

Groundwater Chemistry, Achibo-Sombo Underground Coal Mine, Southwestern Ethiopia

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ABSTRACT

Achibo-Sombo mine is the first underground coal mine in Ethiopia and is in operation for more than a decade. It is a small-scale, semi-mechanized, and mined using room and pillar method. Most of the mining operations are being carried out manually. The coal deposit is inter-trappean, sandwiched between basaltic flows. Seepage is a common problem in the mine. Its intensity varies in three openings and is being drained out by gravity. A preliminary study was conducted to assess the quality of water in the mine. Ten water samples collected randomly from three openings were analysed for major anions using standard colorimetric methods and elemental concentrations using ICP-MS. The results indicate that the concentrations for sulphur, manganese, and iron is relatively higher. The concentration of toxic elements like Cd, As, Hg, and Se is relatively low except Zn. Increased amounts of sulphate in water indicate the sulfides as the source and their chemical breakdown. The relatively higher amount of dissolved sulfur is expected to produce acid mine drainage with time.

Keywords: Mine water, Hydrogeochemistry, Major ions, Trace elements, Achibo-Sombo, Ethiopia.

1. INTRODUCTION

Coal deposits in Ethiopia are mostly found inter-bedded with Cenozoic volcanics of the Ethiopian plateau (Miniye, 1992). These intertrappean coal- bearing sediments are widely distributed in the Dilbi-Moye, Lalo-Sapo, Yayu, Sola, Chida, Chilga, Mush Valley, Wuchale, Arjo and Nejo basins (Wolela, 1992a, 1992b; Wolela et al., 2002; Miniye, 1992; Getahun et al., 1993; Kibrie, 2000) (Fig 1a). Yayo coal deposit in southwest Ethiopia has been the target for detailed exploration and mining since 2007 with an estimated reserve of about 250x10⁶ tons (Gebreyohannes, 2001). The Yayo area is further divided into Wuttete coal field and Achibo-Sombo coal field with about 179Mt and 3.2Mt respectively (Gebreyohannes, 2001). The underground coal mine is situated in Achibo-Sombo coalfield and the coal deposit at Achibo-Sombo covers an area of about 41 km² and consists of lignite to sub-bituminous variety coal (Fig

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1a & b). The Achibo-Sombo area is covered by red and brown colored soil with limited exposures of basement crystalline rocks, younger volcanic rocks mainly of basaltic composition and sedimentary rocks. Based on the detailed study of coal -bearing sedimentary sequences, ten coal seams of varying thickness were reported whereby nine of them have been correlated and numbered 1 to 9 from bottom to top (COMPLANT, 2007). Mulata et al. (2017) have conducted a study on underground mine slope stability, design, factor of safety, and possible recoverable coal. Studies related to mine water quality and aquifer condition and its consequences are yet to be conducted. Thus, the present paper tries to assess the quality of underground coal mine water particularly in terms trace elements.

1.1. About Mine and Groundwater

The underground coal mine is operating for more than a decade and developed using room and pillar mining method. Three horizontal parallel openings, only one level, are developed into the coal-bearing sedimentary formations, referred as OP1, OP2 and OP3 (Fig 1c). The openings are about 2m height, 2m wide and extend laterally maximum about 150m. These parallel openings slight inclination of about 5% to facilitate haulage and water drainage. The mine is overlain by about 150-250m thick overburden comprised mainly of lateritic soils, basaltic rocks and sedimentary rocks (Mulata, 2017). Major part of the overburden about 100-150m is covered by basalt rock. Due to the mine openings, water in the overburden rock aquifers is flowing into the mine through geological structures as pathways. To facilitate the mining operations, the water flowing into the mine is being drained out by gravity through the mine openings. Out of three mine openings, only OP1 and OP2 are being used presently for production operations while OP3, about a meter below to OP1 and OP2, is being used to drain the water from the mine by gravity (Fig 1c & d). The water generated in different parts of the underground mine is directed to flow along OP1 and OP2 and then connected to OP3 through crosscuts. Thus, the water is drained out of the mine continuously into the nearby Geba river. Since, the mine is not a mechanized one and the water is not used for any application inside the mine, the drained water quality is expected to be controlled by the aquifer rocks, and chemical changes taking place at mine due to exposure. The groundwater samples collected in the mine are referred here as mine water for convenience.

