Oscillatory zoned gersdorffite and the Ni-Bi-Au association at Clemence mine and Km 3 locality, Lavrion district, Greece.

Emmanouil Galanos[1], Panagiotis Voudouris[1], Branko Rieck[2], Uwe Kolitsch[3], Constantinos Mavrogonatos[1], Vasilios Melfos[4], Stefanos Zaimis[5], Konstantinos Soukis[1]

[1]Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Greece; [2]Institut fur Mineralogie und Kristallographie, Universitat Wien, Austria
[3]Mineralogisch-Petrographische Abteilung Naturhistorisches Museum Wien, Austria; [4]Faculty of Geology, Aristotle University of Thessaloniki, Greece
[5]Institut fur Mineralogie, TU Bergakademie Freiberg, Germany

1. Introduction and Regional Geology

The Lavrion district in Greece, a part of the Attic-Cycladic metamorphic core complex, is characterized by Late Cretaceous-Eocene deformation and eclogite/blueschist-facies metamorphism, followed by Late Oligocene to Miocene post-orogenic extension in the backarc region of the Aegean continental crust, by exhumation of metamorphic core complexes, and by a greenschist- to amphibolite-facies overprint of the high-pressure rocks.

The three major tectonic units are: a Basal (or Kamariza) Unit composed of a sequence of Triassic-Early Jurassic age rocks metamorphosed to blueschist facies and retrogressed to greenschist-amphibolite facies, the Intermediate Tectonic Unit also referred as the Lavrion or Cycladic Blueschist Unit, comprised of a phyllitic nappe of Late Cretaceous age and the Upper Unit, which is represented in the Lavrion area by late-Jurassic red cherts and a non-metamorphic limestone of Cretaceous age. The contacts between Upper, Intermediate and Basal units are low-angle normal faults that constitute the Western Cycladic detachment system (Figure 1).

Carbonate-sericite altered microgranodiorite dykes and sills at Kamariza are crosscut by porphyry-style quartz-sericite-calcite stockworks hosting sulfide mineralization including pyrrhotite, arsenopyrite, pyrite and galena (Figures 2a and 3a). In addition, east-west trending dykes and sills of andesitic composition crosscut the lower marble and the Kamariza schists in the Kamariza area. They are equigranular rocks consisting of plagioclase and biotite with interstitial quartz. The dykes are propylitic-altered (Figure 2b), whereas adjacent to the orebodies they are pervasively altered to quartz-sericite±carbonates and contain disseminated or vein sulfides.

