



**LOW TEMPERATURE VOLATILIZATION OF SELENIUM FROM ROCK  
SAMPLES OF THE PHOSPHORIA FORMATION IN SOUTHEASTERN IDAHO**

by

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## ABSTRACT

Laboratory study of waste bed samples from the Meade Peak Phosphatic Shale Member of the Phosphoria Formation revealed that selenium (Se) can be partially volatilized at atmospheric oxidizing conditions at temperatures as low as 200°C. For a sample of <0.063 mm material containing 2700 parts per million (ppm) Se, approximately 30 weight percent (relative) of the Se was lost during a 72 hour exposure to a temperature of 200°C open to the atmosphere. Because native elemental Se has recently been identified in these rocks, the volatilization of pure Se<sup>0</sup> metal was investigated and shown to occur at 240°C under atmospheric conditions. The routine energy dispersive x-ray fluorescence method of analysis for Se used by the USGS, Branch of Analytical Laboratories, Denver, Colorado, during 1975 to 1984 utilized a sodium peroxide/carbonate fusion for sample decomposition. This fusion exposed the sample to temperatures in excess of 1000°C. The current study shows that values of Se in certain geological materials determined by the method are suspect. Reported values may be as much as 50 percent (relative) too low.

## INTRODUCTION

Thirty-seven oxidizing-heating experiments (300-500°C) were performed in a preliminary study of samples of the Meade Peak Phosphatic Shale Member of the Permian Phosphoria Formation from the southeastern Idaho phosphate district (Desborough and others, 1999). These experiments were performed to evaluate the effects of the chemical/mineralogical components of the samples on the behavior of Se during heating. For example, samples that appeared to have 100-180 ppm of Se associated with pyrite did not lose measurable Se at temperatures below approximately 340°C, whereas some samples with much higher concentrations (300-400 ppm) of Se lost 90-95 percent of their original Se when heated at 300°C for 48-51 hours. The samples with these higher total Se values were also richer in organic carbon (10-23 wt. %), implying that the Se could be associated with organic carbon. These studies were done for a very limited suite of samples, and only 13 samples were from areas with currently active mines. Ore and waste samples subsequently were collected from several active mines in the fall of 1998, and again in June 1999 (Tysdal and others, 1999a; 1999b).

## CHEMICAL, MINERALOGICAL, AND THERMAL STUDIES

Scanning electron microscope (SEM) studies of a polished surface of a sample containing 75-80 ppm Se revealed that small crystals of elemental Se (Figure 1a) were present in sample WPSB 133T from the upper ore zone of the Solutia Enoch Valley mine (Grauch and others, 1999). Additional SEM work on the freshly broken surface of a sample (WPSC157) from the FMC Dry Valley mine indicates that the primary residence of Se in this waste rock is well crystallized, elemental, selenium (Figure 1b; Grauch and others, 1999).

Samples from a 1 foot-thick bed in the upper waste (above the upper ore zone and below the Rex Chert Member of the Phosphoria Formation) from the FMC Dry Valley Mine (Tysdal and others, 1999b) were found to contain as much as 5,000 ppm Se in the least leached inner core zone. The distribution of Se in one sawed slab of this sample (WPSC157H) is shown in Figure 2. The distribution of Se in this slab was determined by

non-destructive energy dispersive X-ray fluorescence analysis as described in Desborough and others (1999). The areas analyzed were 2.2 cm in diameter on solid sawed faces of rock and the distribution of Se in faces of several other slabs from this specimen (WPSC157) was determined. Measured Se concentrations ranged from 200 to 5,500 ppm in more than 40 analyses. Because of the high concentrations determined in this sample, we used it for oxidizing thermal studies to measure the influence of elevated temperatures on Se volatilization. Portions of two of these slabs were crushed and pulverized in tungsten carbide-lined ball mills (with tungsten carbide balls). The pulverized material was sized with stainless steel sieves. For one sample -WPSC153H- two fractions (0.063-0.15 mm and <0.063 mm) were obtained and were exposed simultaneously to thermal oxidizing conditions in the same furnace at temperatures of 240, 260, 280, and 300°C for 48 hours, with Se concentration measurements taken after each thermal treatment. A final exposure to a temperature of 330°C for three additional periods of 48, 67, and 71.5 hours, respectively, was done to maintain temperatures below the pyrite decomposition temperature of 340°C (Desborough and others, 1999). Figure 3 shows the results for these experiments, and illustrates progressive loss of Se with higher temperatures. Initial compositions were determined after air-drying, but are shown as 150°C (to conserve illustration space). Figure 4 shows experiments using a sized sample (<0.063 mm) WPSC157H that contained 2,700 ppm of Se after air drying and before thermal exposures. This illustration shows the progressive loss of Se at oxidizing exposures of 200, 240, 280, 300, and 330°C for the exposure periods indicated. The results illustrate the volatility of Se in these rocks at temperatures in the range of 200-330°C.

