A Mineralogical Note on Boulangerite, Geocronite and Yenerite From Near Işık Dağı (Kızılcahamam-Ankara), Turkey

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Abstract: Microprobe studies have facilitated recognition of the first documented occurrence of geocronite from Işık Dağı (Ankara, Turkey). While yenerite remains a discredited species along the PbS-Sb_2S_3 compositional join, our analyses show significant arsenic as did the original analyses for yenerite; thus, this name might be retained for arsenic-bearing varieties of boulangerite.

Key Words: Pb-Sb sulphosalts, boulangerite, geocronite, yenerite, plagionite, microprobe, slag

Işık Dağı (Kızılcahamam-Ankara) Yakınında Bulunan Bulanjerit, Jeokronit ve Yenerit İle İlgili Bir Mineralojik Not

Özet: Mikroprob çalışmalarının yardımıyla, Işık Dağı (Ankara, Türkiye) yakınında bulunan jeokronitin varlığı ilk kez saptanmıştır. Yenerit, PbS-Sb_2S_3 bileşimsel çizgisi üzerinde ayrı bir mineral türü olarak kabul edilemezse bile, orijinal analizlerin gösterdiği gibi bu çalışmada sunulan analizler de arsenik elementinin önemli miktarda var olduğunu göstermektedir. Dolayısıyla arsenikçe zengin bulanjeritler için yenerit adı tavsiye edilebilmektedir.

Anahtar Sözcükler: Pb-Sb sülfotuzları, bulanjerit, geokronit, yenerit, plajyonit, mikroprob, cüruf

Introduction

In 1943, yenerite (Steiger & Bayramgil 1943) was described as a new mineral species from a complex sulphide deposit near Işık Dağı, ~80 km north of Ankara in north-central Turkey (Figure 1). However, a few years later, yenerite and falkmanite (Robinson 1948) were found to have the same x-ray diffraction pattern as boulangerite and, consequently, those two species were discredited.

In May 1997 and again in May 1999, two of the authors had the opportunity to visit the mine near Işık Dağı. On both occasions, a number of ore specimens were collected from the old mine spoils and taken back to the laboratory for closer examination. The upland meadow, known as Salın Yaylası, in which the old mine is located, is part of a protected natural area and, thus, it is unlikely that any new ore material will become available insofar as additional exploration and development are forbidden.

The old workings are situated just off of the south slope of Işık Dağı at the northern end of Salın Yaylası, adjacent to and immediately west of the road from Yağcıhüseyin village that descends to the upland meadow, which is used as a summer pasture. An averaged GPS-acquired location for the workings/spoils is 40°39'11.2" N latitude, 032°47'05.7" E longitude.

The deposit at Işık Dağı was worked in Byzantine times, as has been documented by C-14 dating of charcoal from within slags found on the upland-meadow flats immediately below the deposit. A previously published result (Seeliger et al. 1985, p. 601) gave an age of 1160 ± 40 B.P., or a date of 880 C.E. This date is now supplemented by dates obtained on samples collected in 1997. A C-14 age of 695 ± 65 BP years was obtained on bulk lumps of charcoal which were collected from among pieces of slag coming out of a stream bank which is eroding through the slag pile (Geochron Labs,
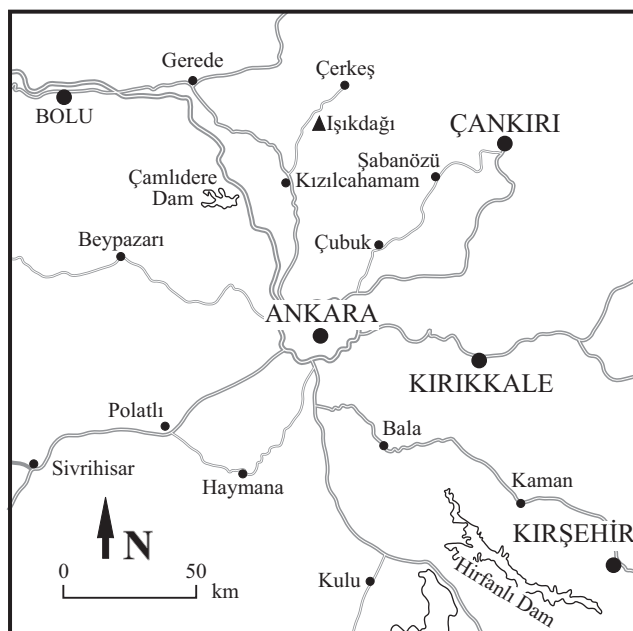
Figure 1. Location map of Işık Dağı.

