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Contrasting Fluids in the Svetlinsk Gold-Telluride Hydrothermal System, South Urals

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Abstract: The large gold-telluride Svetlinsk deposit (~135 t Au) is considered to be a nontraditional one in the Urals and its origin is debated. A specific feature of the deposit is the abundance of various tellurides, such as tellurides of Fe, Ni, Pb, Sb, Bi, Ag, and Au. The new data of microthermometry, Raman spectroscopy, LA-ICP-MS, and crush-leach analysis (gas and ion chromatography, ICP-MS) for fluid inclusions as well as O-isotope data for quartz were obtained for the construction of PTX parameters of ore-formation and fluid sources in the deposit. Mineralisation was formed at a wide range of temperature and pressure (200–400 °C, 1–4 kbar) and from contrasting fluids with multiple sources. At the early stages, the magmatic fluid evolved during its ascent and phase separation and the fluid derived from the host rock decarbonation and dehydration were involved in the hydrothermal system. In addition, mantle-derived fluid might be involved in the ore-forming process during gold-telluride precipitation as well as heated meteoric waters during the late stages. Early fluids were rich in H₂S, S⁰, and CH₄, while the Au-Te mineralisation was formed from N₂-rich fluid.

Keywords: gold-telluride deposit; fluid inclusion; Raman spectroscopy; LA-ICP-MS; native-sulphur-bearing fluid inclusion; hydrothermal fluid; oxygen isotopes

1. Introduction

Gold-telluride deposits are commonly not distinguished as a separate deposit type but are included in epithermal, porphyry, orogenic, or intrusion-related types of gold deposits. Golden Mile, Australia [1], Cripple Creek and Golden Sunlight, USA [2,3], Emperor, Fiji [4,5], Acupan, Philippines [6], and Sacarimb, Romania [7] deposits are well-known examples of large Au-Te deposits. In Au-Te deposits, a significant part of gold occurs as Au(Ag)-tellurides, which can be precipitated simultaneously with or separately from native gold. In addition, there are telluride-rich deposits, where some part of gold occurs as Au(Ag)-tellurides and could contribute to its bulk balance [8]. There are also Au-deposits, where Au(Ag)-tellurides are rare or absent, but with variable amounts of other tellurides (of Bi, Pb, Hg, etc.), associated with native gold (e.g., [8]).

The origin of gold-telluride deposits is debated since several genetic models of these deposits have been proposed. Multiple sources of the hydrothermal fluids, including magmatic-derived,



mantle-derived, metamorphic-derived, and meteoric waters as well as different processes favourable for gold deposition were proposed for gold-telluride deposits [1-14]. In particular, phase separation by boiling and effervescing of CO₂-rich magma-derived fluids played the key role in gold precipitation in the Cripple Creek deposit [3]. The abundance of tellurides in the epithermal systems is attributed to volatile-rich fluids associated with alkaline (particularly shoshonitic) magmatism [9]. For the deposits formed in deeper (>5 km) settings, e.g., orogenic gold deposits, fluid phase separation was associated with a catastrophic drop in pressure [10]. Periodic release of gas due to throttling was put forward as a formation mechanism in the Golden Mile deposit [1]. The position of the deposit at the intersection of different fault systems was optimal for the development of sustained fluid throttling producing effervescence, and it was likely the main mechanism of gold deposition at the Sacarimb [7]. CO₂ effervescence and concomitant H₂S volatilisation were dominant ore-deposition mechanisms in the intrusion-related Yuryang Au-Te deposit, Korea, and the gold deposition by the fluids apparently derived from the S-type granitoid magma [11]. Fluid inclusion and isotope data for the Chinese Au-Te deposits show that pressure release and fluid boiling as well as fluid-rock interaction (Lifanggou and Mofanggou) and mixing of magma-derived fluids with meteoritic waters (Guilaizhuang) played an important role in the ore formation [12]. The large Dashuigou Te-(Au) deposit, Sichuan Province, is a spectacularly telluride-rich (10 wt % Te) deposit interpreted as a product of the Permian Large Igneous Province-related mantle plume [13]. Fluid sources enriched in Te during mantle underplating and/or metasomatism were responsible for the telluride enrichment observed in the deposits ranging from HS-epithermal and LS-epithermal to metamorphogenic gold systems in the Hellenides [14].

The Svetlinsk Au-Te deposit (54°17′ N, 60°25′ E) is located in the Plast district of the Chelyabinsk region, 30 km west of Plast, which is a centre of gold mining and processing industry in the Southern Urals. The deposit was discovered in 1974. The annual gold production is 4-4.5 tons of Au. The remaining reserves of gold to the depth of 800 m are estimated at 80 tons [15,16], and its total reserves, taking into account the output for 25 years (since 1992), is about 135 tons of Au. A specific feature of the Svetlinsk deposit is the abundance of various tellurides, namely tellurides of Fe, Ni, Pb, Sb, Bi, Ag, and Au. The deposit was classified as a quartz-carbonate shear-zone-related Au-Ag deposit [17], which corresponds to "greenstone-hosted quartz-carbonate vein" in [18] or "orogenic gold" in [19]. Our early studies considered the Svetlinsk deposit as a mesothermal low-grade disseminated and vein-gold one [20]. Previous studies showed the polygenetic and polychronous ore formation by fluids derived from different sources [20–22]. Mineralisation was related to granitic magmatism [21]. Generation of the ore-forming fluids resulted from direct magmatic input and from metamorphic devolatilisation reactions in rocks adjacent to the pluton [20]. Gold-telluride ores were formed at decreasing temperatures and at progressively declining tellurium fugacity alternating with some periods of relative stability of f_{Te2}, and under slight variations of sulphur fugacity. The abundance of tellurides is a mineralogical indicator of direct magmatic contributions to the Svetlinsk ore-forming system [23], cf. [24]. In the present paper, detailed study of fluid inclusions using microthermometry, Raman spectroscopy, LA-ICP-MS, and crush-leach analysis (including gas and ion chromatography, and ICP-MS) was performed to evaluate mineral formation conditions and possible mechanisms of ore deposition.

2. Geological Setting

The large Svetlinsk (also spelled as Svetlinskoe) gold-telluride deposit is located within the East Uralian megazone at the junction of the granite-gneissic (with minor greenstones) Neoproterozoic Kochkar anticlinorium with the Middle Paleozoic Aramil-Sukhtel synclinorium (mainly arc-related complexes); see Figures 1 and 2. The deposit is associated with a NS-trending regional fault. This fault gently dips to the west, evolves to a steeply dipping reverse fault with depth, and is related to the submeridional Kumlyak-Linevka lineament zone [25–27].

The deposit is located in the sequence of west-dipping Upper Fransian-Famennian sandstone and shale alternating with horizons of mafic volcaniclastic rocks and small bodies of gabbro and serpentinite

locally altered to talcite and listvenite. The Upper Devonian metavolcanics, mainly andesibasalt, composing the western flank of the Svetlinsk deposit, were thrusted over the terrigenous-carbonate meta-sediments that are the main ore-hosting rocks. The meta-volcaniclastic sequence is underlain by the Visean marbles (Figure 3). All host rocks underwent strong, up to epidote-amphibolite facies metamorphism caused by emplacement of the hidden granitic pluton and by influence of the major west-dipping thrust-fault [21]. In the western part of the deposit, the host rocks dip steeply westward, whereas, in the eastern part, a gentle (up to horizontal) dip is observed (Figure 3). Rocks in the thrust-shear zone were largely brecciated, subjected to cataclasis and schistosity.

The position of the deposit corresponds to the western slope of the Svetlinsk granite-related dome [28,29], which was related to the main collisional stage in the Late Paleozoic [30]. In 2–3 km to the east of the Svetlinsk gold deposit, the Svetlinsk pegmatite-related piesoguartz deposit with miarolic and vein pegmatite bodies is located above the apical part of the hidden granite pluton [31].



Figure 1. Geological setting of gold deposits in the South Urals, modified after [32]. The red square corresponds to Figure 2.



Figure 2. Geological setting of the mineralising district comprising the Svetlinsk gold deposit, modified after [33]. The red square corresponds to the Svetlinsk gold deposit (Figure 3). K—Kochkar anticlinorium zone. AS—Aramil-Sukhtel synclinorium zone.

The gold-sulphide-telluride mineralisation of the Svetlinsk deposit can be subdivided into two types (Figure 4). The first type is represented by disseminated pyrite and pyrrhotite in the hydrothermal-altered (strongly silicified, up to quartzite-like) host rocks forming large stratified lenses. Sulphide content is usually about 3–5 vol %, locally up to 20 vol %. Gold grade in these ores is low (≤ 1 g/t Au). The bulk of gold in the deposit is associated with the second type of mineralisation (average 0.8–2.5 g/t Au) represented by a system of sulphide-quartz veins and veinlets (3–5 g/t Au) that cross-cut and overprint the stratified zones with disseminated sulphides [21,34]. Sulphide-quartz veins occur mainly in the metasedimentary rocks but they are almost absent in talcite and marble. Three types of veins accompanied by gold-bearing beresite-listvenite, pyrite-quartz-biotite, and pyrite-sericite-quartz alteration were found: (1) the largest NS-trending, steep-dipping veins of quartzite-like quartz, (2) the most numerous smaller steep-dipping, east-west-striking veins, and (3) rare, small, gently west-dipping sub-meridional veins and veinlets.