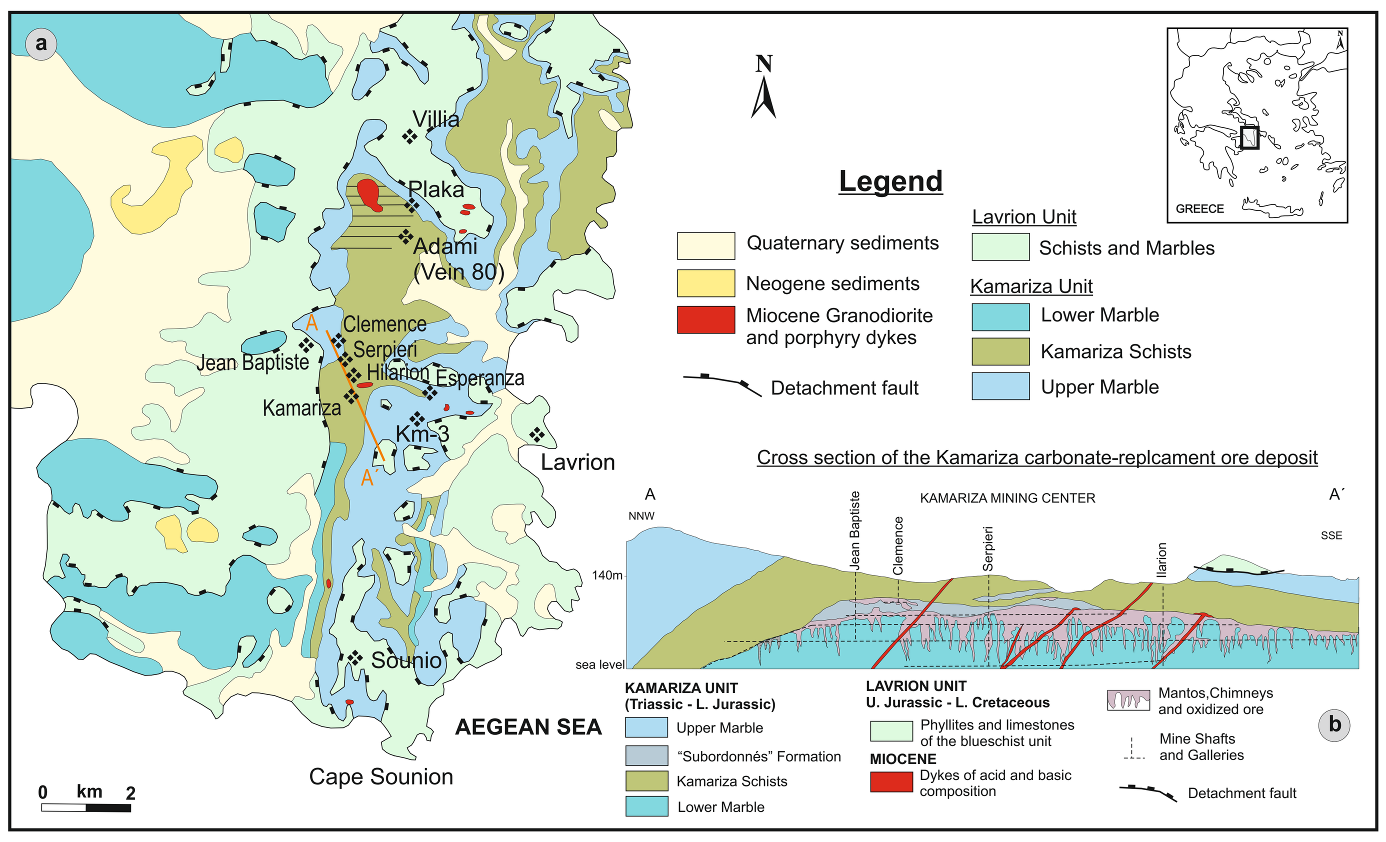

Figure 1. (a) Simplified geological map of the Lavrion ore district; (b) cross-section A–A' of the Kamariza deposit (both modified after Marinos and Petraschek 1956).