GX-23290). In addition, an AMS C-14 age of 910 ± 50 years BP was obtained on small quantities of charcoal which were extracted from freshly broken pieces of slag (Geochron Labs, GX-23366-AMS). These new dates correspond to 1255 C.E and 1040 C.E., respectively, and while somewhat later, are still within Byzantine time.

Later explorations are reported from the early 1800's (Bayramgil 1945, p. 45) and again in 1942 (Bayramgil 1945), but none of these attempts seem to have been successful. Moreover, it is unclear why the first attempt was abandoned. One might presume that the purpose was to extract lead and possibly silver from the complex ores. Perhaps they found the ores to be too poor in lead insofar as the abundant sphalerite (false-galena) might have been mistaken for the less abundant true Pb-bearing species of galena and boulangerite; alternatively, impurities of antimony in the lead extracted may have made it too hard to be useful, such as for gun shot (Bayramgil 1945, p. 45). Furthermore, the ores are quite rich in arsenopyrite. When the ore was smelted, abundant arsenic fumes would have proven quite poisonous to anyone in the neighbourhood; of course, it is possible that the ores were actually used to recover arsenic, not lead. However, there seems to be no mention in Roman sources (e.g., Pliny) or in late medieval sources (e.g.,

Biringuccio and Agricola) of the recovery of white arsenic by fuming. Certainly the recovery of arsenic from arsenopyrite by fuming would have been confounded by the presence of large quantities of SO_2 (Azcue & Nriagu 1994, p. 5).

Ore Mineralogy

The geological setting and mineralogy of the ores at Işık Dağı during the last serious exploration of the deposit have been fully described by Bayramgil (1945). His detailed petrographic examination yielded the following paragenetic sequence (Bayramgil 1945, p. 79, 1946): tourmaline + cassiterite + apatite + epidote, arsenopyrite; sphalerite + chalcopyrite; pyrite; galena-I; calcite; boulangerite/geocronite + para-ankerite; galena-II; and quartz + barite.

