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Mineral Deposits: Research and Exploration Where do They Meet?

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Vein-quartz deposits of northern Greece – Exploitable resources for industrial uses

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ABSTRACT: Significant quantities of vein-type quartz reserves amounting to 2.5 m.t. hosted by Paleozoic or older metasedimentary two-mica gneisses of the Serbomacedonian, Pelagonian, and Rhodope Zones have been located in northern and central Greece. Structural, textural, mineralogical, chemical, fluid inclusion, and genetic studies were conducted to serve evaluation of quartz as raw material for the production of ultra-pure qualities for the European Market. Fluid inclusion studies have assisted in genetically relating vein formation to regional post-Jurassic greenschist facies metamorphism and gradual uplift of the gneissic host-rocks, as well as deciphering the role of inclusion in degrading elemental contaminants to market- quality requirements.

INTRODUCTION

Exploration for vein-quartz deposits, as well as evaluation of known prospects, in northern (Macedonia, Thrace) and central (Thessaly) Greece has been carried out by the Institute of Geology and Mineral Exploration (IGME) of Greece, for the implementation of the BRE2-CT94-1026 E.U. Brite-Euram II Programme entitled "New industrial applications for quartz deposits indigenous to the Community". This on-going project aims at developing advanced beneficiation techniques to produce ultra-pure quartz/silicon for high-tech application needs of the European Market, using Greek vein-quartz as raw material. Targets were subjected to a succession of geological, geophysical, petro-logical, geochemical, as well as trenching and drilling, studies and tests which resulted in the discovery of significant vein-quartz reserves amounting to 2.5 m.t. and the selection of prime targets for further evaluation. Half-way towards the completion of the project the achieved quartz qualities in terms of elemental chemical impurities (Fe, Al, Ti, Na, and K) appear feasible for the optics industry.

Quartz veins are hosted by rocks belonging to the Serbomacedonian (SMZ), Pelagonian (PZ) and Rhodope (RZ) geotectonic Zones. This communication will present to date results on the geological, geochemical, and fluid inclusion studies for quartz veins of the SMZ.

2. GEOLOGIC SETTING

Quartz vein mineralization of the Paleozoic or older SMZ occurs in its western lithostratigraphic and tectonic unit, the Vertiskos Formation (VF). The VF is an NW-SE trending highly deformed and polymeta-morphosed heterogeneous assemblage consisting of meta-sedimentary two-mica gneisses and garnet-, staurolite and kyanite-bearing mica schists, meta-tholeiitic amphibolites, meta-gabbros, serpentinized ultramafics, anatectic granites and pegmatites (Kockel et al. 1977; Dixon and Dimitriadis 1984; Sakellariou 1989; Kourou 1991; Sidiropoulos 1991).

Five metamorphic episodes (M_1-M_5) and four major deformation phases (D_1-D_4) have been recognized in the NW part of VF where most veins cluster(Fig. 1)(Kourou 1991; Sidiropoulos 1991). The area has suffered Alpidic (Late Jurassic) deformation (D_3) and regional metamorphism (M_4) reaching upper greenschist facies conditions(T:400-520°C, P:5-6 or 9 kb). This tectonometamorphic event was followed by post-

