PAPER • OPEN ACCESS

Geochemical behavior of Mo and W in the CO₂rich mineral waters occurring in the East Elbrus area

To cite this article: G A Chelnokov et al 2021 IOP Conf. Ser.: Earth Environ. Sci. 865 012037

View the article online for updates and enhancements.

You may also like

- A computational study of MoS₂ for band gap engineering by substitutional doping of TMN (T = transition metal (Cu).
 M = metalloid (B) and N = non-metal (C)) Muhammad Tayyab, Akhtar Hussain, Qurat ul Ain Asif et al.
- Production of Mo and Ru Isotopes in Neutrino-driven Winds: Implications for Solar Abundances and Presolar Grains
 J. Bliss, A. Arcones and Y.-Z. Qian
- Structural evolution and thermal runaway of refractory W and Mo nanotips in the vacuum under high electric field from PIC-ED-MD simulations Xinyu Gao, Nan Li, Andreas Kyritsakis et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.134.78.106 on 06/05/2024 at 18:49

IOP Conf. Series: Earth and Environmental Science 865 (2021) 012037

Geochemical behavior of Mo and W in the CO₂-rich mineral waters occurring in the East Elbrus area

G A Chelnokov^{1,3}, V Y Lavrushin¹, A S Aidarkozhina¹ and Q Guo²

¹Geological Institute Russian Academy of Sciences, Pyzhevsky lane 7, bld. 1. 119017, Moscow, Russia;

²State Key Laboratory of Biogeology and Environmental Geology, School of Environmental Studies, China University of Geosciences, 430074 Wuhan, Hubei, PR China

³Corresponding author's e-mail: geowater@mail.ru

Abstract. Molybdenum and tungsten concentrations in cold CO₂-rich mineral groundwaters of east Elbrus area lie in two ranges: 0.01-0.43 ppb and 0.01-410 ppb. The temperature of the water varies from 7.9 to 17.6 °C. Mo concentrations have irregular behaviour with temperature and do not demonstrate a significant correlation with any parameters. Tungsten concentrations are strongly and positively correlated only with As, indicating either common sources or common processes controlling their grades. The highest W concentrations are exclusively associated with Na-HCO₃-Cl water types, with a circum-neutral condition (6<pH<7) and lower Eh (-60-+45 mV). The dominant species of Mo and W in mineral waters of eastern Elbrus are molybdate ion (MoO₄), and $[W_7O_{24}]^{6}$ polyanion. Based on the risk assessment results, for two potential contaminants (Mo and W), the concentration level of W exceeded the environmental quality standard, which suggests a severe to moderate ecological risk and, therefore, needs to be considered as the priority pollutant for the studied area.

1. Introduction

The concentrations of Mo and W and processes controlling their chemistry in groundwaters are of environmental interest. From the one side, the enrichment of these elements in aqueous systems is useful to unravel geochemical processes (pollution, water-rock reaction, mixing with geothermal fluids etc.). However, recently, more studies suggest that the exposure to elevated tungsten concentrations may cause various pathological changes or diseases, like rhabdomyosarcoma, lung inflammation, DNA damage in bone marrow, etc. [1].

Several investigations have revealed W and other microelements concentrations in mineral and surface waters within the Baksan river Valley (East Elbrus area), which connected with Tyrnyauz Mo-W deposit [2, 3, 4]. Unfortunately, they contain poorly understood features. Therefore, the adequate geochemical data for tungsten and molybdenum in natural water of the study area are still limited. This article represents new geochemical results on Mo and W in CO2-rich mineral groundwaters of the East Elbrus area.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

The Fourth International Workshop on Environment and Geoscience	IOP Publishing
IOP Conf. Series: Earth and Environmental Science 865 (2021) 012037	doi:10.1088/1755-1315/865/1/012037

2. Sampling and analytical procedures

For the present study, chemical data on ten mineral water manifestations within Baksan river Valley (East Elbrus area, Figure 1), collected by authors during fieldwork in 2016, were interpreted. Sample points were represented by boreholes and spring with water temperatures ranging from 7.9 to 17.6°C.

