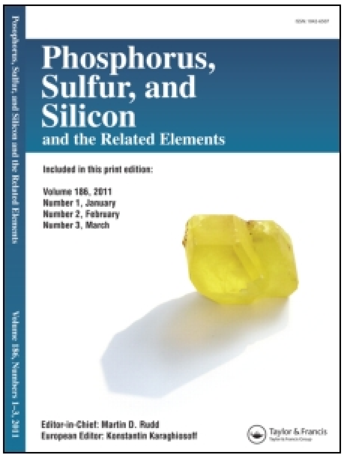

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SELENIUM CONTENT OF NATURALLY OCCURRING ELEMENTAL SULFUR, OF INDUSTRIALLY PRODUCED SULFUR AND OF THE MINERAL SELENSULFUR[1]

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SELENIUM CONTENT OF NATURALLY OCCURRING ELEMENTAL SULFUR, OF INDUSTRIALLY PRODUCED SULFUR AND OF THE MINERAL SELENSULFUR[1]

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Nineteen samples of naturally occurring elemental sulfur or "selensulfur" were investigated by neutron activation analysis, Raman spectroscopy and high-pressure liquid chromatography. The natural sulfur samples contained between < 1 and 682 ppm selenium while nine industrially produced sulfur samples showed Se contents of $\leqslant 4$ ppm. The existence of a mineral "selensulfur" consisting of only S and Se in comparable concentrations seems doubtful. Elemental sulfur minerals containing > 150 ppm Se were found to be yellow at 77 K while pure ordinary sulfur (α-S_8) is colorless at this temperature.

INTRODUCTION

The atomic ratio of sulfur and selenium both in the universe and in the earth's crust amounts to approximately $10^4:1$,[2] and many sulfidic ores contain selenium[3] which is recovered either during the metallurgical roasting process or from the anode slimes during the electrolytic refining of copper.[4] However, sulfur frequently also occurs in the elementary state consisting of S_8 molecules and believed to be formed from either sulfides or H_2S by oxydation, from pyrite (FeS_2) by thermal decomposition, or from sulfates ($CaSO_4$) by bacterial reduction via several intermediates. Earlier reports on the Se content of volcanic sulfur deposits, including so-called "selensulfur",[5] showed concentrations of up to 1% Se;[3,6-8] the frequently cited highest value of 5.18% reported in 1916 by Brown[6] for a sample from Kilauea (Hawaii) has, however, never been confirmed. In some of these reports the analytical procedure has not been published.

We have determined by neutron activation the selenium concentration in 15 naturally occurring crystalline sulfur samples from various localities in Europe (including Turkey) and North America (including Hawaii) as well as of 4 samples of "selensulfur" from the island of Vulcano (Italy). In addition, 9 samples of industrially produced elemental sulfur based on sulfur sources of various types have been investigated.

RESULTS AND DISCUSSION

The results for the naturally occurring sulfur deposits are shown in Table I (samples nr. 1–15). Most samples contained only trace amounts of Se ($\leqslant$ 3 ppm) and there is clearly no relationship between color and Se content. Some brown or even red-brown samples (e.g., nr. 3 and 6) exhibited very low Se concentrations ($\leqslant$ 2 ppm) while the yellow crystals of sample nr. 10 showed a relatively high Se content of 25 ppm. For one sample a substantially higher selenium concentration of 251 ppm was found and this result may be significant not only for potential industrial users of such sulfur deposits but also for the understanding of the metabolic pathway of sulfur in bacteria living on either elemental sulfur or related reduced sulfur compounds.[9a]

According to older reports,[5] the mineral "selensulfur" or "volcanit" occurring on the Liparic Islands as well as on Hawaii is characterized by unusually high selenium concentrations. However, Garavelli[7] analyzed 5 Italian samples for S, Se, Te, As and unsoluble components and found only between 0.09 and 0.82% Se with sulfur (60–76%) and arsenic (38–21%) as the major constituents. The four samples of Italian selensulfur analyzed in this work and obtained from different sources (see Table I, nr. 16–19) seem to support these results. The selenium content of 150–680 ppm in these samples does not justify the name selensulfur, and it is obvious from our findings that selenium concentrations of 1000 ppm (0.1%) in natural elemental sulfur are obviously very rare. On the other hand, trace amounts of Se were present in many if not in all sulfur samples investigated.