The ore-bearing vein-disseminated zones were traced for 500–700 m along strike and downdip to a depth of 900 m (Figure 3). The vertical extent of the mineralisation exceeds 1500 m. However, gold grades markedly decrease down the depth of 350–400 m.



Figure 3. Schematic geological map of the Svetlinsk gold deposit, based on the Kochkar geological team data [25], and cross-section I-I, modified after [21,25].

Ore mineralogy consists of pyrrhotite, pyrite, chalcopyrite, minor sphalerite, tetrahedrite, scheelite, galena, various tellurides, and native gold. Native gold (fineness 873–948) in the ore veins is commonly associated with tellurides of gold and silver (Figure 4). Thin horizons of disseminated mineralisation occur in the footwall marble (Figure 4c). The marble-hosted mineralisation consists of pyrite, sphalerite, pyrrhotite, magnetite, rutile, rare native gold, bournonite, galena, and frohbergite (Figure 4j,k). Unusual mineralisation was found in the marble of the eastern part of the Svetlinsk open pit: small cavities in marble contain fluorite, muscovite, rhinestone, and pink topaz, together with later calcite and native sulphur. Topaz, muscovite, quartz, and fluorite could be formed in marble due to greisenisation in the apical part of the above-mentioned hidden granite massif.

Three mineralisation stages were recognised [20,21,23]: (1) disseminated quartz-pyrite-pyrrhotite stage, with rare chalcopyrite, fahlore, galena, and native gold; quartz forms crystals in marble (Q1a) and grey massive quartzite-like, locally sugar-like aggregates in metaterrigenic rocks (Q1b); (2) quartz-pyrite vein stage, with scheelite, quartz is translucent, locally milky (Q2); (3) gold-telluride veinlet stage (main productive), with several mineral assemblages separated by local tectonic events; quartz is mainly milky (Q3). Late water-translucent quartz (Q4) post-dates the mineralisation.



Figure 4. Mineralisation of the Svetlinsk gold deposit. (**a**,**b**)—systems of gold-bearing sulphide-quartz veinlets and veins with thickness from the first centimetres to 0.2 m, superimposed on the stratiform bodies of disseminated sulphide mineralisation. (**c**)—thin horizons of disseminated sulphide mineralisation in marble. (**d**)—0.2 m thick gold-bearing sulphide-scheelite-quartz veins, intersected the disseminated pyrite mineralisation. (**e**)—quartz vein with chlorite and sulphide mineralisation. (**f**–**i**)—telluride mineralisation in quartz veins. (**j**,**k**)—mineralisation in marble (**j**—native gold, **k**—intergrowth bournonite with galena and frohbergite). Width of image is 3 m (**a**) and 50 cm (**c**,**d**). Td—tetrahedrite, Cp—chalcopyrite.

Structural analysis [28,35] and our unpublished data reveals the following sequence of brittle deformations and mineralising events. At the early stage, the sub-concordant, east-west-trending silicification (disseminated pyrite, pyrrhotite) zones formed in schists, large quartzite-like veins composed in the core of these zones. Later, reverse fault (rarely normal fault) displacements occurred, mainly along the east-west-trending and WNW-trending fracture systems. Subsequently, they were filled with quartz and quartz-carbonate veins and veinlets. At the third stage, intense shear and strike-slip deformations occurred, with the renewal of the old fractures and the formation of the new ones. These deformations were widely manifested as fracturing of the veined quartz. The fractures in quartz were then filled with gold-telluride-sulphide mineralisation, including vein selvages.

Samples for the study (~200) were taken from both the boreholes (depth from 145 to 600 m) and the open pit (levels from 160 to 320 m). Representative samples (n = 28) were selected for the microthermometric study (3—for Q1a, 8—for Q1b, 8—for Q2, 7—for Q3, and 2—for Q4).

Petrographic examination and microthermometric analysis of fluid inclusions (FIs) were carried out at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM RAS, Moscow, Russia). Individual inclusions were studied on a total of 28 double-polished, 100–300-µm thick sections, using a microthermometric system consisting of LINKAM THMSG 600 chamber with 50× longfocus objective lens, installed on BX-53 Olympus microscope, video camera, and control computer. Samples were rapidly cooled to about –180 °C to detect a possible occurrence of clathrate, ice, salt hydrates, and carbonic solid phases. Upon progressive heating, up to seven phase transitions were observed in the inclusions, namely eutectic melting (T_e), melting of the carbonic phase ($T_{m(CO2)}$), melting of the ice ($T_{m(ice)}$), clathrate melting ($T_{m(clathrate)}$), homogenisation of the carbonic phase ($T_{h(CO2)}$), melting of the solid phases $(T_{m(solid)})$, mainly halite, and total homogenisation (T_h) temperatures. The accuracy of temperature measurements is ± 0.2 °C within the temperature interval from -60 to +60 °C, decreasing at higher and lower temperatures. The bulk salinity of the fluid was calculated from $T_{m(ice)}$ for two-phase inclusions or $T_{m(solid)}$ for multi-phase inclusions [36], or from $T_{m(clathrate)}$ for aqueous-carbonic inclusions [37]. Salinity of dense CH₄-N₂ fluid with $T_{m(clathrate)} > 10$ °C was estimated based on ice melting temperature that was corrected for H₂O content in clathrate. The predominant salt composition in aqueous solutions was identified from the melting temperature of eutectic (T_e) [38]. The CO₂ and CH₄ concentrations in the solution (C_{CO2} , C_{CH4}) were calculated based on volume and mass ratios of fluid components [39]. To calculate the proportions of phase volumes in the inclusions of the regular shape, the linear dimensions of fluid inclusion and the phase of liquid CO₂ were measured (in three axes, using Fedorov's table). The volumes of fluid inclusion and the phase of liquid CO_2 were calculated, according to the formulas for the volume of an ellipsoid or a sphere. Pressure was determined on the basis of the intersection of isochore and isotherm [40] for syngenetic fluid inclusions. The gas mixtures (CO_2 - CH_4 - N_2) were interpreted according to [41,42]. Salinity, density, and pressure were estimated using the FLINCOR program [43,44]. The measurements were carried out for fluid inclusion assemblages with similar phase proportions to exclude possible errors due to the necking down of the vacuoles after fluid entrapment [45].

The crush-leach analysis of FIs was carried out for the selected samples (n = 5) with only one dominant type of fluid inclusions at the Central Research Institute for Geological Prospecting on Base and Precious Metals (TsNIGRI). The standard technique [46] includes cleaning of a sample, opening of fluid inclusions, and determination of the element composition. The ~0.5 to 1.0 g samples were crushed to 0.25–0.5 mm and were cleaned by HNO₃ (50 vol %) solution and by electrolytic and ultrasonic cleaners. Before analysis, samples were dried and then placed into a single-shot reactor, filled with helium, and preheated at 110 °C. Subsequent heating to 400 °C and milling with corundum beads (at ~120 °C) allows complete opening of the inclusions. The extracted gas phase was analysed using an Agilent 6890 gas chromatograph to determine the concentration of water, CO₂, CH₄, and other gases. The residual liquid phase was analysed by ion chromatography (Tsvet-3006, for determination of Cl⁻, F^- , SO_4^{2-} , and NO_3^- , detection limit 0.01 mg/L) and ICP-MS (Elan-6100, for determination of Br, B, Li, Rb, Cs, Sr, Ba, As, Sb, Ge, Cu, Zn, Cd, Pb, Au, Ag, Bi, Mo, W, Sn, Tl, Hg, Co, Ni, Cr, V, U, Mn, Fe, Th, Si, Te, and Se) after the addition of 7 mL of ultrapure deionised water and centrifugation. Calculation of fluid composition includes: (1) subtraction of the element contents in the used water from the extract analysis, (2) subtraction of the element contents in the blank extract from the working extract analysis, (3) calculation of the element mass in the quartz sample, (4) calculation of element concentrations in solutions of inclusions (normalisation on H_2O), and (5) calculation of HCO_3^- content based on the balance of cations and anions. Measurement accuracy is within about 5% for ion chromatography and 0.5-2% for ICP-MS.

Compositions of the gas and solid phases in individual fluid inclusions (n = 18) were studied by Raman spectroscopy using a Jobin Yvon LabRAM HR800 spectrometer (Sobolev Institute of Geology and Mineralogy Siberian Branch Russian Academy of Science (IGM SB RAS), Novosibirsk, Russia) and LabRAM-HR (Horiba Jobin-Yvon) spectrometer UV-VIS-NIR version (Geological Institute, Slovak Academy of Sciences, Bratislava, Slovakia). The daughter phases in multi-phase fluid inclusions were identified with the RRUFF database of Raman spectra (http://rruff.info/).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was carried out at the Institute of Geochemistry, Irkutsk, Russia on a NexION 300D quadruple mass spectrometer with inductively coupled plasma combined with a New Wave UP 213 laser ablation system. Contents of B, Na, Mg, Al, S, K, Ca, Mn, Fe, Ni, Co, Cu, Zn, As, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Au, Pb, and Bi in the inclusions (*n* = 11) were determined using the NIST 612 glass as an external standard ([47], http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp, Table A1), and Na content as an internal standard. The Na concentration (the internal standard) in the inclusions was estimated based on cryometric determination of the total salt concentration in FI solutions. Then, the Na concentration in solutions of two-phase inclusions was calculated and corrected considering the content ratios of predominant (Na, K, Cs) cations in the solution, calculated from the LA-ICP-MS data. Te and Hg are absent in NIST 612 and Te and Hg contents are presented as Sb and Au ppm equivalent, respectively. Concentration of elements was calculated, according to the Longerich formulae [48].