Because Grauch and others (1999) identified metallic crystalline Se in SEM studies using an energy dispersive detector to identify Se crystals, we decided to examine the volatility of metallic Se using crystalline, high purity (>99.999 %) Se pellets that weigh about 0.025-0.04 g each. Several experiments were done using the high purity pellets, which were placed in ceramic crucibles upon thermostat controlled hotplates. The temperature of the surface of the inside bottom of the crucibles was measured with a Cole Parmer® Digi-sense thermometer system with digital readout. Volatilization of the metallic Se was observed at a temperature of 240±5°C. An overnight exposure of a 0.027 g pellet of Se to the 240±5°C oxidizing conditions entirely volatilized the Se. All of these experiments in both furnace and hotplate conditions were done under conditions using a forced-air fume hood for withdrawal of any vapors that evolved from the samples exposed to thermal treatments. We caution that others follow this procedure to avoid potential human health hazards when heating Se-bearing rock samples.

Because our studies herein show much higher Se values than had been previously reported for these rocks, we are concerned that previous methods for analyzing similar rocks for Se might be in error. We investigated the method of Se analysis most commonly used in the latter half of the 1970's and early part of the 1980's in our USGS laboratories which was the X-ray fluorescence (XRF) method of Wahlberg (1981). Selenium concentrations considered being of significant interest for rocks, soils, and coals during that period were in the range of about 0.1-500 ppm. The XRF method involved digesting pulverized rock, soil, or coal samples by "fusing with a mixture of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>O<sub>2</sub> " in zirconium metal crucibles with a torch until the mixture of sample plus flux was melted to a liquid. This treatment, under oxidizing conditions,

exposed the sample to temperatures that could have exceeded 1,000°C. The fusion cake was then cooled, “dissolved in distilled water, buffered with NH<sub>4</sub>Cl, and filtered to remove Si and the R<sub>2</sub>O<sub>3</sub> group.” The melting point of sodium carbonate listed by the CRC Handbook of Chemistry and Physics 57<sup>th</sup> edition, 1976, is 851°C (p. B-159). The melting point of Se in the same CRC volume is given as 217°C, and the boiling point is given as 684.9±1.0°C (p. B-153). Our current results indicate that this previously used sample preparation method may have volatilized a portion of any metallic Se present in the rock, soil, and coal samples analyzed for Se.

In a preliminary study of metals of potential economic interest in the Meade Peak Member of the Phosphoria Formation in southeastern Idaho, Desborough (1977) reported Se values as high as 165 ppm in a “Carbon Seam” at the Maybe Canyon mine. The analytical and sample preparation methods used were those of Wahlberg (1981). Fortunately, the remains of the pulverized and homogenized bulk sample were retained and were reanalyzed using the methods and standards of Desborough and others (1999). Results of the reanalysis show that the untreated sample contained about 400 ppm of Se, rather than 165 ppm. The results strongly suggest the loss of Se by volatilization during fusion in the method of Wahlberg (1981) used for the period of about 1975 through 1983 might have volatilized Se before analysis. Consequently, the Se data presented by Desborough and others (1999, Table 1 and Figure 3) for the Pritchard Creek, Caribou Range, locality which were obtained using the method Wahlberg (1981) are probably significantly underestimated. The other Se values given by Desborough and others (1999) are considered acceptable.