The water samples were filtered through 0.45 μ m mixed cellulose ester filters (Advantec, Japan) and collected in acid-washed, high-density polyethylene sample bottles. Waters for the cation analysis were acidified to pH<2 with ultrapure HNO₃. Water temperature, conductivity, and pH were measured directly in the field using Mettler Toledo probe. Major cations and anions were analyzed by ion chromatography. Carbonate species were titrated in-situ with 0.1 N HCl. Trace elements concentrations in groundwater were determined by ICP-MS (Agilent 7500) analysis. Trace elements, Mo and W concentrations were analyzed by ICP-MS (Agilent 7500 and ELEMENT XR) in the Analytical Department of GIN RAS (Moscow). The chemical results of the water samples are presented in Table 1.



Figure 1. Location of sampling sites, Tyrnyauz Mo-W deposit, and Elbrus volcano.

3. Results and discussion

According to classification diagrams (Figure 2), three chemical types of waters are presented (Table 1). The Ca-HCO₃ type has TDS 0.4-1.0 g/l, temperature less than 10°C, slightly acidic to neutral pH, and slightly reducing conditions (Eh from 0 to 78 mV). Geochemical characteristics of this water show that it is shallow groundwaters with a short period of circulation and their mineralization controlled by CO_2 -water-rock interaction processes.

Na-HCO₃ mineral waters with TDS 0.7- 5.0 g/l also display slightly acidic to neutral pH and more oxidizing conditions (Eh from 45 to 112 mV). These waters often have elevated concentrations of SO₄, up to 512 ppm.

Alkali carbonate Na-HCO₃-Cl groundwaters are generally cold (T= $16.6-17.6^{\circ}$ C), demonstrate highest TDS (5.6-6.1 g/l) and reducing conditions (Eh vary from -60 to 45 mV). Concentrations of SO₄ and Fe vary in a wide range (Table 1).

All studied waters show good Na, Cl and B correlations (r=0.93). These values are well-correlated with the geological history of the region since that the main part of are comprises Late Paleozoic biotitic granites and Middle Paleozoic metamorphic crystalline schists [5]. The highest TDS are recorded in mineral waters far from the Elbrus mnt., on an elevation of about 1300 m, in a sector where is found a contact between biotitic granites and Carbonic limestones (points 17-16, 20-16). Lowest TDS = 0,4 and 0,7 mg/l characterized for springs located on upper parts of the territory (2000 m a.s.l.) (points 10-16-12-16).

The Cl and Br concentrations are highly correlated in all analyzed groundwaters (Figure 3). Mass ratios of Cl to Br range from 358 to 1157 (average 501) for all saline groundwaters, which is an indication of fresh water and NaCl dissolution components.

					Springs				Bore	holes
	Unit	10-16	14-16	11-16	12-16	13-16	15-16	16-16	17-16	20-16
		Ca-HCO3			Na-HCO3				Na-HCO3-Cl	
TDS	g/L	0.4	1.0	2.2	0.7	2.0	2.6	5.0	6.1	5.6
Т	°C	9.9	7.9	11.6	8.5	10.3	14	16.4	16.6	17.6
pН	Unit	6.1	6.8	6.2	6.5	6.8	6.5	6.5	6.5	6.7
Eh	mV	2.3	78	112	45	103	84	96	-60	45
Na		5.7	34	304	108	224	283	829	1508	1542
Ca	ppm	74	172	159	75	193	251	406	213	85
Mg		18	26	65	16	75	124	88	48	15
ĸ		2.8	3.6	21	14	15	41	84	96	113
Cl		8.1	81	228	179	195	179	1043	1605	1524
SO_4		11	6.6	11.5	8	111	512	252	9.6	312
HCO ₃		327	673	1364	313	1242	1177	2279	2526	2006
Fe		13	11	21	13	4.4	25	6.4	73	1.8
Al		0.1	0.04	0.05	0.2	0.04	0.05	0.07	0.04	0.03
Мо		0.07	0.13	0.14	0.17	0.43	0.10	0.18	0.4	0.001
W	рро	0.08	-	0.02	0.01	-	-	-	0.55	411

Table 1. Chemical composition of the studied mineral water ^a.