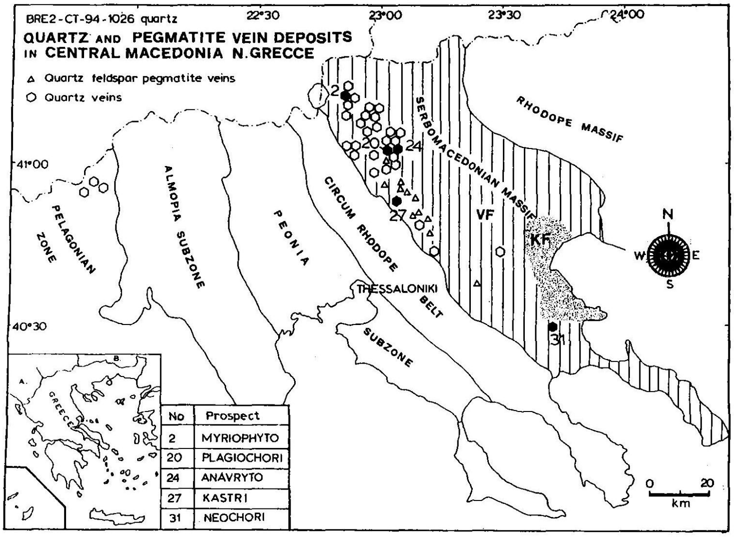

Figure 1. Quartz and pegmatite vein deposits in central Makedonia and northern Greece

Jurassic deformation (D_4) and retro-gression under greenschist facies (M_5) (T:300-550°C, P<5kb). Post-D_4 brittle pheno-mena have been ascribed to gradual uplift of the Vertiskos basement (Kourou 1991; Sidiropoulos 1991).

Evidence for Hercynian (Amphibolite Facies-M_3-D_2 and M_2 - D_1) and pre-Hercynian (Eclogite Facies - M_1) tectonic and/or meta-morphic events exist locally.

3. VEIN GEOMETRY, MINERALOGY AND DEFORMATION

Figure 1 shows the locations of the discovered and known veins of VF. Quartz veins routinely occur in two-mica gneisses and biotite gneisses occupying extensional fractures, except for rare cases when they partly transect granitic bodies. They form disrupted and boudinaged steeply dipping (90° to 40°) bodies, srtiking NNW-SSE concordant to the regional schistosity. Veins measure from 30 up to 100 m in length, rarely reaching 300 or 500 m; thickness vary from 3 to 15 m.

Veins are composed chiefly of milky or yellowish-brown quartz (up to 99,5 % by volume) with traces of white mica, sulphides, feldspar and iron oxides. The quartz grains are deformed, subhedral to anhedral, elongated and slightly dimensionally oriented, with relative dimensions of up to 8 mm in their longest axis and up to 4 mm in width.

Vein quartz has suffered : a) An early episode of ductile deformation (quartz 1), post-dating the vein filling, attributed to emplacement of the veins in a dynamic tectonically active environment; b) Brittle fracturing that took place after the ductile deformation accompanied by cataclasis and recrystallization (quartz 2)

4 VEIN CHEMISTRY

SMZ raw quartz compositions show ranges of Fe = 1 - 28 ppm, Al = 22 - 73 ppm, Na = 12 - 37 ppm, K = 4 - 28 ppm, Ca = 11 - 40 ppm, Mg = 4 - 10 ppm, Ti = 1.4 - 4.8 ppm and Li = 0.1 - 0.9 ppm.

The problem for electronic high-tech applications of quartz arises from high Na contents, and Na appeared to be the hardest element to degrade to quality requirements by the purification techniques used to successfuly eliminate other elements (i.e. Fe, Al, Ca, Ti).

Chemical removal of fluid inclusions and subsequent degradation to 2.39 ppm Na resulted to substantial quality improvement of quartz.

5. FLUID INCLUSIONS

The scope of the fluid inclusion study of the veins was two-fold. First, to determine the physicochemical conditions and mechanisms of vein crystallization and decipher the relation between vein genesis and regional geology, and, second, to investigate the role of fluid inclusions as quality "contaminants", in terms of chemical composition, distribution density, morphology and size.

Fluid inclusions have so far studied by microthermometry techniques in samples from five (5) major quartz veins of VF, namely Kastri (currently exploited quarry), Myriophyto, Plagiochori, Neochori and Anavrito (Fig. 1). Microthermometry was conducted on a LINKAM THMS 600 / TP92 heating / freezing system calibrated with pure CO_2 inclusions, pure H_2O and various organic solvents.The accuracy of the measurements was defermined to be better than $\pm$ 0.5° C over the temperature range of - 70° C to + 30° C and $\pm$ 2 - 3° C for higher temperatures.