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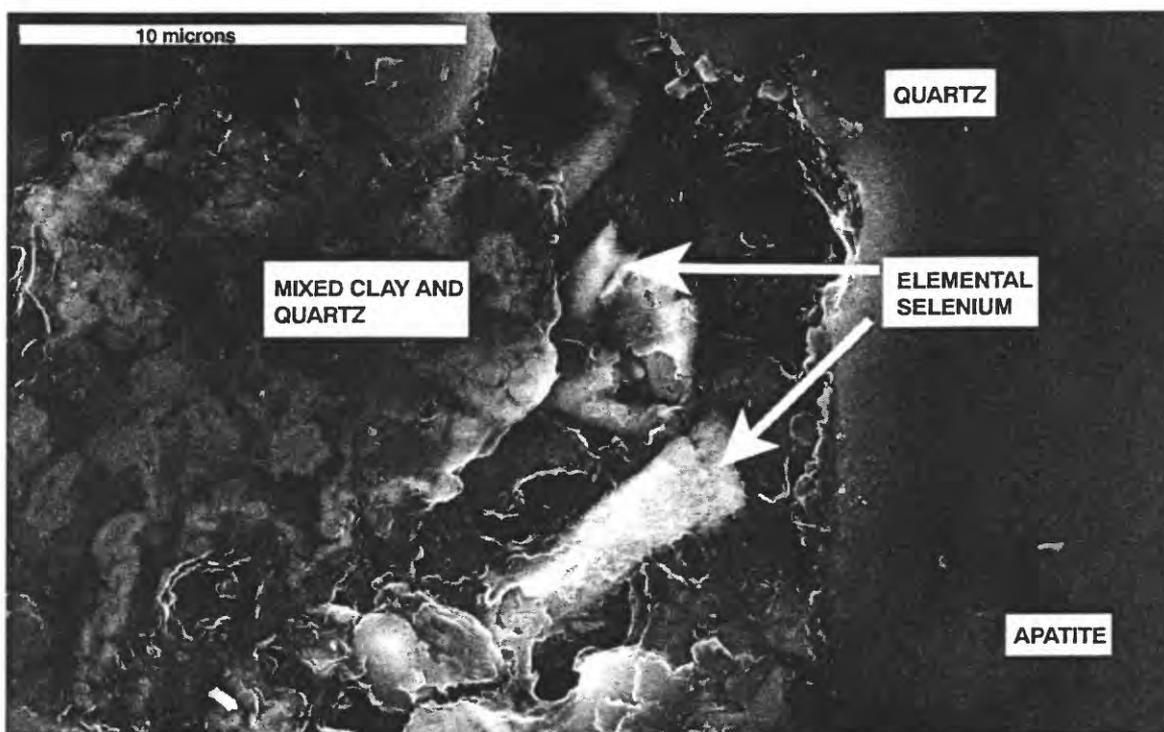


Figure 1 A. Scanning electron microscope image of elemental Se grains in sample WPSB133T from the Solutia Enoch Valley mine. Dark gray is quartz, adjacent lighter gray is apatite.