Oxygen isotope composition of quartz (n = 15) was studied at the Analitic Centre of the Far East Geological Institute RAS (Stable Isotopes Laboratory, Vladivostok, Russia, analyst T.A.Velivetskaya) by standard techniques. The results of O isotope measurements ($\delta^{18}O_{VSMOW}$) for quartz, combined with fractionation factors and fluid inclusion homogenisation data, were used to calculate the O isotopic composition of hydrothermal fluid, according to the equations of fractionation in hydrothermal systems [49].

4. Fluid Inclusion Study

4.1. Fluid Inclusion Petrography

The study of fluid inclusions (FIs) using the standard techniques was carried out for the various generations of vein quartz and carbonate. The fluid inclusions range from 1 to 25 μ m in size and have irregular, ellipsoidal, or negative crystal shapes. The primary, pseudo-secondary, and secondary fluid inclusions were identified, according to the criteria of [45]. The widespread primary fluid inclusions are distributed along the growth zones or as random clusters within the quartz grains. The pseudo-secondary inclusions occur as trails in healed fractures, which do not cut grain boundaries. The secondary fluid inclusions are less abundant and fill cracks or form the chain-like clusters intersecting the grain boundaries. Four major types of inclusions were revealed based on phase assemblages at room (21 °C) temperature (Figure 5):

- type I (L_{H2O} + V_{CO2} ± L_{CO2}) is two-phase or three-phase aqueous-carbonic FIs containing liquid water as well as liquid and gaseous CO₂;
- type II (V_{CO2 ± CH4,N2}) is vapour-rich CO₂ one-phase or two-phase FIs, with minor CH₄ and N₂, sometimes with a thin liquid rim;
- type III (L_{H2O} + V_{H2O}) is two-phase liquid–vapour aqueous inclusions;
- type IV (L_{H2O} + V_{H2O} + S) is three-phase or multi-phase FIs, consisting of H₂O liquid, gas bubble, and one or more daughter minerals. The cubic crystals in such inclusions are usually halite, based on a refractive index. Rarely the solid phase is represented by calcite and solid phases of complex composition (chalcoalumite group) based on Raman spectroscopy data. Additionally, a spherical native sulphur phase was detected in some FIs of I, II, and IV types (subtypes Ia, IIa, and IVa, respectively).

Contemporaneous entrapment of liquid-rich and vapour-rich inclusions suggests that the mineralising fluid underwent phase separation.

Additionally, pseudo-secondary and secondary fluid inclusions of type I, II, and III were recognised in studied quartz.



Figure 5. Photomicrographs of fluid inclusions trapped in quartz of the Svetlinsk deposit. (**a**,**b**)—aqueous-carbonic inclusion, type I (**a**—at 20 °C, **b**—at –10 °C). (**c**)—multi-phase inclusion of chloride brine, type IV. (**d**,**e**)—vapour-rich (CO₂ \pm CH₄ \pm N₂) inclusion, type II (**d**—at +20 °C, **e**—at –5 °C). (**f**)—two-phase liquid-vapour aqueous inclusion, type III.

4.2. Microthermometry

The microthermometry data for about 1300 fluid inclusions, from 28 thick section, in the various generations of quartz from the Svetlinsk deposit are shown in Table 1 and plotted in Figure 6.

4.2.1. Q1a (in the Footwall Marble)

Primary fluid inclusions of I, II, III, and IV types were revealed in quartz crystals in marble of this stage while only FIs of type II were identified in carbonate. Aqueous-carbonic FIs of type I show $T_{m(CO2)}$ between -58.6 °C and -57.4 °C. CO₂ homogenises at 33.1 °C in the vapour phase, which indicates the presence of additional gas species. Native sulphur melts at 85 °C (subtype Ia of FIs). Salinity is 15.6 wt % NaCl equiv. Homogenisation temperatures range between 315 and 286 °C. T_e is about -53 °C, which corresponds to the CaCl₂-NaCl-H₂O system. Mean fluid density is 1.11 g/cm³. CO₂ in FIs of type II melts at -60.5 ± 0.3 °C (FIs in quartz) and at -61.7 °C (FIs in carbonate). Homogenisation of CO₂ in liquid phase occurs at 9.4 °C (FIs in carbonate) and between 16.6 and 32.8 °C (FIs in quartz). Fluid in FIs in carbonate is denser (0.9 g/cm³) compared to FIs in quartz (0.5–0.8 g/cm³). Type III of fluid inclusions is rare and trapped the Ca²⁺ dominated medium-salinity ($T_e = -54 \text{ °C}$, 10.5 wt % NaCl equiv.) solution homogenised at 354 °C. Native sulphur melts at 75 °C (subtype IIIa of FIs). Most inclusions of type IV exhibit uniform eutectic temperatures ($T_e = -52 \,^{\circ}$ C), indicating the dominance of Ca²⁺ cations in the fluids. The halite dissolution temperature in these inclusions is 181 °C, which corresponds to salinity 31 wt % NaCl equiv. Total homogenisation of the type IV FIs occurs at 269 °C. The density of the fluid is 1.05 g/cm³. The FIs of type I contain 1.4 mol of CO₂ per kg of solution and 0.1 mol of CH₄ per kg of solution.

Sample	FIs Type ¹	n^2	T_h , °C	T _e , °C	$T_{m \ ice \ (NaCl) \ [S0]}, {}^{\circ}\mathrm{C}^{3}$	$T_{m(CO2)}$, °C	$T_{h(CO2)(N2)}, ^{\circ}C$	H.m. ⁴	T _{m (clatrate)} , °C	C _{salt} , wt% NaCl Equiv.	C _{CO2} , mol/kg Solution	C _{CH4} , mol/kg Solution	d, g/cm ³
							Q1a						
	ΙP	17	286-315	-53	$-20.5(85)^3$	-57.458.6	33.1	V	0.0	15.6	1.4	0.1	1.11
	II P	15	-	-	-	-60.260.8	16.6 32.8	L	-	-	-	-	0.47 - 0.81
CM	III P	5	354	-54	$-7.0(75)^3$	-	-	-	-	10.5	-	-	0.75
50	IV P	18	269	-52	$(181)^3$	-	-	-	-	31.0	-	-	1.05
	I PS	2	246	-50	-11.8	-58.4	33.6	V	-0.1	15.8	2.2	0.2	1.03
	II PS	2	-	-	-	-60.1	14.5 24.0	L	-	-	-	-	0.73-0.83
CV/0/10	I PS	32	296-300	-5156	$-24.1 \ldots -28.6 (148)^3$	-59.462.2	33.5 34.1	L	-2.3-3.2	23.0-28.8	2.1-2.4	0.1 - 0.4	0.91-0.95
5702/18	II PS	54	-	-	-	-59.763.8	18.8 31.0	L		-	-	-	0.51-0.79
S64/18	II P	9	-	-	-	-61.7	9.4	L	-	-	-	-	0.87
							O1b						
01 (// 10 F	ΙP	3	265-310	-35	-8.3	-56.8	-8.8	L	4.1	12.0	5.4	-	1.09
216/148.5	II P	32	-	-	-	-56.656.8	-29.8 0.6	L	-	-	-	-	0.92-1.08
21 (1400 (ΙP	37	275-320	-3133	-7.611.1	-57.157.2	-6.5 15.6	L	1.3-7.9	11.2-15.0	4.2-7.6	-	1.06-1.10
216/409.6	II P	51	-	-	-	-57.457.5	-13.6 7.0	L	-	-	-	-	0.88-0.97
202/200 2	ΙP	8	315-365	-3132	-4.14.7	-57.457.8	-12.4	L	4.1	12.5	6.4-7.2	-	1.06
202/289.2	II P	47	-	-	-	-58.158.7	-21.1 1.7	L		-	-	-	0.94-1.04
	ΙP	8	260-315	-34	-7.7	-57.5	21.0 26.3	L	3.2-3.9	10.7-11.7	2.9-3.6	0.3	1.05 - 1.06
202/318.8	II P	25	-	-	-	-57.257.8	-25.6 23.8	L		-	-	-	0.73-1.06
	III S	13	275-300	-31	-5.8	-	-		-	8.9	-	-	0.82 - 0.85
	ΙP	7	240-270	-32	-8.3	-60.6	-31.0	L	12.2	12.1	2.7	0.7	1.03
202/601.2	II P	32	-	-	-	-59.361.0	-37.612.5	L	-	-	-	-	1.00 - 1.11
202/001.2	III S	6	310	-31	-9.1	-	-			13.0	-	-	0.85
	II S	4	-	-	-	-	-131	V		-	-	-	0.16
S12/96	I P	9	295-340	-37	-12.8	-57.5	2.1 18.0	L	1.2	14.2	4.9-6.2		1.07 - 1.08
512/70	II P	66	-	-	-	-57.560.2	-35.7 13.1	L	-	-	-	-	0.84 - 1.10
470/293 5	I P	3	325-350	-37	-11.1	-58.6	-9.7	L	1.3	15.3	4.4-4.9	0.2-0.3	1.09
470/200.0	II P	40	-	-	-	-57.759.4	$-22.7 \ldots 4.4$	L		-	-	-	0.95 - 1.05
38-33	I PS	10	250-280	-2833	-8.013.0	-58.460.0	17.0 32.0	L	7.0-12.0	11.4 17	-	-	
	II PS	3	-	-	-	-58.559.1	19.1 24.0	L	-	-	-	-	0.73-0.78
							Q2						
202/593.0	III P	15	285-315	-30	-4.25.9	-	-	-	-	6.7 9.1	-	-	0.80 - 0.81
202/393.0	II P	45	-	-	-	-57.958.7	-26.80.9	L		-	-	-	0.92 - 1.06
	I P	9	300-345	-32	-5.56.7	-56.9	-9.1	L	4.7	11.3	5.3-5.4	-	1.08
S1p/95	II P	31	-	-	-	-56.959.9	-29.2 10.2	L					0.86 - 1.07
	II S	14	-	-	-	-	-153	V					0.13
	I P	3	305-320	-33	-8.2	-59.2	-21.2	L	6.2	11.2	6.6	-	1.09
S3/95a	II P	16				-58.659.4	-28.57.5	L	-	-	-	-	0.97 - 1.07
	II S	2	-	-	-	-	-149	V	-	-	-	-	0.17

Table 1. Microthermometric study of individual fluid inclusions (FIs) in quartz from the Svetlinsk deposit.