In general, the quality of groundwater is understood with reference to the nature of lithologies, geological structures, type of the mineralization, duration of water-rock interaction etc. In the present case, the water flowing towards mine is modified due to coal-bearing lithologies. This change involves in the dissolution of minerals, weathering, and erosion of fine size clay minerals in the form of suspended matter. The intensity or degree of modification is reflected in total dissolved solids content (TDS) and suspended particulate matter. Generally, pH of water in a mine is mostly neutral to weakly alkaline if the water is not much affected due to mineralization (Xinfeng et al., 2021). In the case of coal mines, pyrite being the common sulphide mineral associated with coal is expected to cause acidic condition and acid drainage as the mine progresses. Such condition facilitates more dissolution and increasing amounts of dissolved solids which includes toxic elements.

In the case of Achibo-Sombo underground coal mine, the water flowing into the mine through the faces of the mine openings carry clay size particles, fine coal, and organic matter in suspension. The drained water is mostly colorless and is being drained into the nearby Gaba river without any treatment (Fig 1b). If the contamination level is high or water is polluted, the water can attain greyish black colour with suspended impurities and microorganisms (Zhang, 2013).



Figure 1. a) Coal deposits of Ethiopia (modified after Mulata et al (2019), Wolela (2007); b) location map of the study area; c) three underground coal mine openings (OP1, OP2, OP3); and d) coal haulage using opening one (OP1).

2. METHODOLOGY

Ten water samples were collected in this study. Out of ten, eight were collected from the underground mine, one from outside the mine at exit point and one from the nearby spring. Out of eight water samples were collected in the mine, two are from OP1 (AMWS1OP1 and AMWS9OP1), three each from OP2 (AMWS2OP2, AMWS7OP2, and AMWS8OP2) and OP3 (AMWS5OP3, AMWS6OP3, and AMWS10OP3) (Fig 2). At each site in the mine, the sample was collected in situ at base of the pillar where water was flowing into the mine and care was taken to avoid possible mix of water coming from other openings particularly the samples collected from OP3. Two water samples collected at exit point and spring are from outside the mine. Out of which one is spring water (AMWS4SP) from a spring nearby the mine and another is a mixed sample (AMWS3MIX) collected from the mine outlet representing the mix of groundwater generated in the mine. The sample AMWS4SP is from the nearby spring whose location is outside the sample location map and hence its location is not shown in figure 2.



Figure 2. Water sampling points, Achibo-Sombo underground coal mine. Sample 4 is related to spring which is away from the mine, not shown here.

At each site the water sample is collected in two 1 litre properly rinsed and numbered plastic bottles separately for anions and cation analysis. The bottle collected for cation analysis was acidified with 3-4 drops of conc HCl. The parameters like pH, TDS and EC were collected in the field itself while the major anions were analyzed using UV-Vis Spectrophotometer and

titration procedures at Mekelle University Hydrogeochemistry laboratory. The acidified water samples were submitted to ALS Geochemistry Lab at Addis Ababa for major, minor and trace elements analysis using ICP-MS. The data is given in appendix 1 and 2.

3. RESULTS

The results presented in appendices 1 and 2 are shown in plots in figures 3 to 6, with reference to mine openings from 1 to 3 for a better comparison. The groundwater samples collected in the mine are referred here as mine water for convenience. Mine water samples show neutral to slightly basic pH including the spring water sample where pH is ranging from 7.36 to 8.29 (Fig 3). Alkalinity values in mine water range from 35 to 130 mg/l CaCO₃ and TDS from 205 to 745 ppm and differ significantly with the values of spring water and mixed mine water (AMWS3MIX). The spring water shows lower values while the mixed mine water shows higher values compared to mine water (Fig 4a). Chloride values for mine water range from 7 to 23 mg/l and bicarbonate from 42 to 158 mg/l. These two parameters are lower relatively in spring water compared to mine while in mixed mine water, chloride is much higher, and bicarbonate is quite low compared to mine water (Fig 4b). Sulphate values range from 12 to 56 mg/l and nitrate from 0.02 to 11.17 mg/l in mine water. In the mixed water sample, sulphate is very high (56.15mg/l) while nitrate is low (0.08mg/l) compared to mine water. In the case of spring water, both sulphate and nitrate values are lower compared to both mine water and mixed mine water (Fig 3 and Fig 4b). Among anions, bicarbonate is the dominant anion, from higher to lower abundance it can be indicated as bicarbonates > sulphate > chloride > nitrate.



