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Rare Ni-Co and W accessories in the East-Carpathian metasedimentary manganese belt

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The East-Carpathian manganese belt featured an extended mining activity, lasting from the second half of the 18th century, meantime recording intercalated episodes of decline and revival, until its all-out closedown in recent years. From supergene oxide concentrations, the mining activity extended to carbonate-primary oxide and carbonate-silicate-oxide ore types.

The manganese accumulations are hosted in the medium to low grade metamorphic basement of the Central-East-Carpathian Bucovinian-Subbucovinian nappe system, emplaced during the terminal Early Cretaceous and involving the same sequence of Variscan thrust sheets [1, *and refs. therein*]. The manganese rocks occur as boudined lenses in a definite structural position in the Alpine units, being confined to the Holdița quartzite Formation belonging to the Tulgheș Group in the Variscan Putna Unit, extending hundreds of kilometres over the outcropping basement of the East Carpathians. An account of the mineralogy of the deposits is given in [2], as well as an impressive listing of mineral species by [3].

We identified in a typical banded carbonate-silicate-oxide rock from the former Iacobeni-Arșița Mine, consisting of manganese carbonate, tephroite and jacobsite, with minor alabandite and spessartine-quartz intercalations, a rich assemblage consisting of Co-Ni sulfides and sulfoarsenides, and W-bearing minerals. The assemblage contains intergrowths of maucherite, cobaltite, zoned tučekite-arsenotučekite, pentlandite, millerite and polydymite with sphalerite, galena and alabandite. Welinite, a rare Mn, Mg, W – bearing orthosilicate appears both as coronas around hübnerite, and as grains associated with rhodochrosite, tephroite and jacobsite.

This find identifies the second occurrence of arsenotučekite, often richer in As than that in the type locality Eretria, Greece - [4], and a Mo-bearing, essentially anhydrous, partly (M1)-vacant variety of welinite.

References

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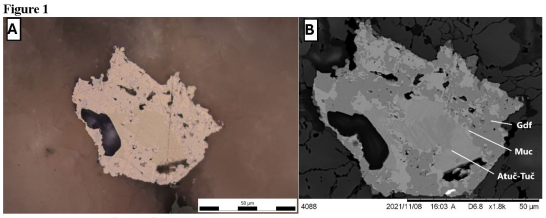
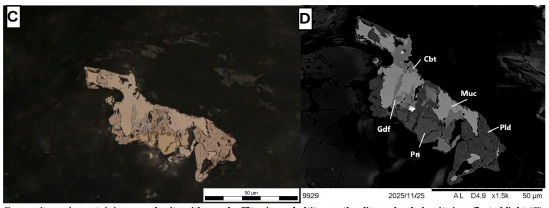
[4] Zaccarini, F., Bindi, L., Tsikouras, B., Grammatikopoulos, T., Stanley, C. J., Garuti, G. (2020) Arsenotučekite, $Ni_{18}Sb_3AsS_{16}$, a new mineral from the Tsangli chromitites, Othrys ophiolite, Greece. *Mineralogy and Petrology, 114/5, 435-442*

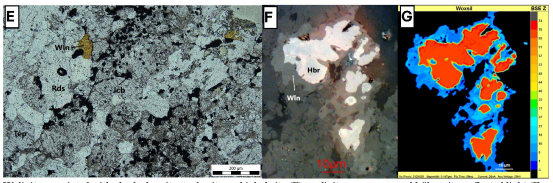
Figure 1



Strongly zoned arsenotučekite-tučekite surrounded by a maucherite-cobaltite intergrowth in reflected light (A) and BSE image (B).



Composite grain containing maucherite with gersdorffite rim, cobaltite, pentlandite and polydymite in reflected light (C) and BSE image (D). Small bright grains in BSE image are galena.