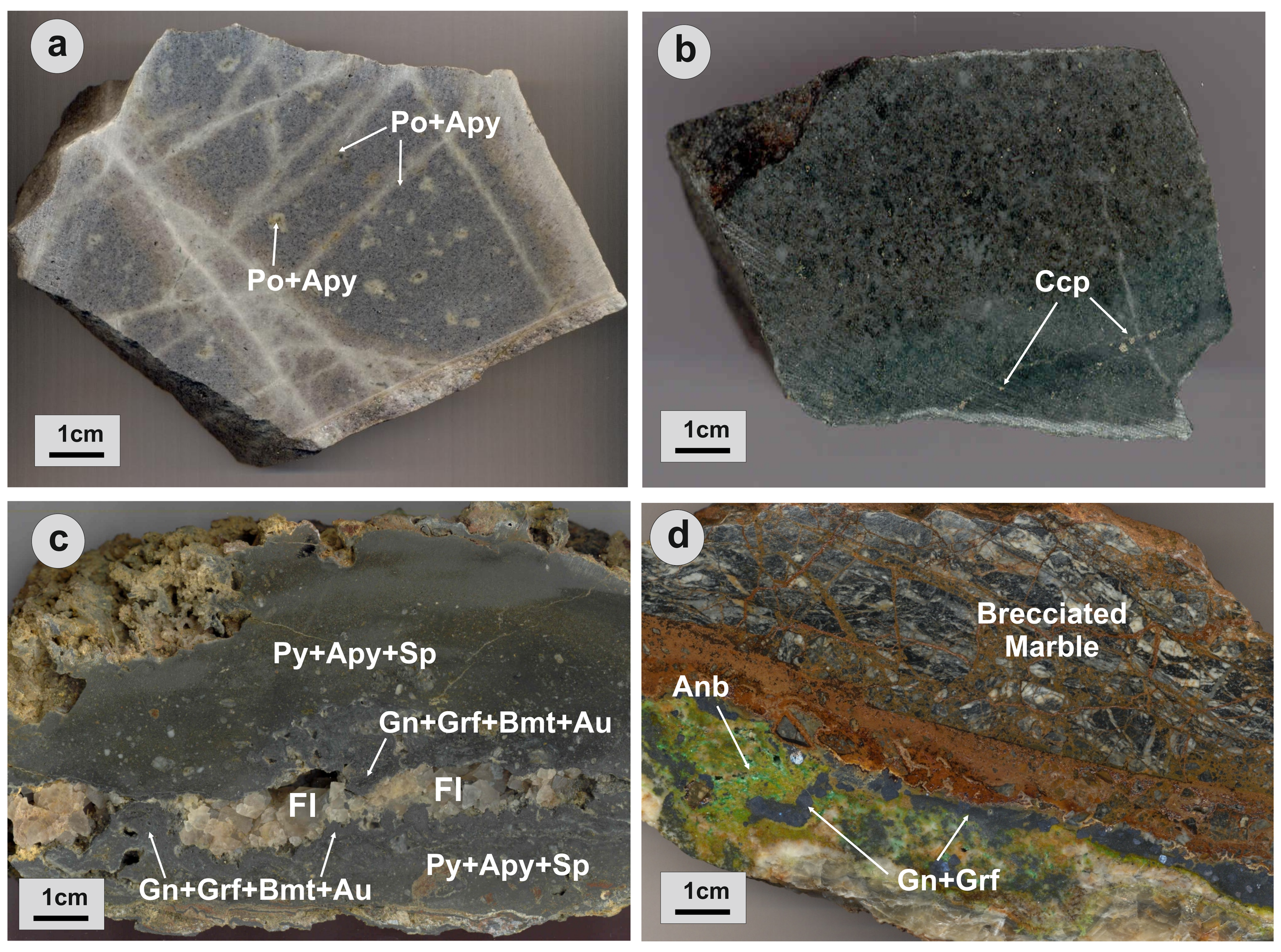

Figure 2. Hand specimens of granitoids and Ni-bearing ores at Lavrion area.

(a) Carbonate-sericite-quartz veinlets with pyrrhotite (Po) and arsenopyrite (Apy) crosscutting a felsic sill at Serpieri Mine;

(b) Propylitic altered andesitic dyke from Jean Baptiste Mine;

(c) Banded vein-style mineralization from Clemence Mine, consisting of initial deposition of pyrite (Py) + arsenopyrite (Apy) + sphalerite (Sp), followed by the deposition of galena (Gn) + gersdorffite (Grf) + bismuthinite (Bmt) + gold (Au) and finally the deposition of fluorite (Fl);

(d) Brecciated marble cemented by galena (Gn)+gersdorffite (Grf) mineralization. The Ni-arsenate annabergite (Anb) is a supergene alteration product of gersdorffite.