Four types (with subtypes) of fluid inclusions were identified in quartz 1. In order of decreasing abundance they are: type III, two-phase aqueous H_2O-NaCl($\pm CO_2$) inclusions; type II, three-phase aqueous-carbonic H_2O-CO_2-NaCl($\pm CH_4$) inclusions; type I, monophase or two-phase carbonic CO_2($\pm CH_4$) inclusions, and type IV, naturally decrepitated and/or leaked inclusions. Type II inclusions are differentiated in types IIa and IIb with contrasting, high (70-90) and low (10-40), respectively, volumetric carbonic/aqueous phase ratios, and contrasting homogenization modes, to the carbonic, and aqueous, phases, respectively; type III inclusions are divided according to the presence of carbonic content in subtypes IIIa (traces of CO_2) and IIIb (no CO_2). All types are not necessarily present in every sample or in every vein studied.

Types I and II are not associated to fracturing and healing episodes of the host quartz; they occur isolated, in small low-density randomly distributed clusters, or between healed fractures, and are thus considered primary. Type IIIb inclusions show transgranular intersecting fracture control indicating a secondary origin, whereas type IIIa inclusions occur in both primary and secondary settings. Sizes of primary onclusions range from <4 mm up to 12μm(type I), 10 μm (type IIa). 15μm (type IIb) and 20 μm (type IIIa) on a side. Secondary inclusions range from <4 up to 20 μm in diameter. Inclusion shapes are variable from irregular to elliptical or subrounded. Decrepi-tated and leaked inclusions have sizes up to 200 μm on a side, possibly constitute ruptured early inclusions due to internal overpressures as a responce to reduction in confining pressure, and are thus considered secondary.

Relatively high Na - content of host quartz are directly related to the salt (equivalent wt% NaCl) content of fluid inclusions. For example, as displayed in Fig. 2A the low - sallnity Myriophyto quartz corresponds to low Na - content (average 16 ppm), whereas the high - salinity Plagiochori quartz averages 110 ppm of Na.

Homogenization temperature versus salinity relationships of primary and secondary inclusions (Figs. 2A, 2B) in conjuction with homogenization behaviour indicate fluid phase unmixing for Kastri and Plagiochori, and simple cooling and/or dilution for Anavrito, Myrio-phyto and Neochori, as mechanisms for primary vein formation. The trends depicted by secondary inclusions may be attributed to post - vein cooling / dilution phenomena (Fig. 2B) Calculated homogenization pressures using FLINCOR, (Brown 1989) for primary fluid inclusions (trapping pressures for unmixed fluids- Kastri, Plagiochori) range between 1.7 and 5.6 kb, and cluster around 3.2 kb. These mineralizing fluid pressures, combined with calculated fluid densities and trapping P-T paths, inclusion Th,tot-salinity trends, and the presence of naturally decrepitated and leaked inclusions, indicate quartz vein growth during the wanning stages of post-Jurassic regional retrogressive greenschist facies metamorphism (M_5)(P<5kb, T=300-550°C), and during decompressive post-metamorphic regional uplift in the VF, allowing the influx of meteoric water into the mineralizing systems.

6. CONCLUSIONS

Vein - type quartz reserves amounting to 2. m.t. have been discovered in northern and centra Greece, and were evaluated as raw materials for th production of ultra - pure qualities for the Europea Market. The deposits are hosted by Paleozoic or olde metasedimentary two - mica gneisses of th Serbomacedonian, Pelagonian and Rhodop geotectonic zones. Vein - quartz is plasticall deformed with superimposed brittle fracturing an minor recrystallization. Quartz is laden with aqueou (H_2O - NaCl $\pm$ CO_2), aqueous - carbonic (H_2O - CO_2 NaCl $\pm$ CH_4), and carbonic CO_2 ($\pm$ CH_4), primary an secondary (aqueous only), as well as naturall decrepitared and leaked fluid inclusions. Flui