Our examination of polished thin sections and backscatter images shows a fine-grained equigranular texture, with the ore minerals embedded in a matrix of fine-grain quartz. The ore minerals – in decreasing order of abundance – are pyrite, arsenopyrite, sphalerite, boulangerite and galena. Our sections did not show any gangue mineral other than quartz. The grains of pyrite and arsenopyrite are euhedral, while those of sphalerite,
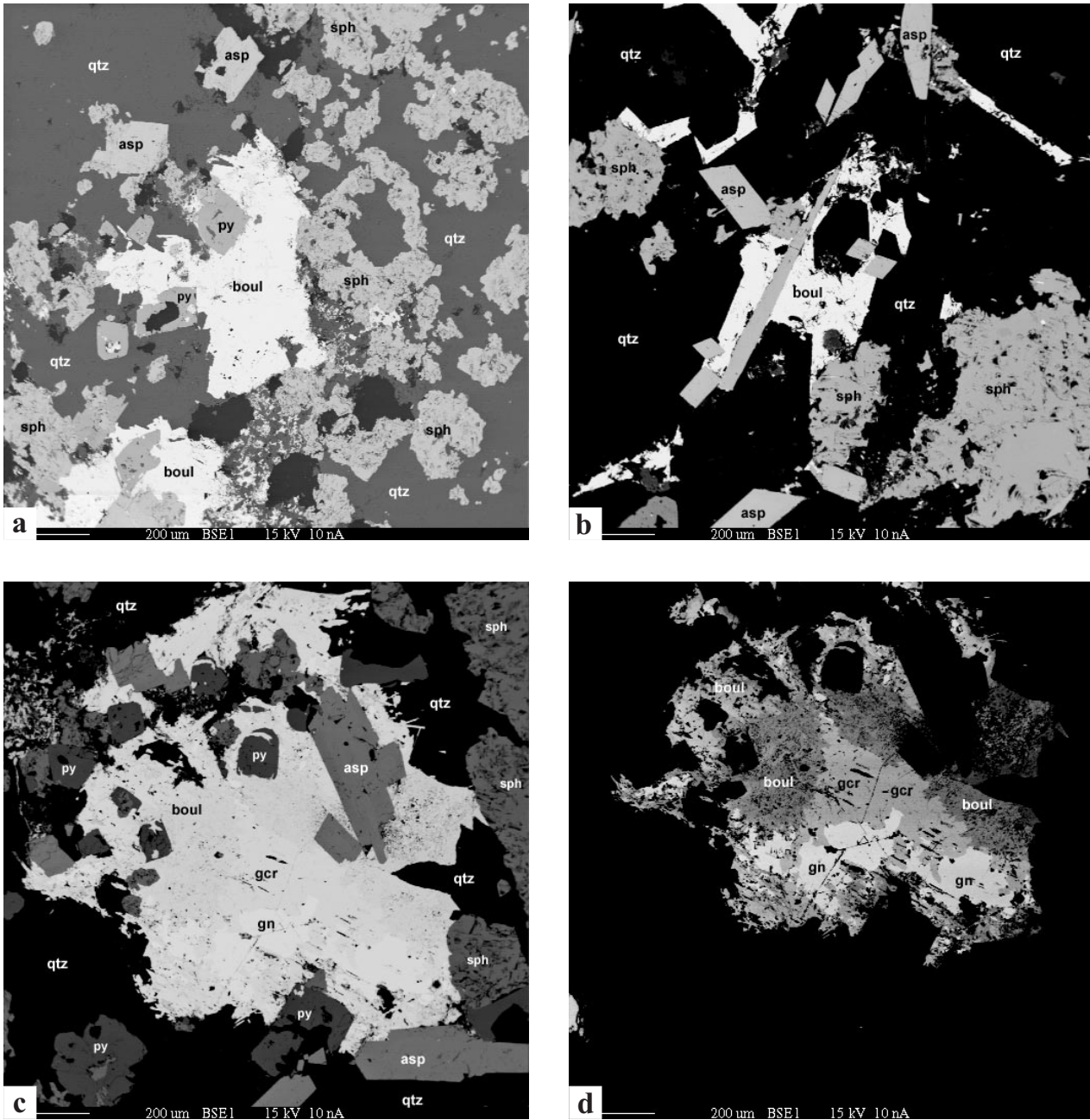
Figure 2. **(a)** A backscatter image from section idg2 showing an anhedral grain of boulangerite (boul) with euhedral grains of pyrite (py) and arsenopyrite (asp), and anhedral grains of sphalerite (sph), all embedded in a matrix of quartz (qtz). **(b)** A backscatter image from section idg1 centred on a grain of boulangerite (boul) surrounded by euhedral grains of arsenopyrite (asp) and anhedral grains of sphalerite (sph), all embedded in a matrix of quartz (qtz). **(c)** A backscatter image from section idg2 centred on an anhedral grain of galena (gn) with geocronite (gcr), and boulangerite (boul), accompanied by euhedral grains of pyrite (py) and arsenopyrite (asp), and anhedral grains of sphalerite (sph), enmeshed in a matrix of quartz (qtz). **(d)** An enhanced backscatter image of an anhedral grain in **(c)** of galena (gn), geocronite (gcr) and boulangerite (boul). Note the decrease in brightness with decreasing content of Pb as one progresses from the core of galena through the overgrowth of geocronite to the outer rim of boulangerite.

boulangerite and quartz are anhedral (Figure 2a). The occurrence of chalcopyrite as fine disseminated grains within the sphalerite is best observed in reflected light.