2. Mineralization and Mineral chemistry

The nickeliferous assemblage from Clemence mine is a vein-type mineralization, characterized by open space filling and mineralogical zonation. Bulk ore analyses yielded an extreme Au and Bi enrichment (> 100 ppm and 2000 ppm respectively. Pyrite, arsenopyrite and sphalerite dominate at the outer parts of the vein, whereas galena and fluorite at the vein center (Figure 2c). Paragenetic relationships in the vein suggest initial deposition of pyrite, arsenopyrite, stannite and Fe-rich sphalerite, followed by gersdorffite, bismuthinite and native gold, then by chalcopyrite, tennantite/tetrahedrite, bournonite, enargite and Fe-poor sphalerite, and finally by galena containing exsolved grains and inclusions of semseyite, boulangerite, native antimony, Ag-rich tetrahedrite, stephanite and miargyrite. Quartz is the main gangue mineral in the early stage of ore deposition followed by fluorite which accompanies galena. In Km 3 locality, the nickeliferous assemblage is associated with veins of calcite and galena crosscutting brecciated upper marble of the Kamariza Unit (Figure 2d).

Early sphalerite is Fe-rich (up to 24.7 mole % FeS) and associated with arsenopyrite, whereas late sphalerite is Fe-poor (2.9 mole % FeS) and associated with the Cu-As bearing association including chalcopyrite-tennantite and enargite. Galena includes gersdorffite, semseyite, bismuthinite, bournonite, native antimony and native gold (Figure 3).

Bismuthinite is included in gersdorffite and galena (Figure 3e to g). Native gold usually forms up to 150 µm grains enclosed in gersdorffite, but can also be found as intergrowths with bismuthinite and/or as isolated grains, enclosed in galena (Figure 3e,g).

Gersdorffite occurs as zoned idiomorphic crystals enclosed in galena and rimming pyrite and arsenopyrite (Figure 3d,f). It displays oscillatory zoning (Figure 4) in respect to its Fe, Ni and As content, varying from ~1.5 to 9 wt.%, ~24 to 32 wt.% and 47 to 60 wt.% respectively (Table 1). The Clemence gersdorffite contains up to 0.2 wt% Se substituting for sulfur in the structure. At "km3" locality, gersdorffite, contains ~ 0.5-2 wt.% Fe, 46-48 wt.% As and ~31-34 wt% Ni (Table 1). Millerite (NiS) is found in association with gersdorffite, as small inclusions or as euhedral needle shaped crystals enveloped by galena (Figure 3j). Ulmanite Ni(Sb,As)S, occurs as inclusions in gersdorffite (Figure 3k) and vaesite is rimming gersdorffite (Figure 3l). Cobalt (up to 0.35 wt.%) substitues for Ni in vaesite and millerite (Table 1).

