

USSR Tellurium (and Selenium)

Sindeeva, N. D. "Selen i Tellur v Mestorozhdeniyakh Razlichnykh Geneticheskikh Tipov" ("Selenium and Tellurium in Deposits of Different Genetic Types"). Izv. Akad. Nauk, Ser. Geolog, 1958 (5): 78-94. October 24, 1958.

These two dispersed minerals, selenium and tellurium, form 37 and 40 independent minerals respectively. Their minerals may be formed in any stage of the ore-forming process, from the magmatic to the exogenic. Also, the bulk of selenium may be captured by supergenic sulfides. Independent Se minerals are formed, as a rule, only where sulfur (or sulfides) are deficient.

Te tends to form minerals with Au, Ag, Pb, and other heavy metals; its dispersion in or admixture to sulfide minerals is generally insignificant.

In practice, both Se and Te are recovered economically from polymetallic ores of different kinds.

In practice, the data on Se and Te reserves are so scarce as to offer no basis for estimation of their potential values. Also, there has been no production of these metals from some of their deposits (in the USSR) in which they are sufficiently abundant to be economic. Hence, the generalized character of this report.

Types of Deposits

(1) Magmatic. Chiefly pyrrhotite-chalcopyrite-pentlandite; Se dispersed in sulfides; independent minerals of Te are present; disseminated ore bodies and breccias at the bottom of intrusives; transverse veins; basic and ultrabasic rocks associated with the intrusives; pre-Paleozoic, rarely younger. Very large deposits, e.g. Noril'sk, Pechenga, Monchegorsk, Sudbury.

(2) Volcanic. Native sulfur; Se and Te as crystals mixed with sulfur; flows and veins; generally small deposits, e.g. Kamchatka, the Kuriles, the Hawaii. (Selenites, selenates, native Se in volc. tuffs and bentonites).

(3) Hydrothermal (a) Quartz-wolframite-bismuthite. Te minerals present; Se is isomorphous in sulfides. Veins; rarely; network of veins, stocks, pipes; acid and ultra-acid granites; Paleozoic and Mesozoic; no data on size. Examples: Belukha, Bukuka (Trans-Baikal), Karaoba (Kazakhstan).

(b) Cassiterite-quartz-sulfide. Independent minerals (tetradymite, jessite, calaverite, altaite, guanahuitite, platinite); veined zones, veins, lenses, brecciated zones); acid and ultra-acid rocks; Mesozoic; no data on size; examples: Nevskoe, Ingoda, Sokhondo.

(c) Chalcopyrite-molybdenite. Se dispersed, chiefly in molybdenite; Te minerals may be present; networks of veins, vein zones, zones of dissemination; rarely quartz-ore (Se, Te) veins; moderately acid granites; Tertiary. Large deposits, e.g. Kadzharan, Dastakert, Agarak, Paragachaisk.

(d) Pyrite. Se dispersed in sulfides; Te minerals present; Lenses, ore beds, irregularly shaped bodies; in effusive rocks; probably related to subvolcanic intrusions. Large and very large deposits (Paleozoic-Mesozoic), e.g., Blyava, Sibai, Dagtyarka in Ural and Nikolaevskoe in Altai.

(e) Cobaltite-selenide-telluride. Se and Te minerals (tetradymite, hessite, crennerite, claustolite, guanahuitite); networks of veins along major fissures, possibly veins; moderately acid granites; Mesozoic; large deposits, e.g. Verkhe-Seimchanskoe, Vetrovoe, Volochek, Akdzhil'ga.

(f) Selenide. Se minerals (blockite, naumanite, claustolite, etc.); veins of siderite-hematite-barite; may or may not be related to intrusives; Tertiary, Paleozoic; generally small, e.g. Bolivian and German deposits (Pacahaca, Tilkerode, Lehrbach, Sorge, San Andreasberg).

(g) Nasturane-selenide. Se and Te Minerals (selenides of Cu, Pb, Hg, Ag, Bi and tellurides of Ag and Ni); veins; acid and moderately acid rocks; Paleozoic-Proterozoic; probably large. e.g. Catanga, Atabaska.