In addition to the elemental analysis the samples nr. 2, 13 and 16 through 19 of Table I have been analyzed by Raman spectroscopy. In the last five samples (nr. 13, 16, 17, 18, 19) only the lines of orthorhombic α-S_8[10] were observed and no indication for SeS bonds could be detected which is in agreement with the very low selenium content (250 ppm Se corresponds to one molecule of SeS_7[11] per 1250 molecules of S_8 or two SeS bonds per 10^4 SS bonds). Sample nr. 2 showed in addition to the strong α-S_8 lines weak and broad features of unknown origin near 280 cm^{-1} and in the region 320–350 cm^{-1}. Furthermore, samples nr. 6 and 18 were analyzed by reversed-phase HPLC which has recently been used to separate and identify both homocyclic sulfur molecules and cyclic seleniumsulfides Se_8S_{n-8} with $n = 1$–7.[11,12] However, only S_8 and no seleniumsulfides or other compounds were found even with a very high instrument sensitivity.

Finally, nine samples of commercially available elemental sulfur were analyzed by neutron activation including formed sulfur (from the Prill, Procor and Sandvik processes) produced by continental European oil refineries and natural gas plants (Claus sulfur), polymeric sulfur (Crystex [based on Spanish $BaSO_4$]), Crosor [based on Claus sulfur from Algerian crude oil and natural gas], high-purity sulfur (Fluka), sulfur "DAB 6, sublimed" (Merck) and Frasch sulfur (Grand Isle, Louisiana, USA). Eight of these samples contained less than 1 ppm Se; only the Merck sulfur had a concentration of 4 ppm Se.

We conclude that elemental sulfur produced and used by the chemical industry does not contain significant amounts of selenium while certain naturally occurring sulfurs do.

TABLE I

Naturally occurring sulfurs and selensulfurs, their selenium content as determined by neutron activation analysis and their colors at 293 K and 77 K.

Sample	Locality	Appearance at 293 K	Se content (ppm)	Color at 77 K
1. sulfur[a]	Baja California	yellow crystals	< 1	colorless
2. sulfur[a]	Col. County, USA	orange-yellow crystals	251	yellow
3. sulfur[a]	Racalmuto, Sicily	brown-yellow crystals	2	pale rosé
4. sulfur[a]	Ciauciana, Sicily	large yellow crystals	< 1	colorless
5. sulfur[a]	Sicily	yellow and brown-yellow cr.	< 1	almost white, pale brownish hue
6. sulfur[a]	Agrigent, Sicily	red-brown cryst. mass	< 1	brown
7. sulfur[a]	Perticara near Rimini	dirty-yellow crystals	< 1	colorless with dark spots
8. sulfur[a]	hot springs at Aachen	grayish-yellow powder	< 1	colorless
9. sulfur[a]	Lüneburg near Hannover	dirty-yellow crystals	< 1	colorless with dark spots
10. sulfur on anhydrite[a]	Moosegg near Salzburg	yellow crystals	25	colorless
11. sulfur[a]	Kalinka, Hungary	green-yellow crystals	< 1	colorless with dark spots
12. sulfur on gypsum[a]	Cubukdage-Tekkehaman, Turkey	brown-yellow crystals	3	almost colorless, pale brownish hue
13. sulfur[b]	Racalmuto, Sicily	yellow crystals	$\leqslant 1$	colorless
14. sulfur[c]	Mauna Loa, Hawaii	yellow solid	< 1	almost colorless
15. sulfur on limestone	Jackson Hole, Utah, USA	yellow crystals	< 1	colorless
16. selensulfur 1[d]	Vulcano Island, Italy	yellow powder	386	pale yellow
17. selensulfur 2[d]	same	yellow mass	147	yellow
18. selensulfur 3[d]	same	orange-yellow mass	682	yellow
19. selensulfur[e]	same	yellow powder	425	yellow