Welinite associated with rhodochrosite, tephroite and jabobsite (E); welinite corona around hübnerite, reflected light (F) and false-colour BSE image (G)

Table 1. Representative mineral compositions in the banded carbonate-silicate-oxide Mn-rock

Mineral	Muc		Alb	Pld	Gdf	Cbt	Pn	Atuč	Tuč	Wlm*			
Analysis	20a/1	20/24	20/2	20/18	20/21	20/26	20b/30	20/6	20/1	20/5	12Ar(24)	12Ar(82)	18-12Ar1(35)	18-12Ar1(36)
As	47.81	48.02	Ca 0.04	Mg 0.02	0.00	0.00	0.02	As 5.43	4.28	1.05				
Sb	1.02	0.47	Mg 0.00	As 0.13	45.26	45.04	0.00	Sb 15.04	17.91	22.09	Mg	1.10	1.38	1.06	1.12
Fe	0.23	0.19	Fe 0.80	Sb 0.01	0.30	0.13	0.01	Fe 0.48	0.49	0.57	Si	7.53	7.72	7.74	7.87
Co	0.07	0.43	S 36.35	Fe 14.56	1.54	0.08	25.14	Co 4.89	4.60	4.70	Ti	0.02	0.06	0.10	0.06
S	0.15	0.42	Zn 0.25	Co 0.59	1.08	31.97	0.04	S 25.32	25.02	24.09	Mn	46.20	45.70	48.21	48.01
Zn	0.00	0.19	Ni 0.03	S 41.32	19.27	19.37	32.06	Zn 0.21	0.00	0.18	Mo	2.17	2.41	2.69	2.18
Ni	50.03	49.88	Mn 61.65	Zn 0.25	0.26	0.34	0.29	Ni 46.89	46.36	45.57	W	15.18	14.66	12.08	12.63
Mn	1.51	0.55	**Sum 99.12**	Ni 39.57	31.54	3.14	39.09	Mn 0.02	0.10	0.06	Mn^{3+}	**6.00**	**6.00**	**6.00**	**6.00**
Sum	**100.82**	**100.15**	Ca 0.00	Mn 0.62	0.47	0.65	0.31	**Sum 98.28**	**96.76**	**98.31**	Mg	0.34	0.41	0.32	0.33
Fe	0.05	0.04	Fe 0.01	**Sum 97.07**	**99.72**	**100.72**	**96.96**	Fe 0.18	0.18	0.22	Mn^{2+}	0.23	0.06	0.37	0.24
Co	0.02	0.09	Zn 0.00	Fe 0.81	0.05	0.00	3.60	Co 1.68	1.59	1.66	Ti	0.00	0.01	0.02	0.01
Ni	10.54	10.54	Ni 0.00	Co 0.03	0.03	0.89	0.01	Ni 16.14	16.12	16.24	Mo	0.17	0.18	0.20	0.16
Mn	0.34	0.12	Mn 0.99	Ni 2.10	0.89	0.09	5.32	Mn 0.00	0.04	0.02	W	0.61	0.58	0.48	0.49
Zn	0.00	0.04	**Sum 1.00**	Mn 0.04	0.01	0.02	0.05	Zn 0.06	0.00	0.06	**Sum**	**1.35**	**1.24**	**1.39**	**1.23**
Sum	**10.95**	**10.83**	**S 1.00**	Zn 0.01	0.01	0.01	0.04	**Sum 18.06**	**17.93**	**18.20**	**Si**	**1.99**	**2.00**	**2.00**	**2.00**
As	7.89	7.95		**Sum 2.99**	**0.99**	**1.01**	**9.02**	As 1.46	1.16	0.30	H	0.00	0.38	0.13	0.69
Sb	0.10	0.05		As 0.01	1.00	0.99	0.00	Sb 2.50	3.00	3.80	O	6.00	5.62	5.87	5.31
S	0.06	0.16		Sb 0.00	0.00	0.00	0.00	**Sum 3.96**	**4.16**	**4.10**	SiO_2	16.11	16.52	16.56	16.84
Sum	**8.05**	**8.16**		S 4.01	1.00	1.00	7.99	**S 15.96**	**15.92**	**15.72**	WO_3	19.14	18.49	15.23	15.93
				Sum 4.02	**2.00**	**1.99**	**7.99**				MoO_3	3.26	3.62	4.04	3.27
											TiO_2	0.03	0.10	0.17	0.10
											Mn_2O_3	2.48	0.62	3.97	2.60
											MgO	1.82	2.29	1.76	1.86
											MnO	57.43	58.45	58.68	59.65
											H_2O	0.00	0.30	0.04	0.99
											Sum	**100.27**	**100.39**	**100.45**	**101.24**

EDS analyses, mineral abbreviations according to Warr (2021).