Table 1. Cont.

Sample	FIs Type ¹	n^2	T_h , °C	<i>T</i> _e , [°] C	$T_{m \ ice \ (NaCl) \ [S0]}, ^{\circ}\mathrm{C}^{3}$	$T_{m(CO2)}, ^{\circ}C$	$T_{h(CO2)(N2)}, ^{\circ}C$	H.m. ⁴	$T_{m (clatrate)}, ^{\circ}C$	C _{salt} , wt% NaCl Equiv.	C _{CO2} , mol/kg Solution	C _{CH4} , mol/kg Solution	d, g/cm ³
							O2						
(10/1/2	ΙP	6	255-275	-32	-7.4	-57.7	~ -6.8 5.3	L	6.6	6.8	4.0-5.0	0.4-0.5	1.08
618/162	II P	53	-	-	-	-57.457.7	-15.8 1.8	L	-	-	-	-	0.92-1.01
	ΙP	5	302	-33	-5.0	-57.8	17.5 25.1	L	4.6	9.6	4.6	0.4	1.02
S2/10	II P	13	-	-	-	-57.8	-1.3 8.0	L	-	-	-	-	0.88 - 0.94
	III S	3	159	-32	-4.9	-	-			7.7			0.97
C14/10	ΙP	7	278-289	-3536	-4.16.4	-57.259.6	3.5 20.4	L	6.7-7.8	4.3-6.8	5.2-5.3	0.5	1.02 - 1.04
514/10	II P	13	-	-	-	-59.259.6	-7.8 12.6	L	-	-	-	-	0.97 - 0.84
01//	I PS	13	230-260	-2732	-4.0	-57.057.8	11.0 23.0	L	5.8-8.3	3.5-7.5	-	-	
5766	II PS	2				-57.557.8	19.5 22.0	L					0.74 - 0.78
CV/E1	I PS	9	195-220	-3739	-6.98.0	-58.158.8	1.6 27.9	L	2.8-4.6	10-12.0	-	-	
5721	II PS	2	-	-	-	-58.5	22.0 25.2	L	-	-	-	-	0.71-0.75
							O3						
	ΙP	17	295-320	-3436	-7.810.1	-56.657.6	~ -30.824.1	L	9.4-12.6	7.2	5.9-6.0	0.6-0.9	1.11-1.12
202/592.7	II P	69	-	-	-	-56.857.6	-24.3 22.1	L	-	-	-	-	0.75-1.05
	III S	23	190-230	-30	-4.9	-	-	-	-	7.7	-	-	0.90-0.94
	ΙP	17	370-405	-32	-5.25.7	-74.4	-146.9147.5	V	9.3-10.5	8.1-8.8	0,8	-	0.83
CE/OEh	II P	76	-	-	-	-57.860.8	-38.8 6.3	L	-	-	-	-	0.89-1.11
55/ 950	III S	29	265-305	-3233	-4.76.2	-	-	-		7.4–9.5	-	-	0.81 - 0.84
	II S	40	-	-	-	-82.9	-149152	V	-	-	-	-	0.14-0.17
470/170	ΙP	7	330-350	-32	-8.19.2	-56.7	16.3 26.5	L	7.1	5.6	5.0-6.3	0.6-0.7	1.01 - 1.04
470/170	II P	26	-	-	-	-56.857.9	2.5 25.0	L	-	-	-	-	0.71-0.91
	ΙP	5	358	-35	-5.9	-57.3	-7.0	L	4.8	10,9	6.3	0.7	1.07
	II P	22	-	-	-	-57.257.4	-1.0 13.4	L	-	-	-	-	0.84-0.93
S1/10	I PS	3	280	-37	-5.4	-57.2	2.9	L	8.3	4.2	4.6	0.4	1.06
	II PS	10	-	-	-	-57.4	-3.1 9.1	L	-	-	-	-	0.87-0.95
	III S	2	262	-30	-0.8	-	-			1.3	-	-	0.78
	I PS	6	363	-33	-5.0	-58.2	2.7	L	7.2	6.1	7.1	0.7	1.04
S9/10	II PS	11	-	-	-	-58.0	-13.60.2	L	-	-	-	-	0.93-1.00
	III S	3	347	-35	-0.3	-	-		-	0.5	-	-	0.58
S35/10	III P	6	308	-33	-0.5	-	-	-	-	0.8	-	-	0.68
	ΙP	6	312-331	-3334	-1.92.7	-58.659.9	2.1 11.4	L	8.1-8.9	3.3-3.8	6.7-8.3	0.7-0.9	1.01 - 1.02
S41/18	II P	43	-	-	-	-58.360.5	-9.8 1.9	L	-	-	-	-	0.92-0.98
	III S	8	203	-22	-0.3	-	-	-	-	0.5	-	-	0.87
							Q4						
63-1	III P	2	220-250	-2122	-1.04.6	-	-	-	-	1.7-7.3	-	-	0.85-0.87
S10/95	III P	28	130-230	-2324	-2.9	-	-	-	-	4.8	-	-	0.85-0.95

¹ inclusion type: I—liquid H₂O + liquid CO₂ ± vapour CO₂. II—vapour CO₂-rich (±CH₄, ±N₂), III—liquid H₂O + vapour H₂O, IV—liquid H₂O + vapour H₂O + solid NaCl. P—primary, PS—pseudo-secondary, and S—secondary inclusions. S⁰—native sulphur. ² number of studied inclusions. ³ the values in round brackets denote the T_{m NaCl}, and the values in square brackets denote the T_{mS}⁰. ⁴ homogeneous mode (H. m.) of CO₂: L—Liquid, V—Vapour.

In addition, *pseudo-secondary* fluid inclusions of I and II types were revealed in quartz. FIs of type I contain CaCl₂-NaCl solutions ($T_e = -56$ to -50 °C) with higher salinity (15.8 to 28.8 wt % NaCl equiv.). The values of $T_{m(CO2)}$ for the majority of FIs vary from -62.2 to -58.4 °C and indicate the variable concentrations of N₂ and/or CH₄ within this inclusion type. The homogenisation temperature ranges from 300 to 246 °C. The density of the fluid is 0.91–1.03 g/cm³. Type II of FIs contains CO₂ with admixture of other gases that melts at -63.8 to -59.7 °C and homogenises at 14.5 to 31 °C. The FIs of type I contain 2.1–2.4 mol of CO₂ per kg of solution and 0.1–0.4 mol of CH₄ per kg of solution.

4.2.2. Q1b (in Metaterrigenic Rocks)

Primary FIs of I and II types are abundant in quartz of this stage, and inclusions of type II prevail. The homogenisation temperature for type I FIs ranges between 240 to 365 °C. Type I of FIs contains Na-, Mg-Na-, and Fe-Na-chloride solutions (T_e from -28 to -37 °C). The values of $T_{m(CO2)}$ range from -60.6 to -56.8 °C. This indicates the variable concentrations of other gas species (i.e., N₂ and CH₄) within this inclusion type that corresponds to the wide variations of the temperature of CO₂ homogenisation into liquid (from -31.0 to +31.0 °C). Melting temperatures of clathrate ($T_{m(clathrate)}$) vary from 1.2 to 12.2 °C, corresponding to the narrow salinity range of 10.7–16.9 wt % NaCl equiv. The density mainly ranges from 1.03 to 1.10 g/cm³. Type II of FIs contains high-density CO₂ with $T_{m(CO2)}$ between -56.6 and -61.0 °C and homogenises at -35.7 to 23.8 °C, which implies the presence of additional gases apart from CO₂. The FIs of type I contain 2.7–7.6 mol of CO₂ per kg of solution and 0.2–0.7 mol of CH₄ per kg of solution.



Figure 6. Homogenisation temperature (T_h) vs. salinity (C_{salt}) (**a**) and homogenisation (T_h) vs. eutectic temperatures (T_{eut}) (**b**) plots for FIs in the quartz of the Svetlinsk deposit.

Secondary inclusions of types III and II are rare. FIs of type III contain Mg-Na-chloride solutions ($T_e = -31 \text{ °C}$). The final ice melting temperatures $T_{m(ice)}$ are between -5.8 and -9.1 °C, corresponding to salinities of 8.9–13 wt % NaCl equiv. The homogenisation temperature ranges from 300 to 275 °C. The density of the fluid is $0.82-0.85 \text{ g/cm}^3$. FIs of type II contain low-density N₂ (0.16 g/cm^3) homogenised at -131 °C in the vapour phase.