Sample sources: a) Institut für Mineralogie und Kristallographie, TU Berlin;
b) Mineralog.-Petrograph. Institut, Univ. Hamburg;
c) Prof. R. Greeley, Deptm. of Geology, Univ. of Arizona, Tempe (USA)
d) Institut für Mineralogie, TH Darmstadt;
e) Institut f. Mineralogie u. mineral. Rohstoffe, TU Clausthal.

THE SURFACE COLOR OF JUPITER'S SATELLITE IO

The surface of Jupiter's satellite Io is believed to be largely covered by elemental sulfur as a result of a number of very active sulfur volcanoes.[13] However, since the thermodynamically stable sulfur allotrope, α-S_8, as well as polymeric sulfur (the likely products of sulfur volcanoes by analogy to sublimation in the laboratory) are colorless at Io's surface temperature of 120 ± 10 K, the yellow and brownish surface colors raise the question what kind of sulfur or sulfur-rich compound is actually present.

Recently the impact of the Sun's radiation on the color of various sulfur allotropes cooled to 77 K has been investigated. It was observed that an intense yellow color is rapidly produced in both α-S_8, polymeric sulfur and other sulfur crystals when irradiated with < 400 nm radiation, thus providing an explanation for Io's yellow surface areas.[14]

However, the data in the last column of Table I provide an alternative explanation: in contrast to pure α-S_8 the sulfur minerals consisting of S_8 molecules and containing between 150 and 680 ppm selenium (probably as SeS_7 molecules[11]) are yellow at 77 K (samples nr. 2, 16, 17, 18, 19; immersed into liquid nitrogen). Therefore, the sulfur-rich material covering parts of Io's surface may be yellow at 120 K due to a small selenium content in the cosmic abundance ratio of the two elements of $10^4:1$ which is equivalent to 250 ppm Se.

EXPERIMENTAL

To determine the element selenium by instrumental neutron activation analysis the nuclear reactions $^{74}Se(n,\gamma)^{75}Se$ (half life 120d) or $^{76}Se(n,\gamma)^{77m}Se$ (half life 17.5s) with thermal reactor neutrons are suitable. However, for non-destructive analysis of minute amounts of Se in a sulfur-matrix the formation of a high radiation background from the activation products ^{35}S and ^{37}S have to be taken into consideration. The measurements of the radionuclide ^{77m}Se after short time irradiation (1 min) has the advantage of a higher activity ratio Se-77m/S-37 = $2.4.10^5$ when compared with the ratio Se-75/S-35 ~ 16 after long time irradiation ($\geqslant 5$ d). Therefore the samples were analyzed using a fast pneumatic transport system especially designed for trace element determination by activation analysis with reactor neutrons.[15, 16] The thermal neutron flux density at the irradiation position in the research reactor BER II was about 1.5×10^{13} n $cm^{-2}s^{-1}$.

Samples and standards were irradiated for 20 s and after a waiting time of 0.5 s their γ-spectra was measured with a coaxial Ge(Li) detector for 30 s. The γ-line at 161.6 KeV was used to identify the radionuclide ^{77m}Se and the mass of selenium was on-line evaluated by means of an Intertechnique IN 90 computer.

The sample masses analyzed ranged from 20 to 120 mg and the corresponding lower limit of detection was found to be 0.1 μg Se. The limit of quantitative determination is in the range of 1 mg/kg (standard deviation $\leqslant 10\%$).

For details of the Raman spectroscopic and HPLC analysis see ref. [13] and [14], respectively.

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