^a Numbers of springs: 10-16– Terskol, 11-16– Badaevka, 12-16– Djan Tugan, 13-16– Irik-Narzan, 14-16 – Adil-Su, 15-16 – Verhni Narzan, 16-16– Nizhni Narzan, 17-16 – borehole, 20-16– Tyrnyauz old borehole. Dash-lower detection limit.

IOP Conf. Series: Earth and Environmental Science **865** (2021) 012037 doi:10.1088/1755-1315/865/1/012037



Figure 2. Classification of studied waters using Piper diagram. Numbers according to Table 1.



Figure 3. Compositions of molybdenum bearing natural waters in the Eh–pH diagram for the Mo–O–H–S system at 25° C, P = 1 bar. [6]

These correlations are unexpected in the Elbrus geological framework, which consists of granites and schists. But this data is in agreement with isotopic and geochemical data presented by [7]. They demonstrate that the salt and the gas composition of these waters were formed at significant depths and high temperatures. The contribution of connate waters, especially in the Elbrus, is not excluded. Upwelling of deep-seated waters was accompanied by decreasing temperature and dilution by meteoric waters. Mineral waters efficiently interact with rocks through leaching.

The measured concentrations of Mo in all water types are much lower the limits of the Russian drinking water (250 ppb) and the WHO (2011; 70 ppb) standards (Table 1). Maximum Mo concentrations (0.4-0.43 ppb) are associated with Na–HCO₃ and Na-HCO₃-Cl waters. There is no Mo anomaly even in the water influenced by Tyrnyauz W-Mo deposit (point 17-16, 20-16). Statistical analyses show that correlation Mo and main parameters and ions are very weak. Maximum coefficients revealed for pH (r=0,3), Ca (0.27), Fe (0.3) and Al (0.27). Figure 3 demonstrates that molybdate (MoO4²⁻) is the dominant species in the studied mineral waters. Molybdenite itself is highly insoluble in water [6], and it is likely to have been oxidized to molybdate and got introduced to the groundwater. Molybdate is the dominant species at a pH > 6. If pH values drop, the molybdate anion becomes protonated. When pH values drop below 4.4 [8], the molybdate anion will fully protonate to MoO₃(H₂O)₃. Thus, the migration state of Mo in cold water is highly dependent on Eh-pH.

Russian drinking water standards is limited W concentration as 50 ppb, and most of studied waters demonstrate much lower tungsten concentration (0.01 to 0.55 ppb). Anomalous high W concentrations (411 ppb) were found in one borehole on the vicinities of the Tyrnyauz town (the area of Tyrnyauz W-Mo deposit, point 20-16, Table 1).

Several mineral water samples with high pH (6.8) do not contain W (#13-16, #14-16). The most probable is that these waters apparently are associated with areas lacking any significant source of tungsten. The highest concentrations of W (0.5-411 ppb) are exclusively associated with Na–HCO₃-Cl water. In general, high pH and low redox potential are favorable for the enrichment of tungsten in water. However, water with lowest redox potential (-60 mV) does not demonstrate high W concentrations. On the other hand, this mineral water provides conditions for tungsten minerals deposition requires low redox conditions and available Fe and Mn (or Ca) ions. These ions were not detected in the water sample with high W concentration [9]. Statistical analysis demonstrates that W have good correlation with As (r=0.99), Eh (0.6), Mg (0.5), Na (0.5) and Ca (0.5). The significant and positive correlation between

The Fourth International Workshop on Environment and Geoscience	IOP Publishing
IOP Conf. Series: Earth and Environmental Science 865 (2021) 012037	doi:10.1088/1755-1315/865/1/012037

concentrations of W and As may indicate that they have similar sources or that similar processes are controlling their concentrations. Tungsten and $A_{S(V)}$ are anions in water and have similar adsorption properties characterized by decreasing adsorption with increasing pH. Whatever the source of W (mineral dissolution, geothermal water, etc.), the high pH, low Fe and Ca of these mineral water samples results in less relative adsorption and greater aqueous concentrations of W.