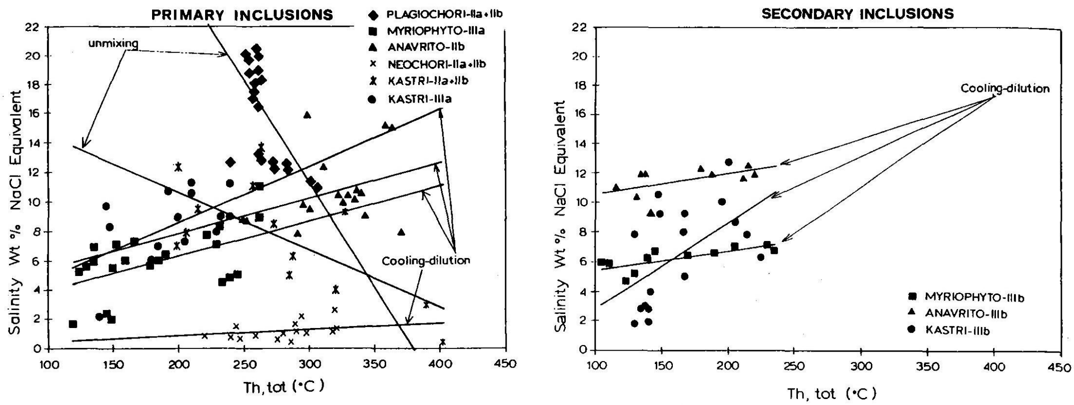

Figure 2. Compositions (wt % NaCl eq.) and homogenization temperatures (Th) of primary (a) and secondary (b) fluid inclusions.

inclusion salinities show positive correlation with bul quartz chemical analyses for Na, suggesting qualitative relation of the Na content of flui inclusions with the «contaminant» Na of raw quartz i terms of market quality requirements. Vein formatio fluid. P- T and T - salinity data are compatible wit regional Alpidic retrogressive greeschist facies meta morphisn, of the gneissic host reocks, and syn - to pos - metamorphic uplift allowing introduction of meteori waters in the mineralizing system.

ACKNOWLEDGEMENTS

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REFERENCES

Brown, P.E. 1989. FLINCOR : a micro-computer program for the reduction and investigation of fluid inclusion data. *Am. Mineral. 74:1390-1393.*

Dixon, J.E. & Dimitriadis, S. 1985. Metamorphosed ophiolitic rocks from the Servo-Macedonian Massif, near Lake Volvi, north-east Greece. In J.E. Dixon & A.H.F. Robertson (eds), *The Geological evolution of the eastern Mediterranean, Special Publication of the Geological Society, n. 17:* 603-618. Oxford:Blackwell.

Kockel, F., Mollat, H. & Walther, H.W. 1977. Erlauterungen zur geologischen Karte der Chalkidiki und angrenzender Gebiete 1 : 100.000 (nord - Griechenland). *Bundesamt. Geowiss. Rohst.* Hannover 119 pp.

Kourou, A. 1991. Lithology, tectonics, geochemistry and metamorphism of part of western Vertiskos Formation. The N-E area of the Agios Vassilios Lake (Koronia). *Unpubl. PhD thesis, Univ. Thessaloniki* (in Greek with English abs.) 461pp.

Sakellariou, D. 1989. Geologie des Serbo-mazedonischen Massivs in der Nordoestlichen Chalkidiki, N. Griechenland : Deformation und Meta-morphose. *Unpubl. PhD thesis, Univ. Mainz, 177 pp.*

Sidiropoulos, N. 1991. Lithology, geochemistry, tectonics and metamorphism of the N-W part of the Vertiskos Formation. The mountain Disoron (Krousia) area, north of Kilkis. *Unpubl. PhD thesis, Univ. Thessaloniki* (in Greek with English abs.) 592 pp.