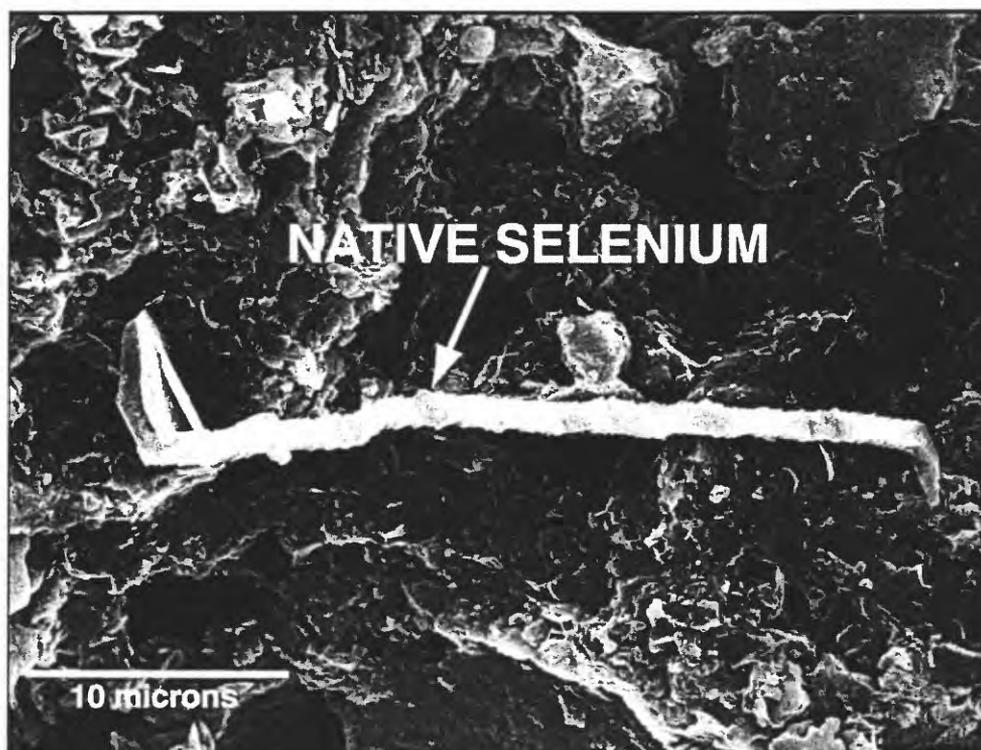


Figure 1 B. Scanning electron microscope image of crystalline elemental Se on a freshly broken surface of sample WPSC157 from the FMC Dry Valley mine.

Three dimensional view of Se concentrations on 11 X11  
cm face of slab WPSC157H

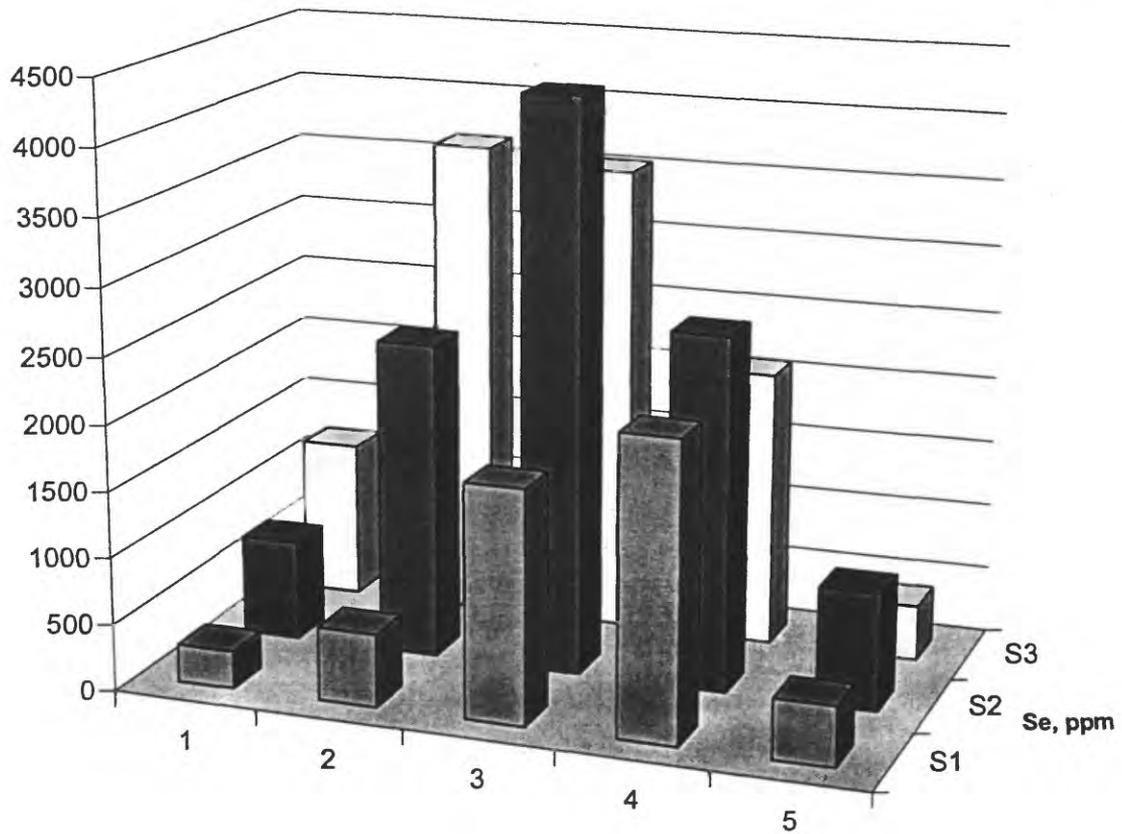


Figure 2. Se concentrations in a 11 X 11 face of a slab of WPSC157H determined by making five analyses parallel to bedding along the lower (S3), middle (S2), and upper (S1) portions.