4.2.3. Q2

Primary FIs of three types (I, II, and III) were identified in quartz of this stage. Type III of FIs was revealed in a few samples. Type I of FIs contains Na- and Mg-Na chloride solutions (T_e from -30 to -39 °C). The melting temperature of CO₂ ($T_{m(CO2)}$) varies from -59.6 to -56.9 °C. This fact indicates the variable concentrations of N₂ and/or CH₄ within this inclusion type. Melting temperatures of clathrate ($T_{m(clathrate)}$) vary from 2.8 to 8.3 °C, corresponding to the salinity range from 3.4 to 11.3 wt % NaCl equiv. The homogenisation of CO₂ ($T_{h(CO2)}$) into liquid occurs at -21.2 to 27.9 °C. Inclusions homogenise at the temperature between 345 and 195 °C. The density of the fluid was 1.02–1.09 g/cm³. Type II of FI contains dense CO₂ with $T_{m(CO2)}$ between -59.9 and -56.9 °C, which implies the presence of additional

gases apart from CO₂. The majority of type II inclusions homogenises into the liquid phase ($T_{h(CO2)}$) from –29.2 and 25.4 °C. FIs of type III contain Mg-Na-chloride solutions ($T_e = -30$ °C) with $T_{m(ice)}$ from –5.9 to –4.2 °C, corresponding to salinities of 6.7–9.1 wt % NaCl equiv. The homogenisation temperature ranges from 315 to 285 °C. The density of the fluid is 0.8 g/cm³. The FIs of type I contain 4.0–6.6 mol of CO₂ per kg of solution and 0.4–0.5 mol of CH₄ per kg of solution.

Secondary inclusions are of types III and II. FIs of type III contain Mg-Na-chloride solutions ($T_e = -32 \text{ °C}$) with 7.7 wt % NaCl equiv. and homogenise at 159 °C. The density of the fluid is 0.97 g/cm³. FIs of type II contain low-density N₂ (0.13–0.17 g/cm³) homogenising at –153 to –149 °C in the vapour phase.

4.2.4. Q3

Primary fluid inclusions of I, II, and III types were recognised in quartz of this stage. Aqueous-carbonic inclusions of type I show $T_{m(CO2)}$ between -74.4 and -56.6 °C, which indicates the presence of additional gas species. $T_{h(CO2)}$ is mainly from -30.8 to 26.5 °C. N₂ homogenises at -147.5 to -146.9 °C in the vapour phase. Positive $T_{m(clathrate)}$ values between 4.8 and 12.6 °C correspond to salinities from 3.3 to 10.9 wt % NaCl equiv. Homogenisation temperatures range between 405 and 295 °C. This inclusion type exhibits T_e from -36 to -32 °C, which indicates the dominance of Mg²⁺ and Fe²⁺ cations in the chloride solution. Densities range from 0.83 to 1.12 g/cm³. In FIs of type II, the melting temperature of CO₂ ($T_{m(CO2)}$) varies from -60.8 to -56.8 °C. This indicates variable concentrations of N₂ and/or CH₄ within this inclusion type. Type III of fluid inclusions is rare and trapped the low-salinity (0.8 wt % NaCl equiv.) solution homogenised at 308 °C. The FIs of type I contain 0.8–8.3 mol of CO₂ per kg of solution and 0.6–0.9 mol of CH₄ per kg of solution.

In addition, *pseudo-secondary* fluid inclusions of I, II, and III types were revealed in this quartz. FIs of type I contain FeCl₃ solutions ($T_e = -37$ °C) with a lower concentration of salts (4.2 wt % NaCl equiv.). The values of $T_{m(CO2)}$ for the majority of FIs are close to -57.2 °C. Small quantities of other gas species (i.e., N₂, CH₄) decrease the melting point (-56.6 °C) of pure CO₂. The homogenisation temperature is 280 °C. The density of the fluid is 1.06 g/cm³. Type II of FIs contains high-density CO₂ with melting temperatures ($T_{m(CO2)}$) of -57.4 °C and homogenises at -3.1 to 9.1 °C.

FIs of type III trapped the dilute Mg-Na-solutions ($T_e = -35$ to -30 °C) with 0.5–1.3 wt % NaCl equiv. Homogenisation temperature ranges from 347 to 262 °C. The FIs of type I contain 4.6 mol of CO₂ per kg of solution and 0.4 mol of CH₄ per kg of solution.

Secondary inclusions are of types III and II. FIs of type III trapped the contrasting fluids. Some of them are Mg-Na-chloride solutions (T_e from -33 to -30 °C) with moderate salinity (7.4–9.5 wt % NaCl equiv.) homogenised between 305 and 190 °C while others are NaCl low-concentrated solutions ($T_e = -22$ °C, $C_{salt} = 0.5$ wt % NaCl equiv.) homogenised at 203 °C. The density of both fluids is similar (0.81–0.94 g/cm³). FIs of type II contain low-density N₂ (0.14–0.17 g/cm³) homogenised from –152 to –149 °C in the vapour phase.

4.2.5. Q4

Primary fluid inclusions of type III were recognised in the late vein quartz. These FIs trapped the low-salinity (1.7 to 7.3 wt % NaCl equiv.). NaCl solution ($T_e = -21$ to -24 °C) homogenised from 250 to 130 °C.

4.3. Crush-Leach Analysis

The reconstructed fluid composition based on the crush-leach analysis of quartz is shown in Table 2.

Quartz	Q3	Q3	Q3	Q2	Q1a	Quartz	Q3	Q3	Q3	Q2	Q1a
Sample	S-1/10	S-9/10	S-35/10	S-14/10	SV	Sample	S-1/10	S-9/10	S-35/10	S-14/10	SV
CO ₂ ,×10 ³ ppm	49.05	293.29	1231.85	406.23	471.05	Ge, ppm	0.52	0.31	0.27	0.11	0.91
CH ₄	0.683	0.652	2.566	1.955	0.026	Cd	1.96	0.53	0.30	0.18	-
Cl-	14.42	< 0.6	<1	6.13	59.96	Pb	35.54	-	13.10	-	-
SO_4^{2-}	< 0.8	< 0.8	<1.5	< 0.5	<1	Au	9.89	_	-	-	_
HCO3-	65.25	11.74	35.30	23.45	93.48	Ag	0.05	_	0.14	-	_
Na	25.31	2.99	8.31	11.43	31.27	Bi	0.07	0.09	-	-	-
K	2.25	0.42	0.78	0.72	3.07	Mo	0.19	0.02	-	0.05	0.13
Ca	3.92	0.70	2.38	0.65	31.83	W	-	-	-	-	1.67
Mg	1.53	0.20	0.94	0.14	2.59	Sn	0.30	_	-	-	_
Br, ppm	-	-	-	-	2824.5	Hg	0.02	-	-	-	_
В	2015.8	408.43	661.34	592.13	596.48	T1	0.12	-	1.47	0.02	0.17
Li	1.04	0.30	0.48	0.11	10.68	Co	0.10	0.06	0.07	0.04	20.06
Rb	3.28	1.10	2.78	2.06	7.00	Ni	5.38	0.64	12.75	1.80	174.94
Cs	0.28	0.23	1.17	1.13	2.23	Cr	0.82	0.38	-	-	_
Sr	30.29	7.20	6.79	27.55	1166.0	V	0.21	-	-	-	0.55
Ba	12.19	0.92	-	9.44	3951.1	U	-	-	-	-	-
Cu	263.86	-	236.34	8.92	-	Mn	34.29	4.74	13.54	32.37	511.06
Zn	1630	54.05	1699.9	65.48	164.87	Fe	126.15	2.69	-	-	_
As	72.51	42.13	68.67	19.76	21.26	Ι	-	-	-	-	116.22
Sb	27.37	52.99	51.53	2.96	19.22	Si	40,127	35,623	31,309	-	-

Table 2. Reconstructed fluid compositions according to crush-leach analysis.

Dash-below the detection limit.

Gas chromatography revealed that CO_2 was the major volatile component trapped in fluid inclusions. Content of CH_4 in the fluids varies from 0.03 to 2.6 g/kg of H_2O . Na dominates in fluids for Q2 and Q3, while Ca is significant in addition to Na for Q1a. Solutions trapped in Q1a are Li-rich. Chlorine-ion is abundant in the early fluids (Q1a), while the mole fraction of HCO_3^- in fluid increases in Q2 and HCO_3^- -rich fluids are predominant in Q3. Fluorine-ion was not determined, and the content of SO_4^{2-} is insignificant. Iodine-ion was determined in the early fluids. Common components (in ppm) in the early fluid (Q1a) are Br (2825), Li (10.7), Sr (1166), Ba (3951), Co (20.1), Ni (175), and Mn (511). Fluids trapped in Q3 are rich in B (408–2016), As (42–73), Sb (27–53), Cu (236–264), Zn (54–1700), Pb (13–36), Fe (3–126), and Au (9.9). Fluid in Q2 is more water-saturated and contents of most elements are comparable to the fluid of Q3 but As and Sb contents are lower.