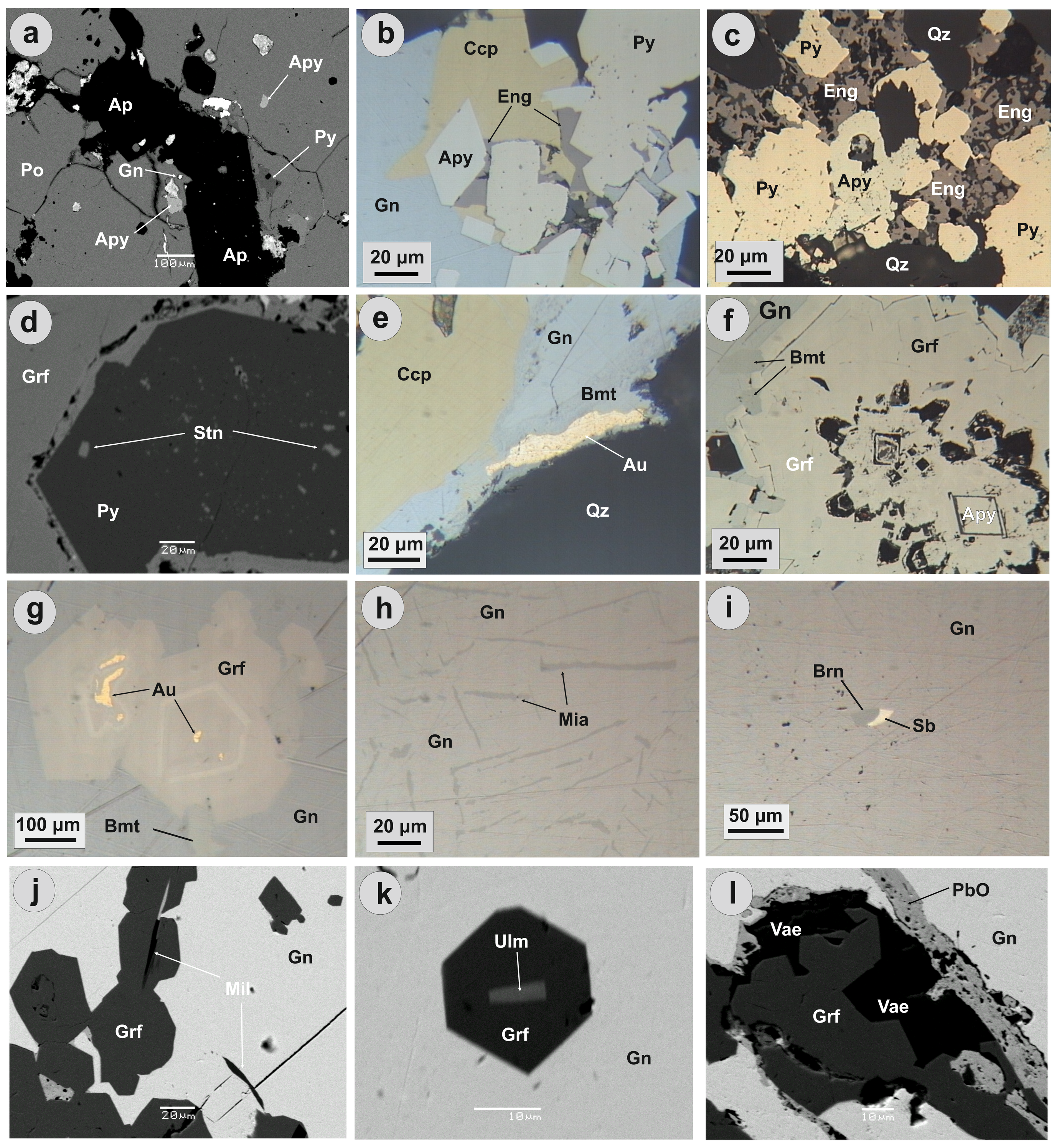

Figure 3. Photomicrographs demonstrating ore paragenesis in the Serpieri, Clemence and 'km-3' areas. a Pyrrhotite (Po) including arsenopyrite (Apy), pyrite (Py) and galena (Gn). Apatite (Ap) is also present. Felsic dyke from Serpieri area; b pyrite and arsenopyrite are followed by chalcopyrite (Ccp), enargite (Eng) and then by galena (CLM2, reflected light – plain polarized); c Pyrite and arsenopyrite rimmed by enargite (CLM6a, reflected light – plain polarized); d Pyrite including stannite (Stn) is surrounded by gersdorffite (Grf) (CLM6a, scanning electron microscope-back scattered electron image); e chalcopyrite postdated by galena including bismuthinite (Bmt) and native gold Au. Quartz (Qz) is gangue mineral (CLM6, reflected light – plain polarized); f arsenopyrite rimmed by gersdorffite, the later surrounded by bismuthinite and galena (CLM6b, reflected light – plain polarized); g oscillatory zoned gersdorffite including native gold and bimsuthinite is surrounded by galena (CLM6b, reflected light – plain polarized); h miargyrite (Mia) as exsolution lamellae within galena (CLM4a, reflected light – plain polarized); i bournonite (Brn) and native antimony (Sb) includedin galena (CLM6a, reflected light – plain polarized); j millerite (Mil) needles included in both gersdorffite and galena ('km3', scanning electron microscope-back scattered electron image); k Ulmanite (Ulm) enclosed in gersdorffite ('km3', scanning electron microscope-back scattered electron image); l gersdorffite surrounded by vaesite (Vae), enclosed in galena (PbS).