Cumulative Se loss after each oxidizing thermal treatment for two size fractions of WPSC 153H

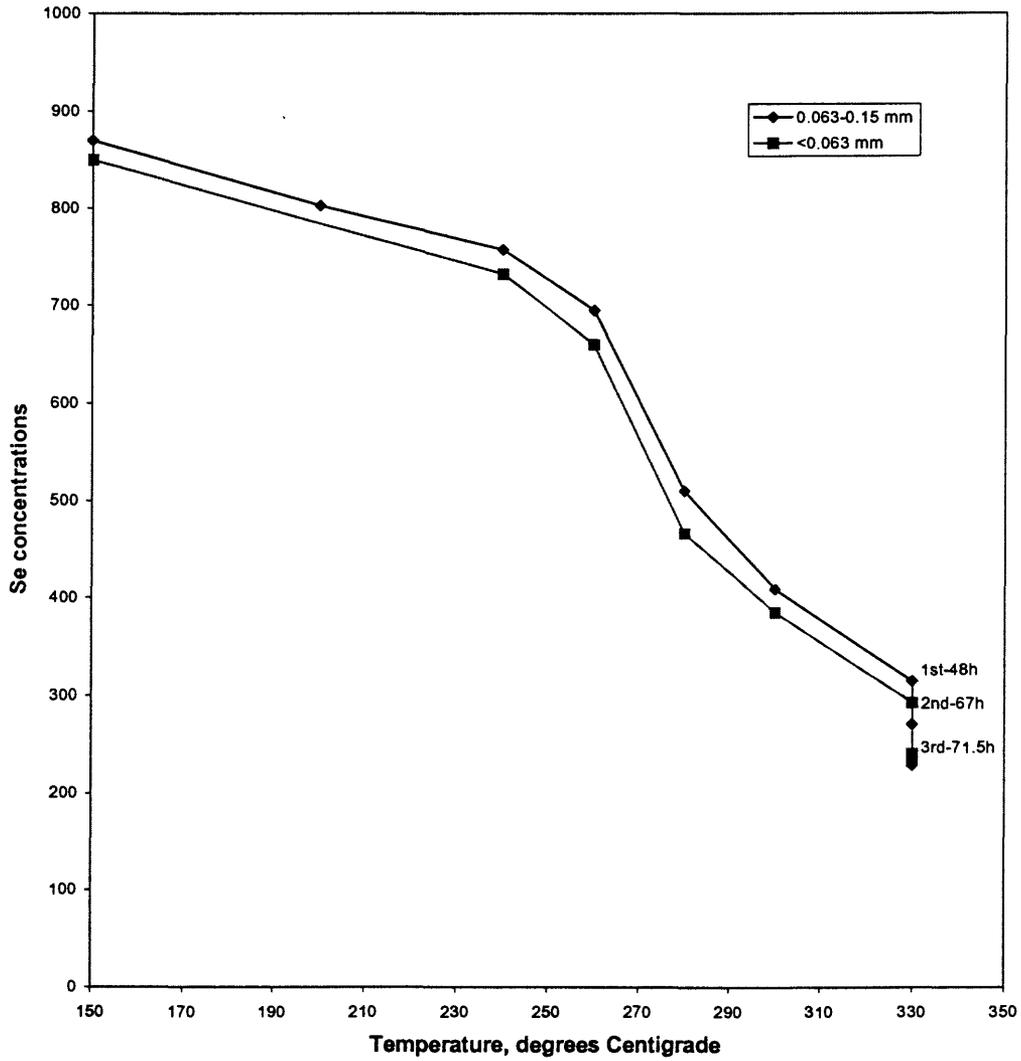


Figure 3. Losses of Se from two size fractions during sequential heating open to the atmosphere.