According to Smedley & Kinniburgh [8], there is a lack of up-to-date thermodynamic and kinetic data for many important reactions for Mo and W in the natural environment and these limits the ability of current geochemical models to predict its fate and transport. Is well known that the WO₄²⁻ anion is the predominant species of natural waters at pH above 4.5 at 25°C. But recent experiments with Raman spectroscopy coupled with capillary technique [10] reveal that $[W_7O_{24}]^{6-}$ polyanion is the predominant species (90%) under circum-neutral condition (6<pH<7) at T 25-100°C. and only 5-10% of the total dissolved W concentration represents by WO₄²⁻. Even more, there is not W precipitation at temperature interval 25-100°C and pH from 1 to 5.5. According to with Carocci [10] the main species in these conditions are $[W_{10}O_{32}]^{4-}$, $[W_7O_{24}]^{6-}$ and WO₄²⁻.

4. Conclusion

The conducted research allowed to identify the main features of the distribution and water migration of Mo and W in the CO₂-rich mineral waters of the East Elbrus area. It was found that the concentrations of Mo and W vary significantly, from 0.01-0.43 ppb for Mo and 0.01-410 ppb, for W. Temperature of the water changing from 7.9-17.6 °C. In these conditions, concentrations of Mo have irregular behavior with temperature and do not demonstrate some significant correlations with any parameters. Mo concentrations in waters are not controlled by molybdenite solubility. The dominant species of Mo in mineral waters of eastern Elbrus are molybdate ions (MoO₄²⁻). Tungsten concentrations are strongly and positively correlated only with As, indicating either common sources or common processes controlling their contents. Tungsten is mobile during water-rock interaction and its concentrations tend to increase with increasing primary rock dissolution and temperature. Highest concentrations of W are exclusively associated with Na–HCO₃–Cl water types, circum-neutral condition (6<pH<7) and lower Eh (-60-+45 mV). Our new data allowed us to suggest that [W₇O₂₄]⁶⁻ polyanion is a primary species of tungsten, whereas WO₄²⁻ dominates in more alkali environment.

Based on the risk assessment results, for two potential contaminants (Mo and W), the concentration level of W exceeded the environmental quality standard, which suggests a severe to moderate ecological risk and, therefore, needs to be considered as the priority pollutant for the studied area.

Acknowledgements

The reported study was funded by RFBR and NSFC, project number 21-55-53005.

References

- [1] Guo Q, Li Y, Luo L, 2019 Sc. Total Environment 657 1523
- [2] Chirkova E, Baranovskaya E, Kharitonova N, Lavrushin V, Chelnokov G, Bragin I 2019 E3S Web Conf., 98 01009
- [3] Gurbanov A, Bogatikov O, Gazeev V, Leksin A 2015 Doklady Earth Sc. 464 967
- [4] Lavrushin Y V, 2012 Subsurface Fluids of the Greater Caucasus and its Surrounding. 348
- [5] Gurbanov A, Gazeev V M, Bogatikov O A et al., 2004 Elbrus active Volcano and its geological history Russian J. Earth Sc. 6 257
- [6] Ryzhenko B N, 2010 Geochemistry International. 48 407
- [7] Dubinina E O, Chernyshev I V, Bortnikov N S, et al., 2005 Geochem. Int., No. 10, 988
- [8] Smedley P, Kinniburgh D, 2017 App. Geo. 84 387
- [9] Seiler R L, Kenneth G, Stollenwerk J, Garbarino R. 2005 Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada *App.Geo.* **20** 423
- [10] Carocci E, 2019 Tungsten transport and deposition in magmatic-hydrothermal environments: the example of Panasqueira (Portugal). Earth Sciences. Université de Lorraine, English.