Figure 3. Relation between pH, alkalinity, and bicarbonate in mine water (pH values as shown in table 1 are multiplied by 10 to see the trend).



Figure 4 Mine water chemistry, (A) TDS and alkalinity; B) major anions; C) major cations; and D) trace elements.

4. DISCUSSION

4.1. Coal Mine Geology and Aquifer Condition

The underground mine is developed in the coal-bearing sedimentary sequences which present between basaltic flows, at few places between volcanic and high-grade basement rocks. Based on age, stratigraphy set up and geochemical variations the basaltic rocks are divided into Lower and Upper basalt (Fig 5a and b). The coal-bearing sedimentary rocks mainly overlie the Lower basalt unconformably. Upper basalt which forms the overburden consists of fine-grained basalt (aphanitic basalt), porphyritic basalt, vesicular basalt, tuffs, and amygdaloidal basalt. Upper basalt is highly weathered at places producing residual soil. Upper part of the residual soil shows reddish to reddish brown color. The soil when wet or moist it shows plasticity but when it is dry the plasticity nature decreases and become loose. The bottom part of the residual clay soil contains highly to extremely weathered and limonitized/ ferruginized fragments of basalt with thin bed of laterite. Below the residual clay soil, basalt grades into completely to moderately weathered varieties. The color also varies from place to place from yellowish brown to gray (Mulata, 2017). The sedimentary succession mainly consists of non-systematic sequences of fine grained clastic sedimentary rocks, siltstones, claystones, sandstones, mudstones, carbonaceous

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shales, and coal bed in the middle of the succession. In the mine area carbonaceous shale and mudstones are associated with the coal beds. The sedimentary sequences together with coal were formed in fluvio- lacustrine environment (Mulata, 2017).



Figure 5 A) Geological map of the study area; B) Cross section profile along A-B of the area. C) Rose diagram showing (i) mining direction, (ii) joints and fractures orientation, (iii) fault orientation, and (iv) bed orientation (Mulata et al., 2017).

Figure 5 indicates the mine direction, coal beds orientation, and associated structures. The Upper basalt which forms the main overburden is affected by minor faults (S70⁰E) and columnar joints (S50⁰W) having spacing ranging from 8 cm-10 cm and aperture of 2 cm-5 cm. The joints are mostly open type and rarely closed or healed. The closed joints are filled with calcite, silica and secondary hydroxides of iron and manganese minerals (Mulata, 2017). The overburden comprised of lateritic soils and upper basalt are possibly the water-bearing formations that form two distinct aquifers in the area (COMPLANT, 2007). It is not clear whether there are two distinct aquifers or only Upper basalt form the main aquifer. The aquifer characteristics and the water yield potential mainly for Upper basalt is weak to medium whereas the water yield property of the coal bearing sedimentary rocks, Lower basalt and basement rocks

is very weak. (COMPLANT, 2007). The elevation of water table is in the range of 1586.82-1624.73m (COMPLANT, 2007). The distance between the minable coal seams (No 6, 5, 4) and the aquifer system ranges from 15.41 m to 283.50m (Mulata, 2017). Flow of groundwater into the mine through joints and fractures is eroding finer particles from the sedimentary formations causing localized small-scale subsidence. Such affected areas in the mine are addressed by providing proper wooden support.

4.2. Mine Water Chemistry

In general, the degree of contamination of mine water like surface water and groundwater, is generally reflected by the color of the water. Un-contaminated water is generally having no color. In the present case, visual observation suggest that the water is almost colorless. In terms of chemistry, mine water shows significant variation in certain anions and cations and distinctly differ from spring water chemistry in terms of TDS, sulphate, calcium, and magnesium (Figs 3 and 4).

pH in mine water is mostly neutral to slightly alkaline (Table 1, Fig 3) and is one of the indicators that suggests the quality of water in terms of acid drainage and role of sulfides. In the present case, the values do not indicate any acid drainage. At the same time, pH broadly shows inverse relation with both alkalinity and bicarbonate (Fig 4). Alkalinity values are slightly above the normal range 80-120 ppm, shows positive relation with bicarbonate and suggests the nature of water-rock interaction and shift towards basic pH.