4.4. Raman Spectroscopy

The gaseous phase of FIs in all studied generations of quartz was examined using laser Raman to investigate the possible presence of condensed gases. FIs in Q1a (in marble) in addition to CO₂ (94.2 to 98.8 mol %) contain H₂S (0.53 to 4.12 mol %) and often N₂ (0.65 to 1.64 mol %). Both vapour-rich and multi-phase FIs have a similar gaseous composition. The anisotropic solid phase in multi-phase inclusions has a complex composition (chalcoalumite group). Additionally, a spherical native sulphur phase (471.8 cm⁻¹ spectral line) was detected in almost all FI types (Figure 7). All FIs in Q1b (in metaterrigenic rocks) mainly contain variable CO₂ (50 to 100 mol %). In three FIs, the significant admixture of CH₄ (20 to 50 mol %) and (in two inclusions) of H₂S (2 to 4 mol %) was detected in addition to CO₂ (Figure 8). Solid phases in two FIs are calcite, which was defined based on the 1085 cm⁻¹ spectral line. The vapour-rich FIs in Q2 contain only CO₂ (100 mol %, 9 FIs) whereas other gases (N₂, CH₄, H₂S) were not detected. The gaseous phase of FIs in Q3 contains CO₂ and N₂. Aqueous-carbonic FIs are N₂-rich (26.7 mol %) when compared to vapour-rich inclusions (1.6 to 10.4 mol %). The content of CO₂ varies from 89.6 to 98.4 mol % and is equal to 73.3 mol % for these FI types (Table 3). No condensed gases were detected in the gaseous phase in FIs (*n* = 4) in the late quartz (Q4).



Figure 7. Fluid inclusions (FIs) with native sulphur in quartz from marble: (**a**)—multi-phase FIs, (**b**)—four-phase FIs with CO₂, (**c**,**d**)—gaseous FIs with dense CO₂, (**e**)—Raman spectra of FI showing the presence of sulphur. L—aqueous solution. Sample SV.



Figure 8. Selected laser Raman spectra of fluid inclusions showing the presence of CO_2 and CH_4 (**a**) and CO_2 (**b**) in gaseous phase of FIs as well as the presence of calcite as a solid phase (**c**). Sample 38-3a. Scale bar is 10 μ m. Q—quartz.

Sample ¹	Q Generation	FIs Type ²	CO ₂	N_2	H_2S	CH ₄
SV	Q1a	II	96.9	1.23	1.82	_
SV	Q1a	IV	98.2	_3	1.81	_
SV	Q1a	IV	94.2	1.64	4.12	_
SV	Q1a	IV	98.8	0.65	0.53	_
S1/10	Q3	II	98.4	1.62	_	_
S1/10	Q3	II	98	2.01	_	_
S1/10	Q3	II	89.6	10.41	_	_
S1/10	Q3	II	95	4.98	_	_
S1/10	Q3	Ι	73.3	26.70	_	_
38-3a	Q1b	Ι	50	_	_	50
38-3a	Q1b	Ι	80	_	_	20
38-3a	Q1b	Ι	70	_	_	30
38-3a	Q1b	Ι	96	_	4	_
38-3a	Q1b	Ι	98	_	2	_
38-3a	Q1b	Ι	100	_	_	_
SV-51	Q2	Ι	100	_	_	_
SV-66	Q2	Ι	100	_	_	_
63-1	Q4	III	_	-	_	-

Table 3. Gas species in the vapour phase of inclusions according to Raman spectroscopy (mol %).

¹ SV and S1/10 samples was studied in IGM SB RAS, other samples—in Geological Institute, Slovak Academy of Sciences. ² inclusion type. ³ not detected.

4.5. LA-ICP-MS of Fluid Inclusions

Fluid composition in individual fluid inclusions in the early quartz (Q1a, n = 6) and in quartz of the main productive stage (Q3, n = 5) was also determined (Table 4). The early fluid is rich in Na, S, Ca, Mn, Sr, Cd, Sn, and Ba, while, in Q3, contents of B, K, Cu, Zn, Ag, Te, Pb, and Bi are relatively high (Figure 9). Bi is absent (below the detection limit) in Q1a and Ca, Fe, and Cd were not detected in Q3. Co and Mo are sporadic in Q1a, and Mn, Mo, and Cs are sporadic in Q3. Fluid in vapour-rich inclusions in Q1a is rich in As, Cd, Sn, Te, Sb, and Hg in comparison with multi-phase FIs. Fluid in vapour-rich inclusions in Q3 is rich in S, Zn, Sr, Ba, Pb, and Bi, and sometimes in Sn and Cs in comparison with aqueous-carbonic FIs. Au and Ag are detected sporadically in both quartz generations, but their contents are typically one to two orders of magnitude higher in Q3 when compared to Q1a.

Table 4. Fluid composition according to LA-ICP-MS of individual fluid inclusions in quartz of the

 Svetlinsk deposit.

Quartz			Q	1a			Q3 (Main Ore Stage)				
Sample	SV (1)	SV (2)	SV (3)	SV (4)	SV (5)	SV (6)	S1/10 (1)	S1/10 (2)	S1/10 (3)	S1/10 (4)	S1/10 (5)
FI type ¹	IV	IV	IV	IV	IV	Π	Ι	Ι	Ι	П	II
	0	Cor -	Co.	0	0	6	- BR	O	D		0
B, ppm	140	100	50	14	39	0	1350	460	350	2580	560
Na	58,900	58,900	58,900	58,900	58,900	13,000	47,200	19,700	19,700	19,700	19,700
Mg	1170	3770	3160	1750	1680	20	4360	0	0	58,500	45
AĬ	0	2390	520	560	36	3830	90	0	3680	1170	1390
S	260	2370	960	530	890	0	0	0	0	0	1290
K	1870	1250	4770	1320	740	970	5550	5480	930	5820	8320
Ca	79,800	45,400	124,000	32,700	23,500	0	0	0	0	0	0
Mn	160	26	140	54	30	8	0	0	0	0	110
Fe	0	0	8	380	9	0	0	0	0	0	0
Ni	0	8	4	25	19	0	1200	1900	1480	0	2000
Co	0	0	0	0.1	0.2	0	0	0	88	0	18
Cu	2	14	0.1	0.3	0.5	12	510	5890	0	150	0
Zn	210	0	39	1130	18	44	400	27	310	830	1220
As	5	0	7	235	0	5150	0	0	3970	0	270
Rb	15	3	2	290	1	0	0	140	0	0	40
Sr	2200	320	220	49,000	100	0	15	0	0	510	100
Mo	0	7	0.2	0	1	0	0	250	0	0	0
Ag	1	0	0	2	0.4	0	30	0	130	60	0
Cd	8	2	1	25	0	480	0	0	0	0	0
Sn	20	0	2	4	35	560	0	0	0	0	28
Te ²	4	17	1	10	1	1050	65	560	2300	80	330
Sb	0.4	1.1	0	1.2	0.0	2504	50	240	0	0	140
Cs	55	11	0.2	4	0.5	0	0	0	0	0	25
Ba	14,000	17,000	160	3900	290	0	0	0	0	3000	110
Au	0	0	0	1.5	0	0	0	110	0	0	0
Hg ²	7	25	1	0	2	1800	0	410	890	620	50
Pb	180	12	20	12	0.2	44	0	0	210	610	340
Bi	0	0	0	0	0	0	12	22	0	80	0

¹ inclusion type: I—liquid H₂O + liquid CO₂ ± vapour CO₂ + N₂, II—vapour CO₂ + N₂, IV—liquid H₂O + vapour H₂O + NaCl + S⁰. ² Te and Hg are absent in the external standard (NIST 612). For this reason, their contents are conventionally estimated in ppm Sb and Au equivalent, respectively. These data reflect only the qualitative result of their determination in the sample.



Figure 9. Sketches of the dependence of the signal intensity on time during ablation of a single fluid inclusions S1/10(2) (**a**) and SV (1) (**b**–**d**) (in Table 4). The photographs (**a**,**b**) show individual phases of fluid inclusions: V—gas, L—solution, H—halite, S⁰—native sulphur.

5. Oxygen Isotopes

The δ^{18} O values in quartz of all studied generations vary from +12 to +26‰ and fall into a narrow interval for each stage (Figure 10). The δ^{18} O values of the early quartz are of +23 to +26‰ and +12.1 to +16.5‰ for Q1a and Q1b, respectively. Quartz from the marble (Q1a) is ¹⁸O-rich. The δ^{18} O values of Q2 fall into a narrow interval from +12 to +12.9‰. The δ^{18} O values of Q3 range from +12.8 to +14.1‰. Our previous data revealed the ¹⁶O-rich (+7.2 ± 0.3‰) values for the late quartz [20]. The calculated δ^{18} O values of the ore-forming fluid in equilibrium with quartz at 270–385 °C (according to T_h data) fall into two intervals: between +5.2 and +8.5‰; between +16 and +19‰ (Figure 10). Temperature ranges for each of the studied samples are up to 50 °C (more often not exceeding 20 °C), which corresponds to the variation of 0.1 to 0.6‰ (rarely 1.3 to 1.5‰) between the estimations at minimum and maximum temperatures. The δ^{18} O values of fluid were calculated using average T_h and the dependence between the temperature and δ^{18} O_{H2O} is shown in Figure 10b. The δ^{18} O_{H2O} value in equilibrium with the metasomatic quartz at 300 °C is +8.5‰ and with the vein quartz ranges from +4.5 to +11‰ and close to 0 (±0.5‰) [20].



Figure 10. Oxygen isotopic composition of quartz (**a**) and ore-forming fluid (**b**,**c**) in comparison with the range of magmatic waters (after [50]) in the Svetlinsk deposit.

