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Chalcogen Elements in Snow: Relation to Emission Source

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■ We have measured the concentrations of S, Se, and Te in samples of 1986 snow and compared our results with those of earlier measurements. We were unable to find any earlier reports on Te in snow, but values of the Se/S concentration ratio in 1986 are about a factor of 6 lower than that in snow and glacial ice of 800 B.C. Measurements on intermediate samples demonstrate that most of the decline in the Se/S ratio occurred during the past 200 years, i.e., since the start of the Industrial Revolution. This temporal change in values of the Se/S ratio probably reflects a shift in the major emission sources—from natural processes such as volcanism and biomethylation to large-scale combustion of fossil fuels.

Introduction

Tellurium (Te) and selenium (Se), usually in association with sulfur (S), are widely distributed in environmental materials such as soils (1, 2), waters (3, 4), and air (5-7). The concentrations of Se and S have also been reported in snow samples collected in Greenland ice sheets (8), in Japan (9), and in Boston, MA (10). Prior to this study, we were unable to find any report on measurements of Te in snow. We initiated a study of chalcogen elements in snow as part of our investigation into the geochemical cycles of Te, Se, and S. The last element has received considerable attention because sulfur oxides are now recognized as the primary culprit of acid precipitation, accounting for about two-thirds of this acidity (11). Since Te and Se routinely occur in association with S in nature, most processes that release S to the atmosphere are also expected to release Te and Se. The concentration of Te in snow is low, and a new analytical procedure was developed that takes advantage of the high sensitivity of atomic absorption spectrometry for the detection of Te after removal of interfering elements by cation exchange (5).

In the work reported here, this analytical procedure was used to obtain new data on the concentrations of Te, Se, and S in snow. Ratios of these elements, e.g., values of Te/S and Se/S, depend on the nature of the emission source and on the atmospheric chemistry of these three members of the Group VIA elements. The advantages of

measuring the concentrations of closely related elements in geochemical studies are well recognized and, in relation to this study (7), could extend our insight into the origin of the Te, Se, and S trapped in snow over the historical period recorded in permanent snow fields.

Experimental Section

Fresh samples of snow were collected during, or immediately after, snowfalls here at Rolla, MO, during the period of February 10 to March 13, 1986. The network of six sampling sites was set up in such a way that the distance of any site from the University of Missouri was about 2-4 miles. The snow was collected in polyethylene bags, transferred to the laboratory to melt, and then filtered to remove any dust or other debris. Each sample was then acidified by the addition of 1 mL of concentrated HNO₃ per liter of melted snow. Next, the volume was reduced to 50 mL by pumping off water vapor with an aspirator at low temperature, 60 °C. The preconcentrated melt was then heated to near dryness, and 1.5 mL of concentrated HCl was added. The HCl reduces Te(VI) to Te(IV), which can be adsorbed onto the cation-exchange column.

The acidity of the solution is reduced to 0.05 N HCl before loading onto a cation-exchange column, 1.2 cm i.d. × 10 cm long. Under these conditions, Te(IV) exists predominately in the form of TeO(OH)⁺ or Te(OH)₃⁺ and is retained quantitatively on the cation-exchange column (5). Other interfering anions are not retained on the column, and Se is released in the first 100 mL of 0.05 N HCl effluent. Te is efficiently eluted from the cation-exchange column with 150 mL of 0.3 N HCl, but most of the interfering metal cations of Cu, Hg, Ni, etc. remain on the column. Yields for the recoveries of Te and Se are each about 92% (5). The 0.05 N HCl portion of the eluant is used for the determination of Se and the 0.3 N HCl portion is used for the determination of Te. Graphite furnace atomic absorption spectrometry is used for the determinations.