TDS values are within the normal range 300ppm for all samples except the mixed one which shows much higher value above 700ppm. Such high value is undoubtedly indicating possible source may be close to the outlet in opening 3, not inside the mine openings 1, 2 and 3 because the values get diluted during drainage. Interestingly, alkalinity shows negative relation with TDS for the same mixed water sample. In all other samples there is no significant difference in the trend between TDS and alkalinity (Fig 4A).

Among major anions, bicarbonate is the dominant anion. But interestingly, the bicarbonate value is low in sample no 3 compared to all other samples including spring water (Fig 4B). Chloride values are relatively higher in mine water compared to spring water. Sulphate on the other hand, shows much higher value in sample 3 compared to spring water and other mine water samples (Fig 4B). However, sulphur values are <1% in coal beads around Achibo-Sombo area which is the lowest among other coal deposits present in southwestern Ethiopia

(Diriba, 2020). Relatively higher values for sulphate and chloride in mine water compared to spring water seems to indicate that the source is possibly the coal-bearing sedimentary sequence which commonly consists of sulphides and chloride-bearing salts (Fig 4b). Bicarbonate on the other hand is possibly from chemical weathering of silicate minerals mostly from the Upper basalt (Fig 4b). Relatively lower bicarbonate values for mixed mine water could be due to dilution. Though, sulphur values obtained by ICP-MS and UV-Vis Spectrometry methods do not compare well, the relative value is high in both analyses. (Table 1 and 2). Nitrate values are lower and do not show any significance. Similarly, among major cations, Ca values are relatively higher than other cations and is expected to be derived from both basalt and sedimentary formations. Whereas Mg values are assigned to basaltic source rocks. Na and K do not show any significant trend and their values are also relatively low compared to others (Fig 4C). Other cations, like iron range from 0.3 to 1.6 mg/l in mine water (Table 2) while the mixed mine water and spring water show relatively much low values, 0.06 and 0.08 mg/l respectively. Iron shows higher than 1 mg/l in all the samples in the mine indicating possible contribution from iron sulphide in sedimentary formations and mafic minerals like amphiboles in the basalt. Relatively lower values for iron for both mixed mine water and spring water suggests possible iron precipitation as hydroxides due to its exposure to atmosphere. Manganese on the other hand, ranges from 2 to 65 μ g/l in mine water and spring water but shows highest in mixed mine water $(653 \mu g/l)$. It is quite contrary to Fe and suggest its selective enrichment and contribution from the coal-bearing carbonaceous sedimentary sequences.

In terms of other elements, Al values range between 101 and 11900 μ g/l in mine water and relatively higher compared to mixed mine water (238 μ g/l) and spring water (101 μ g/l) (Figs 4D & 6). Si on the other hand range in concentration from 14 to 37.2 mg/l in mine water, and the values are relatively lower compared to spring water (37.2 mg/l) and higher compared to mixed mine water (Table 2). Silica content in groundwater is mainly due to water–rock interaction, chemical weathering of silicate minerals in rocks and sediments and is directly proportional to its residence time and contact with silicate minerals (Hem, 1959). Generally, SiO₂ in groundwater range from 1 to 30mg/l, and usually about 17mg/l (about 7.9 mg/l Si). So, Si content is a good indicator of the degree of chemical weathering and is also correlated with TDS and Cl⁻ to understand the role of anthropogenic activities and geogenic processes on groundwater chemistry (Marchand et al., 2002; Pradeep et al., 2016; Khan and Umar, 2010). In the present case, Si shows negative relation with both TDS and Cl⁻ (Fig 4B). Interestingly, both Si and Al shows relatively higher values compared to the suggested drinking water concentrations i.e <30mg/l and <0.9 mg/l respectively (WHO, 1984). Both Si and Al show similar trend for samples from OP2 and OP3 but shows opposite trend with the samples from OP1 and spring water (Fig 6). Since, the data size is small, it is difficult to ascertain the behaviour of Si and Al precisely. Zinc is another trace element range from 6.5 to 4100 ppb in mine water and relatively higher compared to mixed mine water (396 ppb) and spring water (19.2ppb) (Table 2). Higher value for Zn than the WHO suggested value for drinking water (50 μ g/l) is related to the coal-bearing sedimentary sequences. The mine water shows relatively higher values for Si, Al, Mn, Fe, Zn among trace elements, others are within the WHO suggested drinking water guidelines (WHO, 2022) (Table 2).