(h) Gold-Arsenopyrite-tourmaline. Te minerals present, as a rule; isomorphous admixtures of Se; mineralized quartz veins and vein networks; acid rocks (possible also andesites--VPS); no data on size; pre-Combrian, Paleozoic, e.g. Kochkar' (S. Ural), Sovetskii Rudnik (Yenisei Range), Kommunar (Mariinsk Taiga).

(i) Quartz-gold. Te minerals (calaverite, altaite, hessite, tetradymite); Se as isomorphous admixture in sulfides) regular and consistent veins; acid, moderately acid, and (rarely) alkali rocks; Meso-Cenozoic, Paleozoic; size obscure but may be large, e.g. Berezovsk (Ural), and--in Kazakhstan--Dzhelambet and Stalinskoe; also Kalgoorlie.

(j) Gold-silver-quartz-odularite. Se and Te minerals; Au, Ag, Bi tellurides and Ag, Pb selenides; vein networks; in effusive rocks; apparently related to subvolcanic intrusions; Tertiary; size obscure and may be large, e.g. in Sumatra (Redjang-Labong) and Nagyag, Rumania.

(k) Galena-Sphalerite-Quartz-Carbonate. Te minerals; Se isomorphous in sulfides; veins, lenses, metasomatic bodies; related paragenetically to small granitic intrusions; deposits may be in (a) granites, shales, etc., (b) volcano genic-sedimentary beds, (c) carbonate rocks. No data on size of deposits; may be large, e.g. Sadon, Zavodinskoe, Zyryanovskoe, Smirnovskoe, Alpine, Cimmerian, Varissian.

(l) Cinnabar-antimonite. Independent Se and Te minerals; beds, veins, etc.; related to acid granitoids and their alkali derivatives; no data on size which is probably small, e.g. Kwei-Tshou (China), Khaidarkhan (Central Asia); Quaternary-and younger(?).

(m) Carnotite-black. Native Se and Fe, Cu, Pb, Ag selenides; Te not characteristic; beds, metasomatic bodies; reserves of Se may be appreciable, e.g. the Colorado Plateau; Paleozoic-Mesozoic.

(n) Exogenetic. (a) Fa gossan type. Dispersed native Se and Te; iron gossans over sulfides; reserves and size may be appreciable, e.g. Maikain, Kul'yur-Tau, Buribai, Blyava, Chudak.

(b) Gold-telluride. Te minerals; placers; small, e.g. Verkhnyaya Angara, Pad'Khorogocha, Malaya Chirka.

Values

(1) Small deposits, in native sulfur (poorly known, eg.):
Paramushiro Island ___ 0.19% Se; 0.025% Te. Kunashir Island (at Medeleev Volc.) ___ 0.12% Se; 0.001% Te. Elsewhere, in the Kuriles, ___ up to 0.19% Se, up to 0.025% Te.

(2) In pyrites ___ up to 0.0072% Te; up to 0.0063% Se.
In molybdenites ___ up to 0.0053% Te; up to 0.03% Se.
In chalcopyrites ___ up to 0.0031% Te; up to 0.01% Se.
(No data on others).

QUALITATIVE IDENTIFICATION OF TELLURIUM
and/or
SELENIUM IN SOIL SAMPLES

This method of identifying tellurium and selenium was designed to be performed with a minimum of equipment, reagents and separations so that field testing of samples might be possible. By this procedure, a combined concentration of 60 ppm. of Te and/or Se can be positively detected. One test is specific for Te, and the other for both Te and Se. If both tests are made on the same sample, and on approximately the same amounts, a fair estimate can be made of the amount of each of these two elements present.

Approximately 250 mg. of the powdered sample is boiled in a porcelain micro crucible with 3-4 drops of 30% hydrogen peroxide and 4-5 drops of concentrated hydrochloric acid. This process is repeated two or three times, or until a fair portion of the sample has dissolved. The contents of the crucible are then evaporated to dryness in order to decompose all traces of H_2O_2 in the acid solution. The residue is then taken up in 5-6 drops of concentrated HCl, warmed to aid dissolution, then diluted with water to 5-6 ml. in the crucible.