Results and Discussion

The concentrations of Te and Se in snow samples collected during the period of February 10 to March 13, 1986, are shown in Table I. The numerical designations in the

Table I. Concentrations and Ratios of Te, Se, and S in 1986 Snow Samples of the Middle U.S.

sample no. ^a	Te, ng/L	Se, µg/L	S, µg/L	Te/S, ×10 ⁹	Se/S, ×10 ⁴
A1	4.3	0.052	0.72	0.60	0.73
A2	3.8	0.042	1.07	0.36	0.42
A3	4.1	0.084	0.79	0.52	1.06
A4	3.5	0.046	0.64	0.55	0.72
A5	5.1	0.053	0.67	0.76	0.79
A6	4.8	0.051	0.74	0.65	0.69
B1	2.8	0.042	0.60	0.46	0.70
B2		0.051	0.97		0.53
B3	3.6	0.048	0.62	0.58	0.77
B4	2.6	0.038	0.34	0.76	1.11
B5	4.1	0.045	0.55	0.74	0.81
C1		0.065	0.74		0.88
C2	5.6	0.060	0.62	0.91	0.98
C3	4.9	0.054	0.69	0.71	0.78
C4	4.4	0.048	0.85	0.52	0.57
C5	5.4	0.061	0.72	0.75	0.85
mean	4.2	0.053	0.71	0.59	0.75

^a Sample A, February 10–11, 1986; sample B, February 23–24, 1986; sample C, March 13, 1986.

Table II. Concentrations and Ratios of Se and S in 1981 Snow Samples of Japan^a

location no. ^b	date	Se, µg/L	S, mg/L	Se/S, ×10 ⁴
A1	Feb 17	0.053	0.65	0.82
A2	Feb 17	0.036	0.50	0.72
B1	Feb 17	0.031	0.84	0.37
B2	Feb 17	0.175	0.88	1.99
C1	Feb 17	0.070	0.67	1.04
C2	Feb 17	0.048	0.71	0.68
D1	Feb 17	0.036	0.78	0.46
E1	Feb 17	0.061	0.53	1.15
F1	Feb 17	0.062	0.75	0.83
G1	March 3	0.030	0.15	2.00
H1	March 3	0.015	0.09	1.67
H2	March 3	0.030	0.15	2.00
I1	March 3	0.060	0.79	0.76
I2	March 3	0.045	0.64	0.70
J1	March 4	0.079	1.01	0.78
K1	March 4	0.035	0.91	0.38
K2	March 4	0.030	0.49	0.61
K3	March 4	0.047	0.98	0.48
mean		0.052	0.64	0.81

^aData from Kobayashi (9). ^bLocations: A, Tokyo; B, Yokohama; C, Kawasaki; D, Kawagoe; E, Machida; F, Oomiya; G, Mitsumine; H, Fuji; I, Nagaoka; J, Naeba; K, Shiga-Kogen.

sample no. refer to up to six collection sites in the vicinity of Rolla, MO, a small town with a population of 13000 that is surrounded by even smaller villages thinly scattered over a farming countryside within a 100-km radius of Rolla. Smelters associated with the New Lead Belt of Missouri are about 120 km east or northeast of Rolla. The largest municipal area within a 160-km radius in St. Louis. This is about 160 km eastnortheast of Rolla, and prevailing winds are from the westsouthwest.

The average concentrations of Te, Se, and S in these local snow samples were 4.2 ng/L, 53 ng/L, and 710 µg/L, respectively, corresponding to average values of Te/S = 5.9×10^{-6} and Se/S = 7.5×10^{-5} . We are unaware of any other measurements of Te in snow, but Tables II and III show the results of measurements of Se and S in snow samples of Japan (9) and the northeastern United States (10), respectively.

The data tabulated in Table II represent snow samples collected in Japan in late winter 1981. The sampling sites

Table III. Concentrations and Ratios of Se and S in 1964–1965 Snow Samples of Northeastern U.S.^a

location	date	Se, µg/L	S, mg/L	Se/S, ×10 ⁴	remarks
1	Dec 18	0.15			falling snow
2	Dec 18	0.09	3.9	0.2	falling snow
1	Jan 10	0.13			falling snow
2	Jan 10	0.16	3.8	0.4	falling snow
1	Jan 16	0.53	1.2	4.4	falling snow
2	Jan 16	0.52	1.4	3.7	falling snow
1	Jan 24	0.14	2.7	0.5	falling snow
2	Jan 24	0.16	1.3	1.2	falling snow
4	Jan 31	0.08	1.5	0.5	ground snow
3	Feb 22	0.25	2.3	1.1	falling snow
3	March 20	0.08	0.9	0.9	ground snow
2	March 20	0.06	0.9	0.7	falling snow
5	March 20	0.12	0.5	2.4	ground snow
6	March 20	0.04	0.7	0.6	ground snow
6	March 20	0.10	1.5	0.7	ground snow
3	March 29	0.10	1.5	0.7	ground snow
1	March 29	0.09	1.4	0.6	falling snow
2	March 29	0.10	1.2	0.8	falling snow
mean		0.16	1.6	1.0	