Figure 6. Relation between silica and aluminum in mine water.

4.3. Nature of Coal Deposit and its Influence on Water Chemistry

The coal deposit of Achibo-Sombo is an intra to intertrappean type and the type of coal present within the mine varies from sub –bituminous to lignite type with moderate sulphur content (Gebreyohannes, 2001; Diriba, 2020). In Achibo-Sombo coal mine, the structurally affected areas in the mine are being provided with proper wooden support. Since, the Achibo-Sombo mine is occupying the topographic high in the area and few meters above in elevation from the nearby flowing Gaba river and its tributaries (Fig 1) the mine water is drained into the river. This may affect the underlying aquifers of Gaba catchment in the long run. At the same time,

continuous flow of groundwater through overburden into the mine obviously affects the groundwater level though locally around the mine area.

The Achabo-Sombo coal deposit being non-marine and lacustrine type, differs significantly from other marine-related coal deposits in terms of host rocks, variety and volume of sulphides particularly pyrite, salts, organic sulphur, toxic metals etc apart from the type of coal (Tülay, 2013). Coal-bearing sedimentary sequences at Achibo-Sombo are only few meters thick, varying from few meters to tens of meters (Mulata, 2017 and 2019) and the mine water composition is mainly influenced by the percolating water through overburden comprised of upper basalt and residual soil cover. The dominant upper basalt aquifer is controlled by secondary permeability (Fig 5C), and the residence time is obviously controlling the chemistry of the water that reaches the mine. Coal layers and coal-bearing sedimentary sequences are mainly contributing sulphur, manganese, zinc etc. to these waters. But when compared the mine water with spring water, there is an increase of in the content of many elements except in bicarbonate, Si, V etc (Appendix 1 and 2). Interestingly, both Si and Al are showing much higher values than drinking water standards and average Si in groundwater, 0.9mg/l and 8 mg/l respectively (WHO, 1984, McMahon et al., 1995). High content of Si in water is a good indicator of weathering, water circulation conditions, intensity of water-rock interaction, possible role of organic matter, temperature, and enhanced quartz/k-feldspar dissolution in the aquifer (McMahon et al., 1995, Fournier and Potter, 1982). The solubility limit for silica in water is estimated at approximately 120 mg/L at 25°C (Stumm and Morgan, 1970), and in the present case it is much below the solubility limit.

Mine waters can be of different types and can cause different environmental hazards. Acid mine drainage with increased amounts of toxic heavy metals such as Cu, Zn, Mn, As, Pb, and Cd though is common in coal and sulphide mines related mine waters, it is not the case in the Achabo-Sombo coal mine except for Zn and Mn. Monitoring the mine water becomes essential as it is drained into the nearby river (Fig 1) without any treatment. With time it may cause increase in the acidity of river water locally and related groundwater. This may affect the local population who uses this river water and groundwater for drinking and irrigation purposes. Given the nature and size of the coal deposit, though the toxic element content is expected to be low (Appendix 2), slight increase of these toxic elements (Cd, As, Hg and Se) can have health effects like sore throat, increase the risk of cancer (lung, skin, and kidney), fragile bones, hair and fingernail loss, fatigue, darkening of skin for the miners.

Other sources of pollution due to the mine is the dust and burning of mine spoils which can produce gases like carbon dioxide, hydrogen sulphide, carbon monoxide, methane and oxides of sulphur and nitrogen. Mine spoil waste burning is common in Achibo-Sombo coal mines, especially during dry season. Since, there is no proper ventilation system, it can have impact on the working personnel health as they inhale sulphur- related gases, methane etc very common in underground coal mines. Since, mine water samples show relatively higher concentrations of sulphur, it can give rise to acidic, sulphate-rich waters in future. It can further produce acid mine drainage.

5. CONCLUSION

Groundwater from the overlying rock aquifer mainly of basalt is flowing into the mine through small scale structures like joints and fractures. To facilitate mining operations, the groundwater flowing into the mine is drained out by gravity through OP3 into the nearly Geba river without any treatment. Continuous flow is causing voids and localized small-scale subsidence by eroding the clay-size particles from the coal-bearing formations.