Microprobe Analyses

A couple of the better ore specimens collected from the spoil heaps were sectioned with a diamond saw, and doubly polished thin sections were prepared for microprobe analyses. Samples of boulangerite from well-known localities were obtained from the National Museum of Natural History, embedded in epoxy, and polished sections prepared.

Analyses were performed on an electron microprobe (Cameca SX-50) equipped with four wavelength-dispersive counters. The acceleration voltage was 15kV, with a beam current of 20 nA and a focused beam in spot mode of 1 μm. Natural pyrite was used for S-Kα and Fe-Kα, galena for Pb-Mα, stibnite for Sb-Lα, arsenopyrite for As-Lα, and chalcopyrite for Cu- Lα. Peak and background counting times were set for 30 and 15 seconds, respectively. Observed intensities were corrected using the PAP correction program (Pouchou & Pichoir 1991) supplied with the microprobe.

Probe analyses of the arsenopyrite, chalcopyrite and galena (Table 1) gave conventional values. The sphalerite is notably rich in iron (~10%) while the pyrite is clearly As-bearing (2–3%).

In addition, random grains of lead sulphosalts having two distinctly different compositions were encountered in the course of microprobe analyses. The first of these has a composition corresponding to that of boulangerite (Figure 2a, b), but with the distinct presence of arsenic, while the second corresponds to that of geocronite. The nature of the occurrence of geocronite was not understood during the initial analytical stage because of the high brightness of all of the lead minerals in the backscatter images (Figure 2c). However, upon careful adjustment of brightness, it was possible to observe that the geocronite occurs as overgrowths on grains of galena (Figure 2d), and that it in turn is overgrown by boulangerite.

The compositional values obtained for boulangerite (Table 2) can be compared with microprobe analyses of representative material from the Cleveland mine (USNM-97011-1 and 95414), Pribram, Bohemia (USNM - 83983) and Noche Buena, Zachetcas (USNM-115863), as

Table 1. Selected microprobe analyses of some ore minerals from Işık Dağı (in weight percent).

Section	IDG-2	IDG-2	IDG-1	IDG-1	IDG-2
Mineral	Pyrite	Arseno-pyrite	Sphalerite	Chalcopyrite	Galena
Element					
Mn	0.04	0.00	0.41	0.00	0.00
Pb	0.00	0.00	0.00	0.00	87.10
Sb	0.00	0.00	0.01	0.00	0.10
As	2.31	44.88	0.21	0.00	0.00
Zn	0.03	0.08	56.22	0.00	0.02
Cu	0.00	0.03	0.07	34.22	0.00
S	51.19	20.27	33.48	34.83	13.32
Fe	46.01	34.15	10.67	29.08	0.31
Total	99.58	99.41	101.07	98.13	100.85

Table 2. Analyses of boulangerite (in weight percent).

Sample	1	2	3	4	5	6
Element						
Pb	54.59 ± 0.53	56.77	56.69	55.30	55.86	56.42
Sb	24.99 ± 0.13	25.50	25.30	26.41	26.34	25.69
As	1.27 ± 0.40	0.61	0.69	0.64	0.35	.
S	18.89 ± 0.20	18.22	18.18	18.22	18.28	18.89
Fe	.	.	.	0.01	0.01	.
Total	99.74	101.10	100.86	100.58	100.84	100.00

Sample	7	8	9	10	11
Element					
Pb	57.32	55.28	55.34	55.08	58.13
Sb	23.60	25.40	25.30	24.38	22.81
As	1.83	.	.	.	.
S	17.06	18.19	18.08	18.65	18.43
Fe	.	0.39	0.52	trace	0.57
Insol.	.	0.62	0.40	1.10	.
Total	99.81	99.88	99.64	99.21	99.11

