.289    0.243    0.345    0.790    7.332   10.282    0.324    0.192
Pb        0.199    0.185    0.304    0.222      -      0.109    2.318    0.001
Si          -      0.848      -        -        -        -        -        -
O        25.555   24.230   30.156   28.553   40.671   24.806   32.581   26.806
--------------------------------------------------------------------------------
Total   100.000  100.000  100.000  100.000  100.000  100.000  100.000  100.000

Element      46 | Minimum  Maximum  Average    Sigma
As       47.673 |  33.805   62.449   48.039    8.474
Sb       22.648 |  12.045   28.279   20.070    4.896
Fe        0.246 |   0.192   10.282    2.227    3.807
Pb          -   |     -      2.318    0.371    0.738
Si          -   |     -      0.848    0.094    0.283
O        29.433 |  24.230   40.671   29.199    5.092
-------------------------------------------------------
Total   100.000 | 100.000  100.000  100.000      -
No. of data 9
```

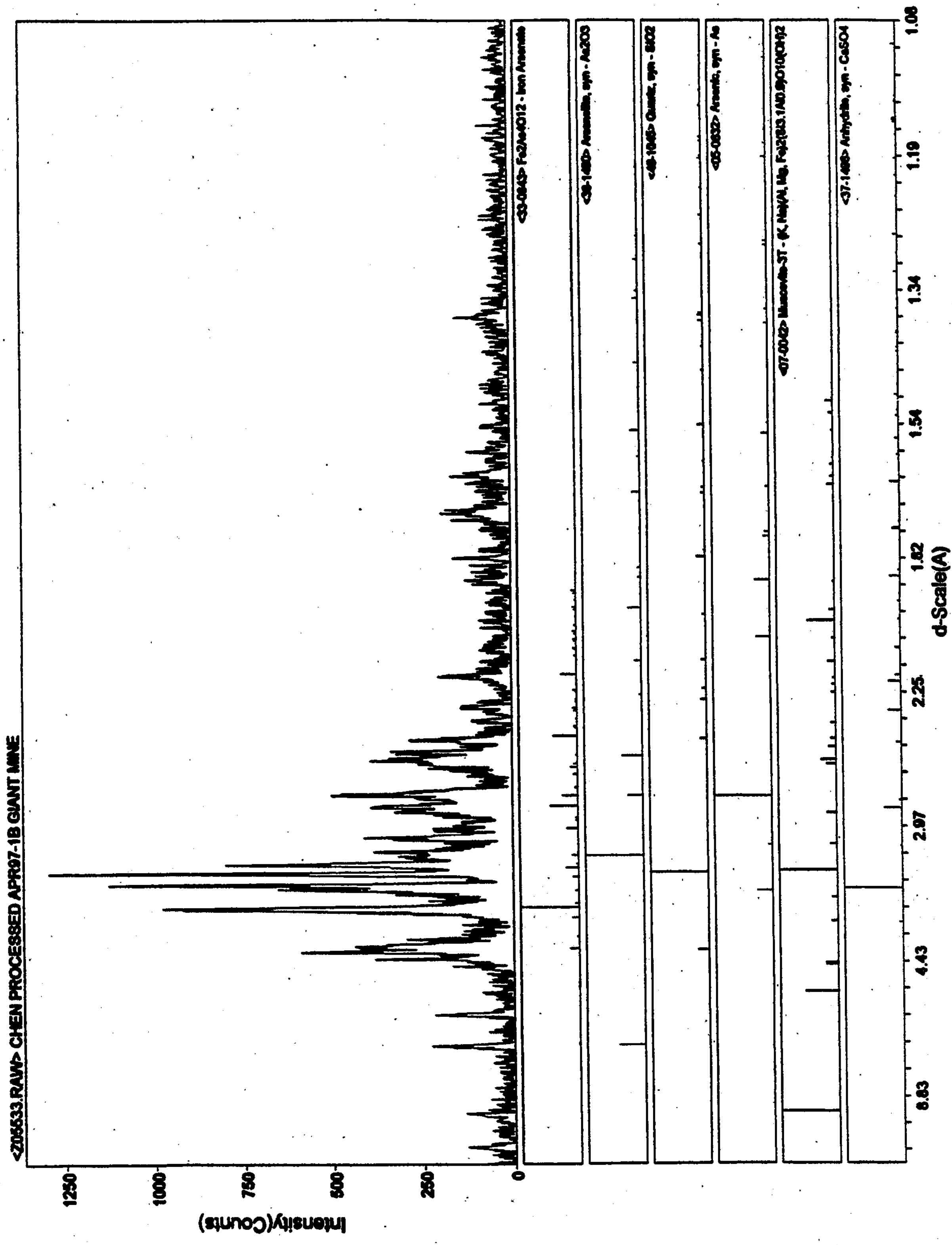
April 97 Composite, 70°C, 150 g/L Solids

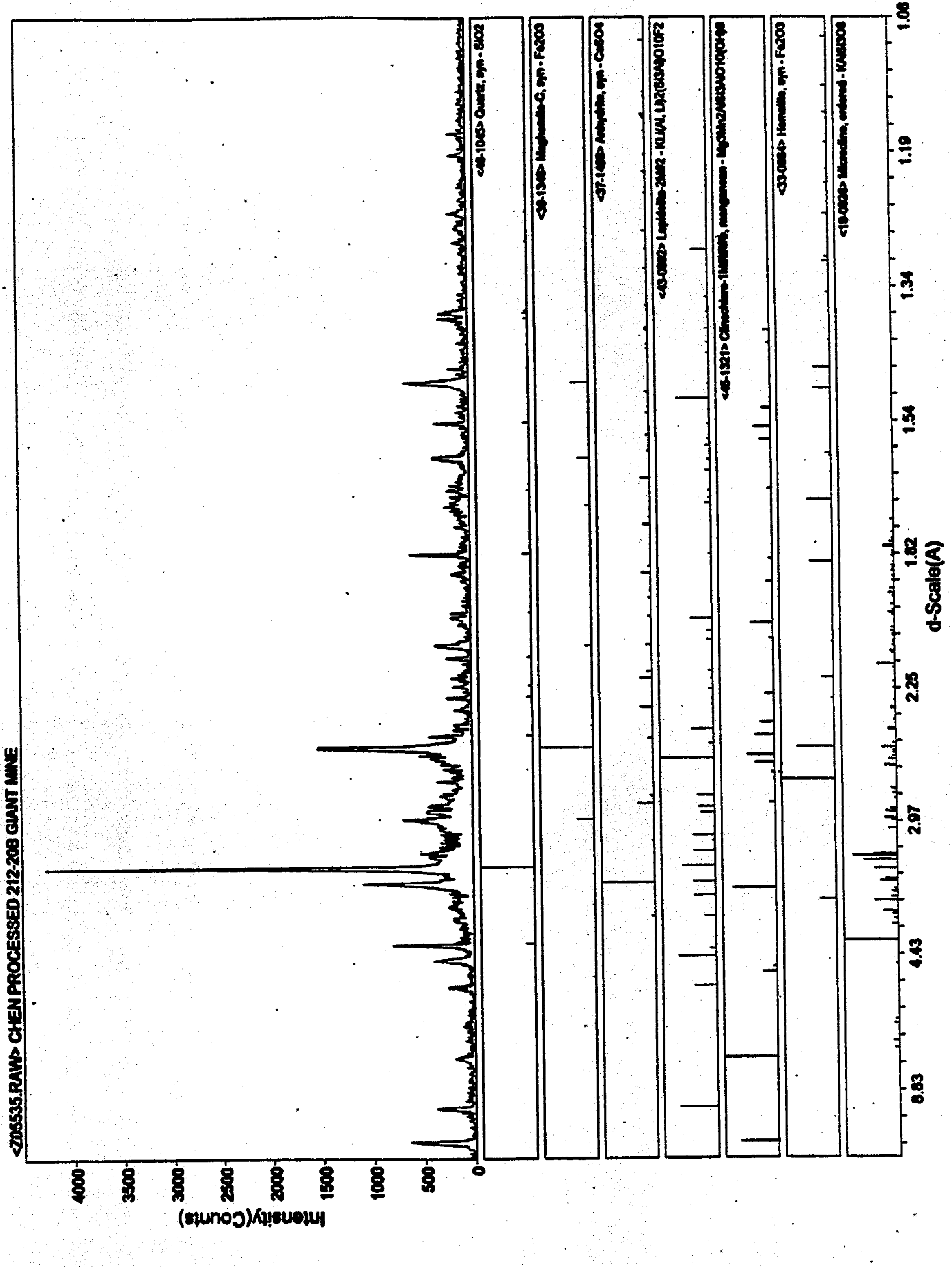
```
Weight percent        Group : CHEN            Sample : As2O3-Residue     Page 1