Table 1. Representative electron microprobe analyses and atomic proportions of gersdorffite (1-8: Clemence Mine; 9,10: 'Km-3'), vaesite (11, 12), millerite (13,14); polydymite (15,16); ullmannite 17,18). bd: below detection limit, na: not analyzed.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Ni	24.12	26.81	32.04	28.67	25.00	27.59	25.04	25.22	34.55	32.65	46.19	45.93	63.18	62.48	56.42	56.67	28.00	27.71
Fe	9.10	7.59	2.23	5.70	8.06	4.46	5.54	5.40	0.49	1.63	0.37	0.05	0.54	0.20	0.16	0.38	0.02	0.11
Co	bd	bd	bd	d	bd	bd	bd	bd	0.13	bd	0.18	0.35	0.06	0.26	bd	bd	bd	bd
Au	0.12	bd	0.07	0.08	0.06	0.25	0.29	0.29	na	na	na	na	Na	na	na	na	na	na
As	50.12	47.55	46.26	47.84	51.61	54.07	58.96	59.95	46.99	47.55	0.97	0.09	0.45	0.16	bd	bd	8.41	8.88
Sb	0.08	bd	0.78	0.10	bd	0.13	0.04	0.02	na	na	na	na	na	na	bd	bd	47.93	46.72
Bi	bd	bd	0.18	bd	bd	0.05	bd	bd	na	na	na	na	na	na	na	na	na	na
S	16.48	18.40	18.46	18.06	15.66	13.22	10.21	9.51	18.71	19.21	52.65	53.60	36.38	36.32	43.47	42.58	15.24	15.15
Se	0.16	0.17	0.19	0.15	0.14	0.20	0.20	0.18	na	na	na	na	na	na	na	na	na	na
Total	100.18	100.54	100.26	100.64	100.59	100.01	100.34	100.60	100.88	100.82	100.36	100.02	100.61	99.42	99.97	99.40	101.11	98.84
Atoms	3	3	3	3	3	3	3	3	3	3	3	3	2	2	7	7	3	3
Ni	0.700	0.759	0.915	0.816	0.730	0.835	0.782	0.792	0.975	0.918	0.962	0.955	0.967	0.963	2.902	2.943	0.977	0.977
Fe	0.278	0.226	0.067	0.170	0.247	0.142	0.182	0.178	0.016	0.048	0.008	0.001	0.008	0.003	0.009	0.021	0.000	0.000
Co	0.000	0.000	0.000	0.000	0.000	0.000	Bd	0.000	0.003	0.000	0.003	0.002	0.001	0.004	0.000	0.000	0.000	0.000
Au	0.001	0.000	0.001	0.001	0.001	0.002	0.003	0.003	-	-	-	-	-	-	-	-	-	-
As	1.140	1.056	1.035	1.067	1.181	1.282	1.443	1.475	1.039	1.048	0.016	0.002	0.006	0.001	0.000	0.000	0.230	0.245
Sb	0.001	0.000	0.011	0.001	0.000	0.002	0.001	0.000	-	-	-	-	-	-	0.000	0.000	0.806	0.796
Bi	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	-	-	-	-	-	-	-	-	-	-
S	0.876	0.955	0.965	0.941	0.837	0.732	0.584	0.547	0.967	0.989	2.009	2.037	1.018	1.027	4.094	4.048	0.973	0.996
Se	0.003	0.004	0.004	0.003	0.003	0.004	0.005	0.004	-	-	-	-	-	-	-	-	-	-