^aData from Hashimoto and Winchester (10). ^bSample locations: 1, MIT campus roof of Earth Science Building; 2, ground location near 1; 3, Cambridge, near Central Square; 4, Topsfield, MA; 5, Boxford, MA; 6, New Haven, CT, Yale University campus.

are classified into four categories: Tokyo and Yokohama represent major urban areas; Kawasaki and Nagaoka represent industrial cities; Kawagoe, Machida, and Oomiya are suburbs of Tokyo; and the other sites of Mitsumine, Chichibu, Naeba, and Shiga-Kogen are located in the mountain district. The average concentrations of Se and S in the snow samples of Japan were 50 ng/L and 640 µg/L, respectively, and the average value of the Se/S weight ratio is 8.1×10^{-5} . Similarities in the weight ratio and in the concentrations of Se and S in snow samples from Japan and Missouri suggest that Missouri's lead industries have little or no influence on the chalcogen elements' content of the snow samples analyzed in this study.

Table III shows the concentrations of Se and S in snow samples from Massachusetts and Connecticut (10). Most of the samples shown there were collected on the MIT campus in the city of Cambridge, a suburb of Boston (10). The average concentrations of Se and S in these 1964–1965 snow samples were 160 ng/L for Se and 1600 µg/L for S, corresponding to an average weight ratio of Se/S = 1×10^{-4} .

Temporal changes in the atmospheric inventory of Se and S can be seen in the results of Weiss et al. (8) from analyses of samples taken from ice sheets of Antarctica and Greenland. These results are tabulated in Table IV, together with the results of more recent studies.

From a comparison of the results shown in Tables I–IV, it should be noted that the concentrations of Se and S are lowest in the permanent snow fields of polar regions, intermediate in the snow samples from Japan and the central portion of the United States, and highest in the snow samples from the northeastern part of the U.S. Differences in the concentrations of Se and S in the U.S. roughly parallel the present geographic distribution of industrial emission sources and acidity of precipitation (12). However, values of elemental ratios, such as Se/S and Te/S, may show a temporal dependence but little, if any, dependence of geographic location.

For example, the average value of the Se/S ratio that was reported (9) in the 1964–1965 snow samples from the northeastern part of the U.S., Se/S = 1×10^{-4} , is not significantly different from the values reported for the

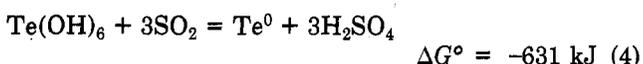
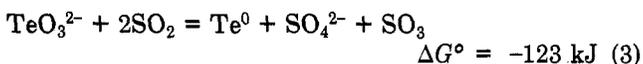
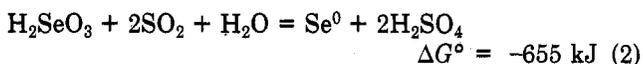
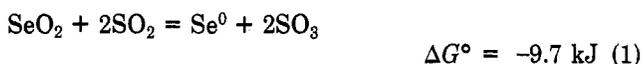
Table IV. Concentrations and Ratios of Se and S in Snow Samples

sample (year)	Te, ng/L	Se, ng/L	S, μg/L	Te/Se, ×10 ⁵	Se/S, ×10 ⁴
800 B.C. ^a		25.5 ± 1.6	56.3		4.5
1724 ^a		14.1 ± 1.6	26.0		5.5
1815 ^a		13.4 ± 2.6	26.7		5.0
1859 ^a		10.1 ± 1.1	34.7		2.9
1881 ^a		7.6 ± 0.3	21.7		3.4
1892 ^a		8.0 ± 0.2	26.0		3.0
1946 ^a		22.0 ± 2.3	37.7		5.9
1952 ^a		11.0 ± 0.2	35.7		3.1
1960 ^a		8.9	41.0		2.2
Fall 1964 ^a		5.1 ± 0.5	38.7		1.3
Dec 1964 ^a		9.7 ± 1.1	72.7		1.3
Winter 1965 ^a		14.2 ± 2.2	98.0		1.5
Spring 1965 ^a		8.0 ± 0.2	71.0		1.1
Summer 1965 ^a		8.7 ± 0.3	53.7		1.6
1964–1965 ^b		160	1600		1.0
1981 ^c		50	640		0.81
1986 ^d	4.2	53	710	0.59	0.75

^aData from Weiss et al. (8). ^bData from Hashimoto and Winchester (10). ^cData from Kobayashi (9). ^dThis work.