The solution is then made alkaline by the addition of 12-15 drops of 20% NaOH, and stirred by the addition of about 1 ml. of water from a jet. The total volume should now be about 7 ml., filling the crucible approximately to the $3/4$ level. The hydroxides of iron, nickel, copper, aluminum, etc., should be allowed to settle for a few minutes, so that several ml. of clear, alkaline solution can be withdrawn with a medicine

dropper without sucking up the precipitates. Each half-filled dropper holds about $3/4$ of 1 ml. At least two droppers (preferably three if possible) half-filled, should be transferred to each of two clean crucibles. If tellurium alone is to be identified, three or four droppers full can be transferred to but one crucible.

Tellurium --I

Evaporate the clear alkaline solution ($1\frac{1}{2}$ -3 ml.) to just short of dryness. Remove from heat and add one drop of 20% NaOH, and let cool for a minute or two. Swirl slightly to mix, adding a drop of water if necessary. Then add one drop of the stannous chloride solution. An immediate green-black precipitate indicates an excess of $4\mu\text{g}$ Te in the test. Smaller amounts may take as long as two minutes to form. A positive test can be expected by two minutes if as much as $1.4\mu\text{g}$ Te is present in the test. The floating, creeping black precipitate is tellurium metal. A considerable excess of selenium does not interfere.

Selenium plus Tellurium --II

The second crucible containing $1\frac{1}{2}$ -3 ml. of clear alkaline solution is acidified by the addition of 3 or 4 drops of 1:1 H_2SO_4 . To this is then added $5\mu\text{10}$ mg. of sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$). The crucible contents are then slowly concentrated by evaporation.

Moderate amounts of Se appear first as a reddish-brown ppt., then Te as a grey through black ppt. as the volume diminishes. If either of these two elements is present, it will appear by the time the volume is reduced to 2-3 drops. A minimum of $2\mu\text{g}$ of Te or of Se can be seen

easily. If the red color is not obscured by black, essentially only Se is present. A half and half mixture is as black as is Te alone.

By comparing tests I and II, the relative amounts of these two elements can often be judged. If Te alone is sought, as much clear alkaline solution as can be withdrawn is added to but one crucible, and Test I is made on it. This will increase the sensitivity two-fold for the test of Te as compared to making both tests. A blank and a control test or two should be made in each batch. If a third of the solution is withdrawn and used in Test I, a positive test should result from soils containing as little as 30-35 ppm. Te.

Equipment

Hot plate or similar source of heat
Medicine droppers, 20-30 each
Porcelain crucibles, 10 ml (Coors size O), several dozen
Spatula
Fine stream wash-bottle
Dropping bottles, 5-6

Reagents

30% hydrogen peroxide (perhydrol) caution!!
Hydrochloric acid, concentrated
Sulfuric acid, 1:1 by volume
Sodium hydroxide, 20% solution
Stannous chloride, crystals (see below)
Sodium hypophosphite, crystals (see below) ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)

Stannous chloride solution is made as follows: 1 gm. of crystalline SnCl_2 dissolved in 1 ml. of conc. HCl, then diluted to 20 ml. with water. A tiny bead of metallic tin can be added to keep this solution reduced. This then should be stable for a week or more at room temperature.

Considerable care should be exercised when handling 30% H₂O₂ to be sure that it does not contact any oxidisable material, particularly organic material. This strength produces a very painful, burning sensation on the skin, producing a white spot that can easily be seen and washed. Its burn is painful, but otherwise not dangerous. It should be kept in a vented and spill-proof bottle. For the tests described here 10% H₂O₂ will suffice, so the 30% reagent can be used full strength, or diluted up to three volumes and used with accordingly larger additions to the sample. The 10% H₂O₂ is much easier to handle, but the above precautions should still be observed.

Sodium hypophosphite must be kept both dry and moderately cool. Take only a little at a time from the reagent bottle, and immediately replace the bottle cap securely to avoid spontaneous ignition of the moist reagent.