The mine waters are slightly alkaline having about 300 mg/l TDS is dominated by bicarbonate and follow the order from higher to lower as bicarbonate > sulphate > chloride > nitrate. In the case of cations, the order from higher to lower is Ca>Mg>Na>K. Among trace elements, Fe, Mn, Si, Al, Zn shows relatively higher values 1.6 mg/l, 65 µg/l, 37.2 mg/l, 11,900 µg/l, and 4100 µg/l respectively compared to WHO drinking water guidelines. When compared with spring water which has no relation with coal-bearing formations, the mine water chemistry is influenced by the coal-bearing formations while spring water by the rock aquifer basalt.

The sample collected outside the mine at exit point interestingly shows higher values for TDS, Cl, and SO₄, Ca, Mg and Mn; and lower values for HCO₃, Fe, Si and Al, Na and K. Relatively higher values of sulphur indicate contribution from sulphides in coal-bearing formations and is expected to increase with time due to mining. This will give rise to acidic conditions in mine waters and can increase dissolution rates, dissolved solids and may produce acid mine drainage. A detailed study is suggested to understand the chemical weathering patterns, suspended clay and organic matter and other chemical species.

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7. CONFLICT OF INTEREST

No conflict of interest.

8. REFERENCE

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Sample code	Sample type	pН	EC	TDS	Alkalinity	Chloride	Bicarbonate	Sulphate	Nitrate
				(<i>mg/l</i>)					
AMWS10P1	Mine water	7.92	288	205	95	7.12	115.89	11.56	0.02
AMWS9OP1	Mine water	7.36	411	293	90	21.32	109.79	16.32	6.12
AMWS2OP2	Mine water	7.90	346	247	95	9.13	115.89	13.63	0.03
AMWS7OP2	Mine water	8.29	390	278	85	12.58	103.69	13.72	5.67
AMWS80P2	Mine water	6.96	360	257	125	12.67	152.49	15.13	11.17
AMWS50P3	Mine water	8.06	452	322	110	12.81	134.19	13.56	5.14
AMWS6OP3	Mine water	8.19	448	320	90	13.23	109.79	14.13	6.12
AMWS100P3	Mine water	7.94	428	305	130	17.43	158.59	14.45	5.57
AMWS3MIX	Mixed water	7.79	1044	745	35	23.56	42.69	56.17	0.08
AMWS4SP	Spring water	7.97	209	149	70	8.18	85.39	12.53	0.04

Appendix 1. Results of anions and other parameters of water samples, Achibo-Sombo underground coal mine, SW Ethiopia.

Appendix 2. Hydrogeochemical result of water samples, Achibo-Sombo underground coal mine, SW Ethiopia.

Code	AMWS10P1	AMWS90P1	AMWS2OP2	AMWS70P2	AMWS80P2	AMWS50P3	AMWS60P3	AMWS100P3	AMWS3MIX	AMWS4SP	
(mg/l)											
Ca	25.8	44.3	34.5	41.5	46.4	40.3	41.8	33.1	128.5	28.6	
Fe	0.604	1.02	0.554	1.035	0.154	1.585	1.16	0.328	0.062	0.085	
Κ	7.82	11.25	7.53	7.57	7.74	12.2	9.11	12.15	12.45	2.51	
Mg	10.9	11.9	12.6	13.5	12.95	12.7	16.35	15.05	42.1	6.38	
Li	3.3	3	2	3.7	1.5	5.4	5.4	1.7	3.5	1.1	
Na	20.3	23.7	14.05	15.15	14.45	29.1	19.4	28.6	24.1	9.01	
Si	24.6	16.15	23.6	25.7	21.8	29.4	21.6	20.1	14	37.2	
S	11	23.7	9.5	17.9	10.6	11.8	28.2	16.5	148	0.8	
(µg/l)											
Al	6420	6360	2090	5660	910	11900	3680	6370	238	101	
Р	0.016	0.017	0.023	0.042	0.028	0.037	0.02	0.019	0.011	0.093	