Se/S ratio in ice sheet samples (8) of the 1964–1965 period. However, it can be seen from Table IV that the value of the Se/S ratio has gradually decreased in glacial ice over the past 150 years, except for one anomalously high value reported for a 1946 sample.

Indirect information on the atmospheric chemistries of Se and S can be inferred from the data shown in Table IV. It can be seen there that the Se content of glacial ice has been relatively constant over the past 200 years, but the concentration of S in these glacial ices increased in most of the post-1960 samples. This observation suggests that fuel combustion has caused a greater fractional increase in the atmospheric inventory of water-soluble S than in water-soluble Se (13). Direct measurements on coal-fired plant emissions provide supporting evidence for this (14). From the absence of tetravalent Se in fly ash or slag, it appears that most of the Se (and the more easily reduced Te) in the vapor phase, fly ash, and slag exists as insoluble elemental Se (and Te). The formation of elemental Se and Te can be described by



In other words, excess SO₂ produced in the combustion process acts as a reducing agent, thus favoring production of the species shown on the right-hand side of the above equations.

It should be stressed that many other species, e.g., the OH radical, may react with the chalcogen elements in air. For example, Seinfeld (15) estimates a 24-h average of 0.7% per h for the rate of oxidation of SO₂ with the OH radical in air. He estimates that the winter rate is somewhat lower because of the lower concentration of OH.

Since Se⁶⁺ is the most thermodynamically stable oxidized form of Se, the Se⁴⁺ that is released to air will undergo oxidation to Se⁶⁺ (16). The Se⁴⁺/Se⁶⁺ ratio will thus decrease with distance from the emission source. However, Te⁴⁺ is more thermodynamically stable than Te⁶⁺, so that

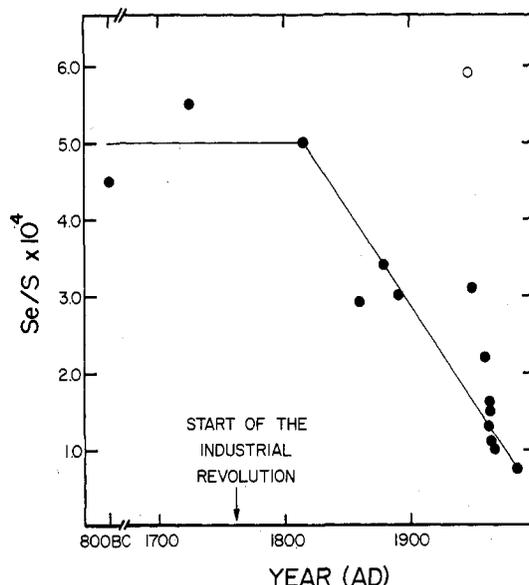


Figure 1. Concentration ratios of Se and S in snow samples over the period from 800 B.C. to A.D. 1986.

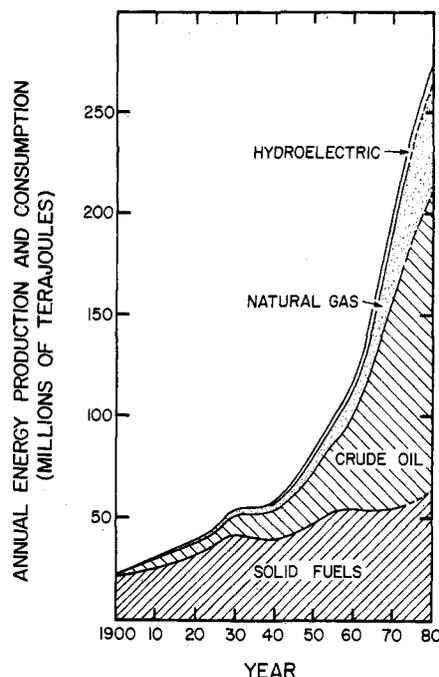


Figure 2. Changes in the major energy sources in the U.S. during the twentieth century.

the Te⁴⁺/Te⁶⁺ ratio will increase with distance from the emission source. Equations 1–4 show that processes which generate high concentrations of SO₂, e.g., fuel combustion or ore smelting, may cause reduction of the heavier chalcogen elements to Se⁰ and Te⁰.