1. Işık Dağı, microprobe, sect. Idg-1, average of 1 spot on 3 grains.
2. Cleveland Mine, Stevens Co., Washington, USNM 95414, microprobe, average of 5 spots, pyrite inclusions.
3. Cleveland Mine, Stevens Co., Washington, USNM 97011-1, microprobe, average of 5 spots, galena inclusions.
4. Pribram, Bohemia, Czech Republic, USNM 83983, microprobe, average of 5 spots.
5. Noche Buena, Zacatecas, Mexico, USNM 115863, microprobe, average of 5 spots.
6. Ideal $Pb_5Sb_4S_{11}$ (Palache *et al.* 1944, p. 421).
7. Yenerite, Işık Dağı (Bayramgil 1945, p. 56).
8. Cleveland Mine, Stevens Co., Washington, USNM 95414, analysed by F.A. Gonyer (Palache & Berman 1942, p. 421).
9. Cleveland Mine, Stevens Co., Washington, USNM 95414 (Shannon 1925, p. 197).
10. Przibram, Bohemia, Czech Republic, USNM 83983 (Shannon 1920, p. 598).
11. Przibram, Bohemia, Czech Republic, analysed by Boricky and Helmhacker (Shannon 1920, p. 592).

well as with wet chemical analyses reported in the literature. Clearly the lead sulphosalt analysed is boulangerite. It is, however, slightly lead deficient when compared to the ideal composition. The probe analyses of boulangerites from known localities are compatible with published analyses, although those from the Cleveland mine are running about 1% higher in Pb (Table 2). Wet chemical analyses all show small amounts of iron, while all of the microprobe analyses show none or only trace amounts. The iron in the wet chemical analyses can be attributed to small inclusions of pyrite that are readily observed in the probe sections. In addition, inclusions of galena were observed and this, in some cases, results in elevated lead values. The reference boulangerites, unlike the wet chemical analyses, show the presence of about 0.5% arsenic. The boulangerite from Işık Dağı is notable in having at least 1% arsenic.

The other lead sulphosalt has a high (> 2) Pb/Sb ratio and a Sb/As atomic ratio of about 2 to 1. A search of Dana's Mineralogy (Gaines *et al.* 1997, p. 150–203) shows that this lead sulphosalt compositionally corresponds closely to geocronite. The composition reported here (Table 3) matches very well with both microprobe and wet chemical analyses reported in the literature. While this represents the first report of the mineral from Işık Dağı, it is not the first report of the mineral from Turkey (e.g., Temur 1991).

Table 3. Analyses of geocronite (in weight percent).

Sample	1	2	3	4	5
Element					
Pb	68.05 ± 1.00	69.18	67.52	68.90	68.60
Sb	10.82 ± 0.99	9.02	11.48	9.27	8.64
As	3.87 ± 0.36	4.37	3.65	4.54	5.32
S	17.42 ± 0.12	16.55	17.45	17.13	17.44
Fe	.	0.10	.	.	.
Cu	.	0.29	.	.	.
Total	100.16	99.51	100.10	99.84	100.00

1. Işık Dağı, microprobe, sect. Idg-2, average of 1 spot on 3 grains.

2. Treore mine, Cornwall (BM 1963, 475), microprobe (Birnie & Burnham 1976, p. 968).

3. Silver King mine, Utah, analysed by R. Klemen, (Douglass *et al.* 1954, p. 913).

4. Sala, Sweden (Anthony *et al.* 1990, p. 178).

5. Ideal - $Pb_{14}(Sb_{0.5}As_{0.5})_6S_{23}$ (Anthony *et al.* 1990, p. 178).

Although the current microprobe analyses reveal the presence of geocronite and boulangerite, none of the analyses have yielded a composition corresponding to that proposed for yenerite. However, an admixing of 20% geocronite with boulangerite would yield a composition of Pb- 57.32, Sb- 22.11, As- 1.79, S- 18.58. This composition would be the same with respect to Pb and As – but lower with respect to Sb and higher with respect to S – as that reported for yenerite (Table 2).