Element      58      61      74      110      113      114      115
As        49.962  50.305  63.050   43.690   44.946   46.965   53.193
Sb        11.385  12.221  18.973   25.097   30.234   29.140   28.692
Fe         1.010   0.348   0.204    0.536    0.135    0.133    0.129
Pb         0.198   0.061   0.147    0.249    0.317    0.175    0.170
Si           -       -       -      0.085    0.673    0.178    0.145
O         37.445  37.065  17.626   30.343   23.695   23.409   17.671
-------------------------------------------------------------------------
Total    100.000 100.000 100.000  100.000  100.000  100.000  100.000

Element| Minimum  Maximum  Average  Sigma
As     |  43.690   63.050   50.302   6.513
Sb     |  11.385   30.234   22.249   8.064
Fe     |   0.129    1.010    0.356   0.325
Pb     |   0.061    0.317    0.188   0.080
Si     |     -      0.673    0.154   0.240
O      |  17.626   37.445   26.751   8.365
------------------------------------------
Total  | 100.000  100.000  100.000   0.000
No. of data 7
```

APPENDIX 8

X-ray Diffraction Patterns of the Four Sublimation Residues


<Z05536.RAW> CHEN PROCESSED JAN96-1B GIANT MINE
Intensity(Counts)
0
500
1000
1500
2000
<46-1045> Quartz, syn - SiO2
<74-2421> Anhydrite - Ca(SO4)
<04-0566> Arsenolite, syn - As2O3
<33-0643> Fe2As4O12 - Iron Arsenate
d-Scale(A)
8.63
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.06


<205533.RAW> CHEN PROCESSED APR97-1B GIANT MINE
Intensity(Counts)
0
250
500
750
1000
1250
d-Scale(A)
6.83
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.08
<33-0643> Fe2As4O12 - Iron Arsenate
<36-1490> Arsenolite, syn - As2O3
<46-1045> Quartz, syn - SiO2
<05-0632> Arsenic, syn - As
<07-0042> Muscovite-3T - (K, Na)(Al, Mg, Fe)2(Si3.1Al0.9)O10(OH)2
<37-1496> Anhydrite, syn - CaSO4


<Z05535.RAW> CHEN PROCESSED 212-20B GIANT MINE
Intensity(Counts)
4000
3500
3000
2500
2000
1500
1000
500
0
<46-1045> Quartz, syn - SiO2
<39-1346> Maghemite-C, syn - Fe2O3
<37-1496> Anhydrite, syn - CaSO4
<43-0662> Lepidolite-2M#2 - K(Li,Al, Li)2(Si3Al)O10F2
<46-1321> Clinochlore-1M#IIb, manganoan - Mg3Mn2AlSi3AlO10(OH)8
<33-0664> Hematite, syn - Fe2O3
<19-0926> Microcline, ordered - KAlSi3O8
8.83
4.43
2.97
2.25
1.82
1.54
1.34
1.19
1.06
d-Scale(A)

PROTECTED BUSINESS INFORMATION