6. Discussion

6.1. Fluid Immiscibility or Fluid Mixing

The contrasting fluids were revealed in the studied hydrothermal system. At the early stage (Q1a), four major temporally-related inclusion types were present: (1) $CO_2 \pm H_2S + N_2 \pm S^0$, (2) hypersaline (31 wt % NaCl equiv.), multi-phase, $H_2O - CO_2 - NaCl - CaCl_2 \pm S^0$, (3) moderate salinity (15.6 wt % NaCl equiv.) $H_2O - CO_2 - NaCl - CaCl_2 \pm S^0$ with variable CO₂ contents and (4) low salinity (10.5 wt % NaCl equiv.) H₂O-NaCl-CaCl₂ inclusions. The first two fluids are interpreted to be end-member fluids of the third fluid, formed during immiscibility. This hypothesis is confirmed by lower T_h of H₂O-rich inclusions, similar CO₂ homogenisation temperature ranges, and higher salinities in more- H_2O -rich inclusions due to the salt preferentially fractionated into the aqueous phase [51]. At the early stage (Q1b), two fluids were revealed: (1) CO₂-rich and (2) moderate salinity (10.7–16.9 wt % NaCl equiv.) $H_2O - CO_2 \pm CH_4 - NaCl - MgCl_2 - FeCl_2$. The appearance of the parent fluid in the same assemblages as two immiscible phases at the early stage implies that these fluid inclusions were trapped along or close to the solvus. The dominance of CO_2 -rich inclusions can be explained by the contrasting wetting properties of H_2O compared to CO_2 with respect to quartz. At stage 2 (Q2), three fluids were revealed: (1) low to moderate salinity (3.4–11.3 wt % NaCl equiv.) $CO_2 - H_2O NaCl - MgCl_2 - FeCl_2$, (2) CO₂-rich, and (3) low-salinity (6.7–9.1 wt % NaCl equiv.) H₂O - NaCl. These FI types show contrasting fluid compositions and homogenisation temperatures that are not in accordance with the criteria for fluid immiscibility [51]. Likely, these fluids are the end product of partial fluid mixing and heterogeneous trapping. The positive correlation between T_h and salinity for the majority of values is compelling evidence of fluid mixing (Figure 6). At stage 3 (Q3), three fluids were revealed: (1) low to moderate salinity (3.3–10.9 wt % NaCl equiv.) $CO_2 (\pm N_2) - H_2O - NaCl -$ MgCl₂ – FeCl₂, (2) CO₂-rich, and (3) dilute (0.5–1.3 wt % NaCl equiv.) H₂O – NaCl – MgCl₂ solution. Contrasting fluid compositions as well as positive correlation between T_h and salinity (Figure 6) are evidence for fluid mixing. Late quartz (Q4) was precipitated from low-salinity (1.7 to 7.3 wt % NaCl equiv.) NaCl solution.

6.2. PTX Parameters of Ore Formation

6.2.1. Temperature

The homogenisation temperatures measured for the FI associations of types I and II with similar phase ratios correspond to the two-phase liquid-vapour equilibrium curve in the $H_2O - CO_2 - NaCl$ system [52]. The T_h values obtained for such heterogenic aqueous-carbonic fluid may be considered the real temperatures of mineral deposition because pressure correction is not required in this case [34]. The fluid inclusion study indicates that the mineralisation was formed from 365 to 240 °C, from 345 to 195 °C, and from 405 to 295 °C during stages 1 (Q1a and Q1b), 2 (Q2), and 3 (Q3), respectively. Mineral formation temperature did not decrease from the early stage to the late one, but temperature decrease within each stage was recorded.

In addition to the microthermometry data, the mineral-forming temperature was calculated using cation (Na/K, Na-K-Ca and Fe/Mn) and mineral geothermometers [53–56]. The obtained values (details are not shown here) are up to 50 °C lower for Na/K and Na-K-Ca geothermometers, but are comparable with microthermometry data for the Fe/Mn geothermometer (304 and 395 °C).

Native gold crystallisation temperature (stage 2) estimated by electrum-fahlore and sphalerite-fahlore geothermometers varies from 216 to 211 °C (Vikent'eva, unpublished data). Temperature calculated based on the composition of telluride parageneses and intergrowths native gold with Au-Ag tellurides from stage 3 varies from 350 to 240 °C [23] and does not contradict the microthermometric data.

6.2.2. Pressure

For the samples where CO₂-bearing FIs were found, the pressure was estimated by crossing isochors and isotherms (Figure 11). For the construction of CO₂ isochors, carbon dioxide inclusions with a minimum impurity of other gases (T_{mCO2} from -56.6 to -58.0 °C) were used, so that their influence on the density estimation could be ignored (less than 5 mol % in bulk fluid composition). Estimated fluid pressure varies from 1970 to 4070 bar at 260 to 365 °C, from 1620 to 2880 bar at 255 to 302 °C and from 1100 to 3220 at 295 to 363 °C for the stages 1 (Q1b), 2 (Q2), and 3 (Q3), respectively (Figure 11). Significant fluid pressure fluctuations as well as intense deformations and fracturing during ore formation suggest the overpressure formation conditions [57–59]. The fluid pressure is relatively low during fluid flow through open fractures at the early periods, and it could increase later as a result of sealing of fractures by precipitation of hydrothermal minerals. This process can repeat itself many times. The fault-valve model helps to explain wide ranges of pressure determinations for FIs from a single sample [60].



Figure 11. Estimated fluid pressure in the Svetlinsk deposit.

6.2.3. Fluid Composition

The complex study of FIs and crush-leach data revealed the various fluid compositions for each stage. Ore-forming fluids in the Svetlinsk hydrothermal system were CO_2 -rich. It is pointed out that the presence of CO_2 can induce immiscibility both within the magmatic volatile phase and in the hydrothermal systems [61]. In addition to CO_2 , early fluid was H₂S-bearing. N₂ and CH₄ are occasionally present in the fluid coexisting with Q1a and Q1b, respectively (Table 3). Quartz of the

quartz-pyrite stage (Q2) was formed from CO_2 -rich fluid. The fluid responsible for the formation of quartz (Q3) with telluride assemblages was a mixture of CO_2 and nitrogen. Late fluid (Q4) was a dilution aqueous solution. Some researchers attribute the presence of N_2 and CH_4 in fluid to the interaction with fluids derived from the metasedimentary host rocks [62–64]. The nitrogen-rich fluid could be produced in-situ, by oxidation-dehydration reactions destabilising ammonium-bearing silicate minerals (biotite, phlogopite, and amphibole). It should be noted that N₂-CH₄-(H₂O) fluids form in equilibrium with biotite at high values of $a_{K+} a_{H+}$ characteristic, whereas N₂-CO₂-(H₂O) fluids would be produced in metapelitic rocks with lower $a_{K+} a_{H+}$ [65]. In addition, the oxidising environment at this temperature range was favourable for the N_2 release from the NH_4^+ -bearing host rocks and stabilisation in the fluid [66]. Mantle-derived fluid could be an alternative source of N_2 -enrichment. The existence of N_2 -rich fluid phase in at least some mantle lithologies at certain conditions is demonstrated in [67]. The presence of N_2 -CO₂-(H₂O) fluids in equilibrium with biotite and reduced nature of hydrothermal fluid (abundance of pyrrhotite in ores and H₂S in FIs) for Q1a and abundance of telluride mineralisation for Q3 suggest the possible participation of mantle fluid in the ore formation. N₂-rich inclusions were also found in the intrusion-related gold deposits [68–71] as well as in quartz from I-type granite [72]. The latter suggests the magmatic fluid enrichment by N₂.

Halogen ratios (Br/Cl and I/Cl) can be estimated only for the early fluid in equilibrium with quartz in marble (Q1a). Br content is below the detection limit in other samples. Br/Cl and I/Cl mol ratios are 0.021 and 532.8 \times 10⁻⁶, respectively. Such high values correspond to a metamorphic interval, according to [73]. However, magmatic fluid could also be Br-enriched as a result of magma degassing with preferential removal of Cl⁻ (as HCl) from interacting NaCl solutions and silica, or at the precipitation of halite from the hydrothermal fluid, where a significant amount of Cl is incorporated into halite and residual fluid is enriched by Br [74,75]. Br-rich fluids within the magmatic systems could also be generated as a result of crystallisation of the Cl-bearing phases (e.g., biotite, amphibole, or apatite) prior to volatile exsolution, which causes the formation of Br-enriched juvenile magmatic brines (e.g., [74]).

Early quartz (stage 1) was formed from the bicarbonate-chloride fluid. Na⁺ \ge Ca²⁺ >> K⁺, Mg²⁺ and Cl⁻ > HCO₃⁻ in the fluid (Q1a) and it was relatively rich in Ba, Br, I, Sr, Ba, Mo, Co, Ni, Sn, and Cd. Quartz of stage 2 also was formed from the CO₂-rich bicarbonate-chloride fluid, but this fluid was Na-rich (Na⁺ >> K⁺, Ca²⁺ > Mg²⁺) and Cl⁻ < HCO₃⁻. Ore-forming bicarbonate-rich fluid of stage 3 was enriched in B, As, Sb, Cu, Zn, Pb, Bi, Au, Ag, Te, and Si.

It should be noted that Au and Te were detected both in the early fluid and the fluid responsible for the main productive stage. This fact suggests that these mineralisations were derived from a single hydrothermal system.

6.2.4. Sulphur in Fluid Inclusions

A specific feature of the early fluid of the Svetlinsk deposit is the presence of native sulphur in fluid inclusions.