Discussion

When yenerite was originally proposed as a mineral, it was thought that it would be a new addition to the series of Pb-Sb sulphosalts along the $PbS-Sb_2S_3$ compositional join that included zinkenite, the plagionite group (fülöppite, plagionite, heteromorphite and semseyite), boulangerite, falkmanite, meneghinite and geocronite, with atomic Pb/Sb ratios ranging from 0.37 to 2.33 (Bayramgil 1945, p. 48, 1946). Since the 1970s, there have been extensive investigations of the Pb-Sb-As sulphosalts (e.g., Pruseth *et al.* 2001 and Mozgova *et al.* 1982). While structurally these minerals are dominated by the plagionite and guettardite (usually As-bearing) groups, there are also a series of diverse other structures, as represented by zinkenite or veenite (see Table 4). Differences within and among these groups are complicated by the presence of superstructures, non-stoichiometry and polymorphism. Synthesis studies indicate that the formation of a particular species is quite dependent on the exact chemical environment. Simple observation (Table 4) shows that most of these species have Pb/Sb ratios between 0.25 and 1.00, and there are relatively few species – both natural (boulangerite and geocronite) and synthetic (e.g., Pruseth *et al.* 2001) – with ratios between 1.00 and 2.50. Naturally back in the 1940s it was hoped that yenerite, with a Pb/Sb ratio of 1.38, would be an important extension of the list of minerals along the $PbS-Sb_2S_3$ join.

While the present work supports the discrediting of yenerite as a species along this join, it is clear that the boulangerite from Işık Dağı has elevated values of arsenic, as did the original analyses of yenerite (Table 2). Thus, yenerite might be retained for arsenic-rich varieties of boulangerite.

Table 4. Mineral sulphosalts along a portion of the PbS-Sb$_2$S$_3$ compositional join (adapted from Strunz & Nickel 2001, p. 123, 134–136, 139).

Atomic ratio Pb/(Sb+As)	Formula	Plagionite Group	Other Structures	Guettardite Group
0.25	PbSb$_4$S$_7$			
0.31	Pb$_3$Sb$_8$S$_{15}$	fülöppite		
0.41	Pb$_6$Sb$_{14}$S$_{27}$		zinkenite	
0.50	Pb(Sb,As)$_2$S$_4$		twinnite	
0.56	Pb$_9$(Sb,As)$_{16}$S$_{33}$			guettardite
0.62	Pb$_5$Sb$_8$S$_{17}$	plagionite		
0.67	Pb$_4$Sb$_6$S$_{13}$		robinsonite	
0.85	Pb$_{22}$Sb$_{26}$S$_{61}$			launayite
0.88	Pb$_7$Sb$_8$S$_{19}$	heteromorphite		
0.89	Pb$_{16}$Sb$_{18}$S$_{43}$			playfairite
0.95	Pb$_{19}$(Sb,As)$_{20}$S$_{49}$			sorbyite
1.0	Pb$_2$(Sb,As)$_2$S$_5$		veenite	
1.13	Pb$_9$Sb$_8$S$_{21}$	semseyite		
1.25	Pb$_5$Sb$_4$S$_{11}$		boulangerite	
1.38	Pb$_{11}$Sb$_8$S$_{23}$		(yenerite)	
1.50	Pb$_{5.4}$Sb$_{3.6}$S$_{11}$		falkmanite	
1.75	Pb$_7$Sb$_4$S$_{13}$			
1.86	CuPb$_{13}$Sb$_7$S$_{24}$		meneghinite	
2.00	Pb$_4$Sb$_2$S$_7$			
2.25	Pb$_9$Sb$_4$S$_{15}$			
2.33	Pb$_{14}$(Sb,As)$_6$S$_{23}$		geocronite	
2.50	Pb$_5$Sb$_2$S$_8$			

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