Temporal changes in the concentration ratios of chalcogen elements in snow are tabulated in Table IV and shown graphically in Figure 1. The unexpectedly high value of the Se/S ratio for the 1946 glacial ice is shown by the unfilled symbol and was not considered in drawing the trend lines in Figure 1. Fuel combustion is now recognized as a primary source of S pollution, and as shown in Figure 2, the twentieth century has been a time of increasing utilization of fossil fuels (17). By 1960, an estimated 21 million tons of SO₂ pollution could be attributed to the combustion of coal and fuel oil, with coal alone contributing 85% of the SO₂ pollution (18). More recently, it was estimated that sulfur oxides accounted for two-thirds

of the acidity of precipitation in 1985 (19).

In contrast to fuel combustion, there are low-temperature biological processes that release chalcogen elements to air by biomethylation. For example, fungi of several genera produce $(\text{CH}_3)_2\text{Se}$ from inorganic selenium (20, 21), and rats fed selenite and selenate salts exhaled this same volatile selenium compound, $(\text{CH}_3)_2\text{Se}$ (22). Microorganisms in lake sediments have been found to convert natural selenium compounds there to volatile selenium compounds such as dimethyl selenide, dimethyl diselenide, and another unidentified selenium compound (23). On the other hand, fuel combustion and natural high-temperature processes, such as volcanism, produce SO_2 that acts to reduce the oxides of Se and Te that are initially generated by these processes.

Thus, the decline in values of the Se/S ratios since the start of the Industrial Revolution, as shown in Figure 1, probably reflects a shift in the major emission sources of the chalcogen elements in air. Prior to A.D. 1850, natural processes such as volcanism and biomethylation most of the chalcogen elements that were deposited in glacial ice. The Se/S ratio of the water-soluble component differed for these two sources, being lower in the volcanic emissions because the abundant SO_2 there reduced most selenium oxides to elemental Se. The scatter of values of the Se/S ratio in glacial ice prior to A.D. 1850 might reflect natural variations in the relative proportions of biomethylation and volcanism as emission sources. Since the start of the Industrial Revolution, fuel combustion has played an increasingly important role as a major emission source for chalcogen elements, as shown in Figure 2. This is probably responsible for the decline in values of the Se/S ratio that is shown in Figure 1.

The value of the Se/S ratio in bulk aerosols of this area, $\text{Se/S} = 8.7 \times 10^{-4}$ (7), is about a factor of 10 higher than that in snow but similar to the value of the Se/S ratio observed in aerosols from other locales, e.g., $\text{Se/S} = 10 \times 10^{-4}$ in St. Louis, MO (24), $\text{Se/S} = 9.6 \times 10^{-4}$ in Steubenville, OH (24), and $\text{Se/S} = 8.9 \times 10^{-4}$ in Buffalo, NY (25). Solubilities of the oxides of the chalcogen elements increase in the order $\text{Te} < \text{Se} < \text{S}$, and this preferential solubility of the sulfur oxides is probably responsible for the lower values of the Se/S ratio in snow than in aerosols.

Values of the Se/S ratio in volcanic ash and in fly ash from coal combustion (7) are similar to those observed in modern aerosols (7, 24, 25), but atmospheric chemistry has modified the Se/S ratio in snow from that of the emission source.

Conclusions

Values of the ratios Te/S and Se/S depend on the nature of the emission source and on atmospheric chemistry. Values of the Se/S ratio in snow in 1986 are about a factor of 6 lower than that reported in glacial snow of 800 B.C. The results of this and other studies of chalcogen elements in snow (8-10) demonstrate a temporal decline in values of the Se/S ratio in snow over the past 200 years. We suggest that this change in values of the Se/S ratio may have been caused by increased usage of fossil fuels since the start of the Industrial Revolution.

Registry No. Te, 13494-80-9; Se, 7782-49-2; S, 7704-34-9.

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