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Ag	0.037	< 0.005	0.055	0.018	0.046	0.013	0.041	0.049	0.015	0.014
As	0.52	0.34	0.44	0.29	0.29	0.68	0.14	0.38	0.3	0.11
Au	0.52	0.34	0.44	0.29	0.29	0.68	0.14	0.38	0.3	0.11
В	173	21	13	14	16	38	17	22	95	5
Ba	105	101	75	76	75	118	73	127	112	14
Be	0.059	0.055	0.035	0.098	< 0.005	0.161	0.06	0.046	< 0.005	< 0.005
Bi	< 0.01	< 0.01	0.01	0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cd	0.134	0.061	0.006	0.023	0.007	0.077	0.08	0.084	0.081	0.013
Со	2.18	0.187	0.164	0.239	0.066	2.47	2.58	1.25	2.12	0.093
Cr	1.3	2.3	1.1	2.3	<0.5	3.8	1.6	0.7	<0.5	<0.5
Cs	0.103	0.093	0.065	0.046	0.051	0.006	0.085	0.084	0.09	0.006
Cu	1.2	1.9	0.9	1.1	0.8	1.6	1.2	2.3	1	1.5
Ga	0.69	1.02	0.47	1.2	0.16	2.25	0.73	0.42	0.07	0.06
Hf	0.133	0.337	0.087	0.286	0.038	0.513	0.513	0.083	0.011	< 0.005
Hg	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
In	0.03	< 0.01	0.01	0.01	< 0.01	0.01	0.01	< 0.01	< 0.01	< 0.01
La	1.375	1.84	0.896	2.42	0.219	3.54	1.96	0.947	0.102	0.078
Mn	65.5	2.28	2.5	2.32	2.12	15.8	5.33	10.55	653	3.78
Mo	6.19	3.84	4.18	4.63	3.84	11.05	5.26	4.4	3.61	0.36
Nb	0.85	1.29	0.505	1.425	0.186	2.68	0.951	0.461	0.03	0.028
Ni	3.1	1.7	0.3	1	< 0.2	3.6	3	1	2.9	< 0.2
Pb	0.98	0.84	0.3	1.27	3.17	0.98	0.36	0.37	0.16	0.08
Pd	< 0.005	0.006	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Pt	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Rb	14.95	21	13.9	13.3	14.4	21.7	17.65	21.8	24.1	2.32
Re	0.003	0.025	0.003	0.002	0.004	0.004	0.002	< 0.002	0.041	< 0.002
Sb	0.13	0.09	0.05	0.15	0.09	0.19	0.12	0.07	0.14	0.01
Se	1.06	1.49	0.57	0.81	0.62	1.54	0.53	0.96	8.15	0.13
Sn	0.06	0.11	0.06	0.16	< 0.05	0.2	0.08	< 0.05	< 0.05	< 0.05

 $\ensuremath{\mathbb{O}}$ CNCS, Mekelle University

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Sr	140.5	204	189.5	418	184	261	217	190	631	153
Та	0.04	0.07	0.03	0.08	0.01	0.17	0.04	0.03	< 0.01	< 0.01
Те	0.01	< 0.01	0.01	0.01	0.01	0.01	0.01	< 0.01	0.01	< 0.01
Th	0.166	0.37	0.142	0.314	0.037	0.688	0.416	0.101	0.026	0.008
Ti	340	290	90	250	40	600	180	400	30	10
Tl	0.007	0.018	< 0.002	0.016	0.011	0.008	0.011	0.015	0.024	0.008
U	0.082	0.235	0.063	0.113	0.033	0.333	0.113	0.057	0.035	0.024
V	6.07	6.24	4.88	6.5	3.7	11.5	3.93	8.75	1.85	10.5
W	0.1	0.06	0.06	0.07	0.04	0.13	0.07	0.06	0.04	0.01
Y	0.705	1.395	0.483	1.49	0.245	3.38	1.9	0.563	0.155	0.187
Zn	4100	123	6.5	193.5	210	19.2	19.2	48.1	396	19.2
Zr	4.04	7.35	2.84	7.71	1.04	15.4	5.05	2.5	0.45	0.25
Ce	3	4.59	2.01	4.58	0.397	9.33	4.21	1.56	0.16	0.159
Sc	0.93	1.57	0.64	1.32	0.55	2.32	1.84	0.57	0.96	2.68