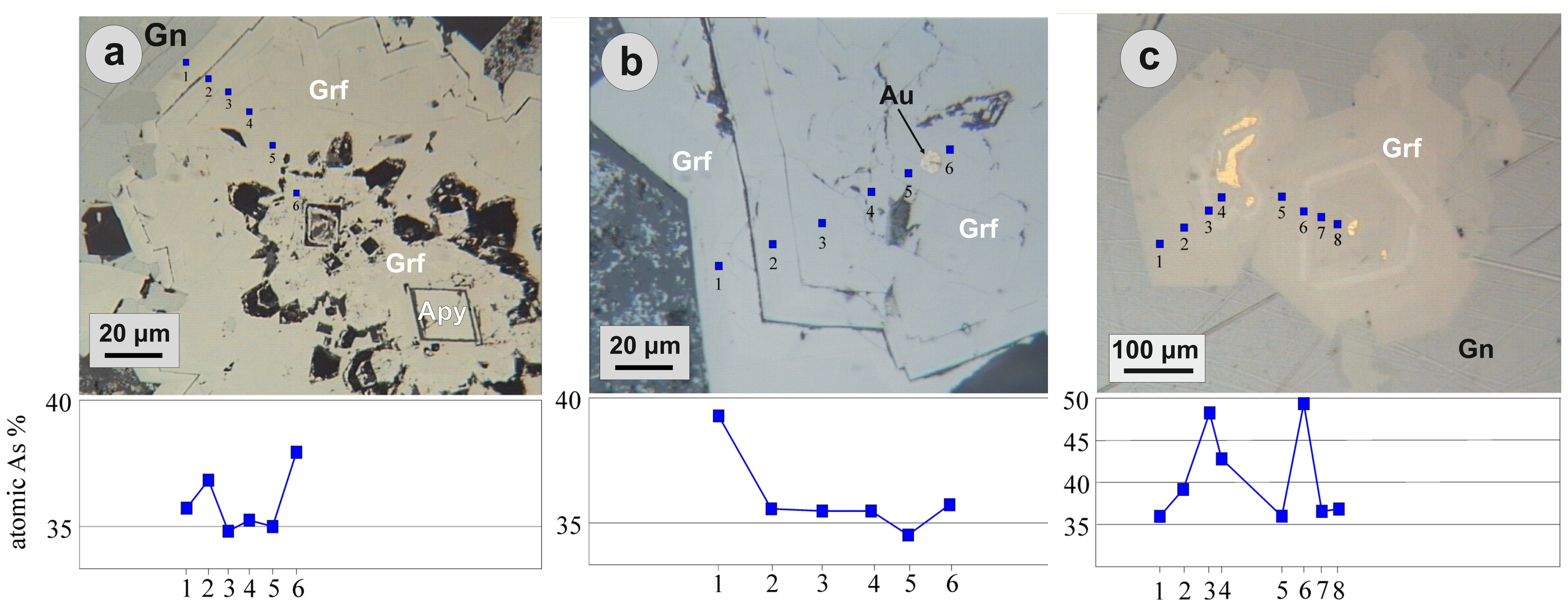

Figure 4. EMPA line scans of As distribution along traverses in gersdorffite.

3. Conclusions

•The variations in the As-, Ni- and Fe-content in individual micro-zones observed within the oscillatory zones of Clemence gersdorffite suggest physical or chemical fluctuations within the bulk system and disequilibrium as stated by Shore and Fowler (1996).

•Changes in the hydrothermal system, such as varying fluid composition, or temperature, led to the gersdorffite zoning at Clemence deposit. Zonation in gersdorffites is attributed to intense fluctuation of arsenic fugacity and activities of Ni and Fe in the hydrothermal fluid.

•For the mineralization at Clemence, has been suggested a path of decreasing temperature (from about 400 to 200 °C), under generally increasing fS2 conditions as indicated also by a decrease of the Fe content of sphalerite from about 25 to 3 mole % FeS (Voudouris et al. 2008).
On the contrary, in the Km 3 locality, deposition of Ni sulfides is followed by formation of homogenous gersdorffite, indicating increasing trends for the As content and decreasing Ni activities in the hydrothermal fluid.

•Late galena associated with fluorite rims gersdorffite in both districts demonstrating a common fluid evolution along the detachment system in the broad Lavrion area.

4. References

corresponding author:
voudouris@geol.uoa.gr

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