Oxidizing thermal treatment of 2 g of <0.063 mm  
WPSC157HN. Note 3 exposures at 240

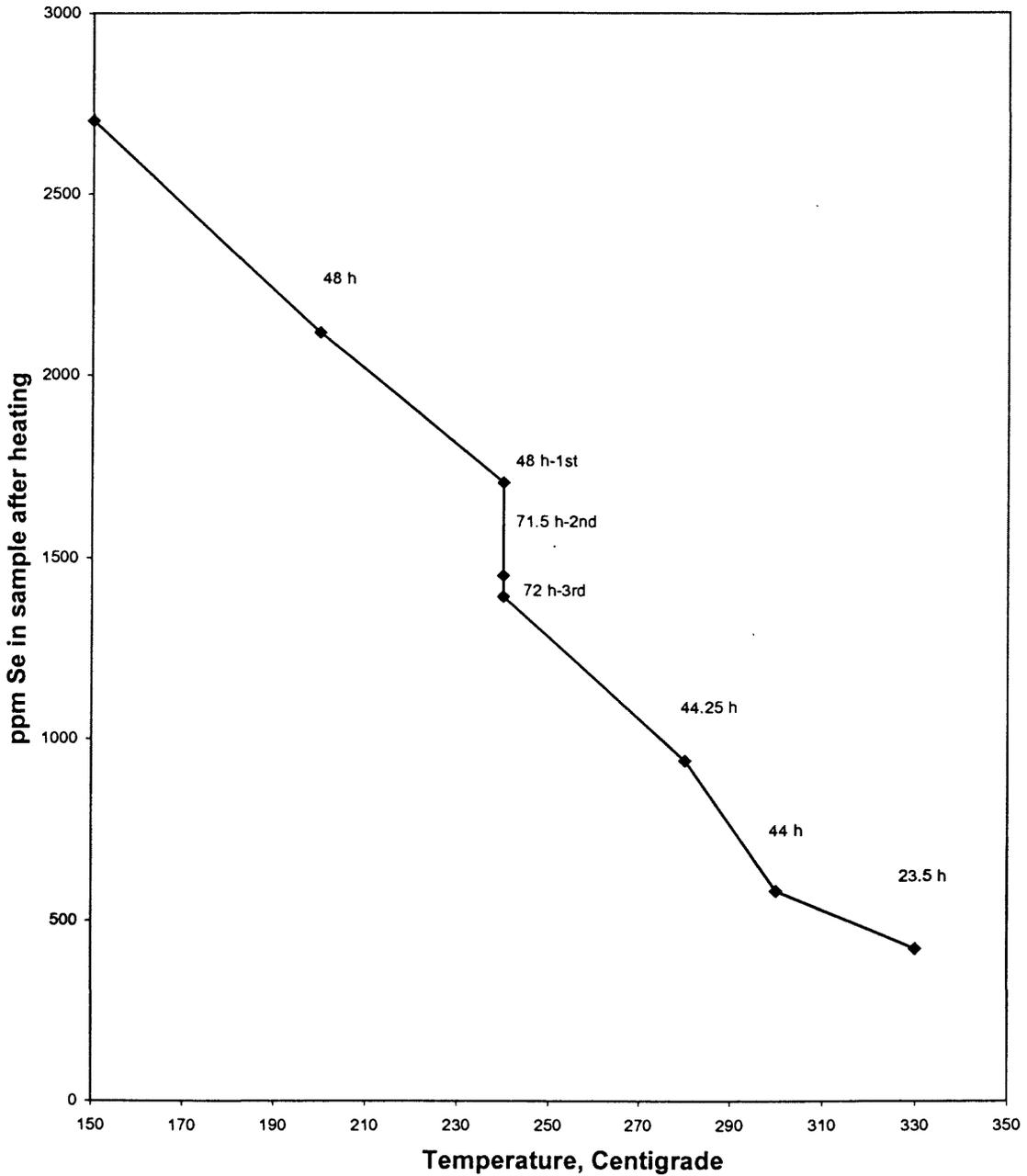


Figure 4. Se losses during heating of a high Se size fraction for several periods of time at different temperatures.