Native sulphur was observed in FIs from the Nordvik salt dome (Taimyr Peninsula, Russia, [76]), and from the stratabound Sierra de Lujar deposit (Granada, Spain, [77]). A mix of different redox states of sulphur species was also found in FIs from various environments. H_2S , COS, and S together with anhydrite crystals were observed in FIs from the meta-evaporite in the Siberian platform [78] and in the metamorphic ruby deposits in Northern Vietnam [79]. H_2S , SO₂, SO₄²⁻, and elemental sulphur are often observed in FIs from porphyry-epithermal deposits [80,81]. Native sulphur-bearing FIs were more recently identified in greisen veins of the Sn-W Alyaskitovoe deposit (Yakutia, Russia) linked with the Li-F granite, in quartz of both the granite porphyry and the veins from the Kalgutinskoe Mo-W(Be) greisen deposit (Gorny Altai, Russia), and in the Samolazovskoe deposit (Central Aldan), which formation was related to alkaline magmatism [82].

Based on experimental studies, the mix of sulphate-sulphide and/or elemental sulphur could produce new sulphur species at an elevated temperature (>200 $^{\circ}$ C), like the trisulphur S₃⁻. The latter

could favour the mobility of sulphur itself and associated metals (Au, Cu, and Mo) in hydrothermal fluids [83].

6.2.5. Oxidation State of Ore Forming Fluid

The abundance of pyrrhotite in the early ores as well as the presence of H₂S (Q1a) and CH₄ (Q1b) in FIs suggests the reduced nature of the hydrothermal fluid. The presence of native sulphur in FIs could be an indicator of the initial oxidation state of parent fluid and of low pH of solution at the moment of trapping [84]. High CH₄ values could be attributed either to the interaction of the hydrothermal fluids with carbonaceous host rock or to the initially lower oxidation state of the fluid (close to the CO₂-CH₄ buffer). Precipitation of scheelite and late telluride assemblages as well as the presence of N₂ in FIs corresponds to a relatively oxidised state of ore-forming fluid. This fact coincides with the slight increase of the CO₂/CH₄ ratio from the early to the late stage. It was previously established that gold-telluride ores were formed at the temperature decrease and at the progressive decline of tellurium fugacity with some periods of relative stability of f_{Te2} and at the slight f_{S2} variations [19]. According to [85], the constant level of f_{Te2} requires a change in the hydrothermal fluid, such as an increase of X_{H2Te} , total Te concentration, or oxidation of fluid. Composition of Bi tellurides, namely the Bi/Te + Se + S (R_{Bi/Te}) ratio, reflects the redox conditions of fluid [86]. Tsumoite (R_{Bi/Te} = 1) coexisting with Au-Ag tellurides indicates the relatively oxidised environment.

6.3. Sources of Hydrothermal Fluids

Oxygen isotope composition of fluid ($\delta^{18}O_{H2O}$) equilibrated with various studied quartz is clustered into two groups, with one from +5.2 to +8.5‰ (Q1b, Q2, and Q3) and the other from +16.1 to +19.1‰ (Q1a) (Figure 10). According to the previous study, $\delta^{18}O_{H2O}$ values are: in equilibrium with the metasomatic quartz at 300 °C – +8.5‰; with the vein quartz – 0 ± 0.5‰ and +4.5 to +11.0‰ [20]. The majority of values corresponds to the typical magmatic water interval (+5 to +9‰, [87]), is close to the mantle value (+5.7‰) and falls into a narrow interval for each stage (+6.1 to +8.4‰ for Q1b, +5.2 to +6.0‰ for Q2 and +6.3 to +8.5‰ for Q3). Since the intervals of igneous and metamorphic water overlap, the contribution of metamorphic fluids to ore formation cannot be excluded. Oxygen isotope composition of fluid equilibrated with the quartz from marble (Q1a) is ¹⁸O-rich and these values are typical for metamorphic fluids. However, the oxygen isotope exchange between the fluid and the host rock could also cause ¹⁸O-enrichment of the magmatic fluid derived from the hidden granitic pluton. The deposition of quartz from ¹⁶O-rich fluid can be a result of the ¹⁸O depleted heated meteoric water input. The $\delta^{34}S_{H2S}$ values (+1.5 to +8.7‰ [20]) are typical of sulphur exsolved from the granite magma.

6.4. Model of the Svetlinsk Hydrothermal System

Formation of quartz veins was related to the development of the Svetlinsk granite-related dome located to the east of the deposit [28,29]. Granitisation seems to trigger silica and gold mobilisation and their accumulation in the metamorphic halo of the dome. The escape of magmatic fluids from the crystallising synorogenic granitic melt caused the formation of miarolic and vein pegmatite bodies above the apical part of the granite pluton [31]. The migration of fluids further from the granite pluton caused the formation of quartz veins and accompanying quartz-sericite and quartz-biotite alterations at the flanks of the pluton-related system [30]. In the areas of gentle layering, the ore mineralisation was additionally controlled by the zone of the thrust, hosting the plate-shaped massive bodies of serpentinite and gabbro. These bodies acted as a geochemical reducing and hydrodynamic (decreasing permeability) barrier. The following hydrothermal processes led to partial gold redistribution. Some late gold together with tellurium could come from the lower crust and the upper mantle through the thrust permeable zone leading to the formation of the deposit of the unusual for the Urals Au-telluride mesothermal type.

The deposit formation was polygenetic and mainly related to the orogenic activity [21,31,88], cf. [26]. Metamorphic mineral assemblages of the host mainly metasedimentary rocks indicate the amphibolitic facies of the metamorphic peak that was assumed to be associated with the Early-Permian regional metamorphism, accompanying the hyper-collision [89,90]. Five stages of ore formation can be distinguished (cf., [21]): (I) deposition of terrigenous and volcaniclastic rock (slightly enriched in Au), Late Fransian–Early Visean, (II) low-grade greenstone metamorphic stage with disseminated sulphide redistribution, Tournaisian, (III) main collision metamorphism (amphibolitic facies) and formation of the synorogenic tonalite-granodiorite pluton and pegmatite and quartz veins in its apical part and, further from the pluton, in the distal peripheral zone, series of gold-scheelite-sulphide-quartz veins accompanied by beresite-listvenite alteration, Visean–Serpukhovian, (IV) formation of veinlet-disseminated gold-telluride mantle-related mineralisation, Moscovian–Early Permian, and (V) supergenic stage with the formation of weathering crust and large gold placers (Mesozoic-Cenozoic).

7. Conclusions

Our detailed fluid inclusions study revealed the contrasting fluid compositions, and stable O isotope data proved the multiple sources of the ore-forming fluids involved in the Svetlinsk hydrothermal system. At the early stages, the magmatic fluid evolved during its ascent and phase separation, and fluid derived from the host rock decarbonation and dehydration were involved in the hydrothermal system. In addition, mantle-derived hydrothermal fluid might be involved in the ore-forming process during the gold-telluride precipitation, as well as heated meteoric waters at the late stages. Early fluids were H_2S -, S^0 - and CH_4 -rich, while the Au-Te mineralisation was formed from N₂-rich fluid. Mineralisation in the Svetlinsk deposit was formed at a wide range of temperature and pressure (200–400 °C and 1–4 kbar). Mineral formation temperature did not decrease from the early to the late stages, but a temperature decrease within each stage was recorded. Significant fluid pressure fluctuations as well as intense deformation events with post-peak fracturing suggest the possibility of periodic overpressure conditions during vein formation.

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Appendix A

Table A1. Composition of the NIST 612 standard [47], Analytic Center of IGM SB RAS.

Component	Content	$\pm\sigma$	Component	Content	$\pm\sigma$	Component	Content	$\pm\sigma$
Na ₂ O, %	13.7	0.3	Ni	38.8	0.2	Pr	37.9	1
Al_2O_3	2.03	0.04	Cu	37.8	1.5	Nd	35.5	0.7
SiO ₂	72.1	0.6	Zn	39.1	1.7	Sm	37.7	0.8
CaO	11.9	0.1	Ga	36.9	1.5	Eu	35.6	0.8
Li, ppm	40.2	1.3	Ge	36.1	3.8	Gd	37.3	0.9
Be	37.5	1.5	As	35.7	5.5	Tb	37.6	1.1
В	34.3	1.7	Se	16.3	1.9	Dy	35.5	0.7

Component	Content	±σ	Component	Content	±σ	Component	Content	±σ
F	80	89	Rb	31.4	0.4	Но	38.3	0.8
Na	101,645	2226	Sr	78.4	0.2	Er	38	0.9
Mg	68	5.1	Y	38.3	1.4	Tm	36.8	0.6
Al	10,747	212	Zr	37.9	1.2	Yb	39.2	0.9
Si	336,467	2800	Nb	38.9	2.1	Lu	37	0.9
Р	46.6	6.9	Mo	37.4	1.5	Hf	36.7	1.2
S	377	70	Rh	0.91	0.02	Ta	37.6	1.9
Cl	142	58	Pd	1.05	0.1	W	38	1.1
Κ	62.3	2.4	Ag	22	0.3	Re	6.63	0.61
Ca	85,000	714	Cd	28.1	1.1	Ir	0.0045	
Sc	39.9	2.5	In	38.9	2.1	Pt	2.51	0.1
Ti	44	2.3	Sn	38.6	1.3	Au	4.77	0.31
V	38.8	1.2	Sb	34.7	1.8	Tl	14.9	0.5
Cr	36.4	1.5	Cs	42.7	1.8	Pb	38.6	0.2
Mn	38.7	0.9	Ba	39.3	0.9	Bi	30.2	2.3
Fe	51	2	La	36	0.7	Th	37.79	0.08
Co	35.5	1	Ce	38.4	0.7	U	37.38	0.08

Table A1. Cont.

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