A metacolloidal dendrite-rich Bi–Ni–Co quartz vein, Pozoblanco, Spain

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Abstract

A Bi–Ni–Co vein in the contact zone of a granite near Pozoblanco, Córdoba, Spain, shows a zoned structure with mm-thin quartz wall zones, up to 20 cm thick Bi-rich quartz zones, and a few cm thick quartz–bismuth transition zones grading into a central quartz vug zone. The Bi-rich zones show textures indicating a metacolloidal origin from a silica gel enriched in adsorbed Bi: (1) globular and chain aggregates of fine-granular allotriomorphic quartz represent morphological relics of a globulated silica gel; (2) quartz rosettes, chain rosettes and stringer-combs radiating from the quartz globules and chains represent crystallised silica gel matrix; (3) crack fillings of quartz, gersdorffite and platy bismuth dendrites represent precipitates of metal-saturated dilute hydrosols filling shrinkage cracks in the desiccating and crystallising gel; (4) quartz spherocrystals in rosettes and combs are clouded with colloidal particles inherited from the silica gel; (5) unsupported wall rock inclusions represent inclusions in a viscous silica gel precursor covering fissure walls. The thin wall zones are quartz fillings of cracks between shrinking gel and walls. The transition and vug zones are recrystallised colloidal silica crusts precipitated by fissure-filling rest-solutions. Tree-like bismuth–gersdorffite dendrites in the transition zones are precipitates of metal-rich solutions infiltrating from the Bi-rich zones into the recrystallising silica crusts. The pre-concentration of metals in silica gels explains the dendrite formation without assuming abnormally high metal concentrations in transporting solutions or long range diffusion processes.

KEYWORDS: metacolloids, dendrites, Bi–Ni–Co veins, Spain.

Introduction

THE Los Pedroches batholith is a concordant Hercynian granite within the WNW–ESE folded Palaeozoic schists of SW Spain. In the Pozoblanco region, Córdoba province, the granite and schist are traversed by ore veins (Defalque *et al.*, 1971) showing a rough metal zoning with a Cu zone in the granite, a Bi–Ni–Co zone adjacent to the granite, and an outer Pb–Ag zone (Triguero, 1966). South of Pozoblanco, Bi–Ni–Co veins occur in NNE–SSW fractures in the schists along the southern contact of the batholith. The San Miguel de Espuela vein was worked in 1967 in a small pit about 20 km SE of Pozoblanco. The vein forms anastomosing, up to 40 cm thick branches in a 1–2 m wide fracture zone. The vein branches show a zoned structure, with a wall zone, a Bi-rich zone, a transition zone, and a central vug zone (Fig. 1).

The *wall zone* is a sharply bounded, 1–3 mm thin zone of white quartz.

The *Bi-rich zone* is an up to 20 cm thick zone of quartz, 10–15 vol.% bismuth, and minor gersdorffite, bismuthinite, bismutite and bismite. Samples show 0.5–1 cm large cells of flinty, dark quartz, bounded by up to 2 mm thick intercellular veinlets of white quartz and bismuth showing the characteristic polygonal pattern of shrinkage crack fillings (Figs. 2A,B). Less common are stringers of dark quartz (Fig. 2C). The dendritic habit of bismuth is revealed by fracture planes showing several cm large hexagonal skeletons of platy bismuth (Fig. 2D). The Bi-rich zone encloses cm-size unsupported wall rock fragments rimmed by thin quartz wall zones.

The *transition zone* is a several cm thick zone of white quartz and 5–10 vol.% tree-like zoned dendrites of bismuth and gersdorffite (Fig. 2E). The transition zone grades into the up to 2 cm thick central *vug zone* of coarse white quartz crystals protruding into vugs.

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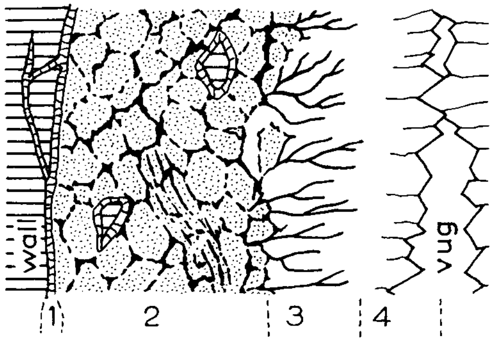

FIG. 1. Zoned structure (not on scale) of San Miguel de Espuela vein. (1) About 2 mm thin wall zone of columnar quartz. (2) Up to 20 cm thick Bi-rich zone showing unsupported wall rock inclusions rimmed by wall zones, cell and stringer matrix of dark quartz (stippled), and polygonal network of shrinkage cracks filled with white quartz and platy bismuth dendrites (black). (3) Transition and (4) vug zone, several cm thick, of white quartz and tree-like bismuth-gersdorffite dendrites.

Mineralogy and textures

Quartz forms fibrous-spherulitic spherocrystals (Grigor'ev, 1965; Lebedev, 1967) of radiating fibres and diffusely spherulitic spherocrystals of radiating subgrains.

Bismuth occurs in cm to dm long dendrites showing coarse twinning and fine polysynthetic parquet-twinning with lamellae in three directions. Locally, the bismuth shows recrystallisation to granular (0.1–0.3 mm) or lamellar aggregates of parquet-twinned grains. Post-parquet-twinning annealing recrystallisation is indicated by fine-granular aggregates of untwinned bismuth. Parquet-twinning of bismuth has been interpreted as inversion in twinning at 75 °C (Edwards, 1947), and as deformation twinning on $(01\bar{1}2)$ of hexagonal bismuth (Ramdohr, 1980). Godonikov and Kolonin (1966) have demonstrated that parquet-twinning in bismuth develops on cooling through 75 °C, not as a result of polymorphic inversion, but consequent to a change of linear expansion coefficient.

Cobaltiferous gersdorffite; 18 microprobe analyses indicate a composition $(Ni_{0.63-0.93}Co_{0.01-0.35}Fe_{0.01-0.04})As_{1.18-1.43}S_{0.82-0.57}$, with As/S ratios between 1.4 and 2.5. The wide range of As and S in gersdorffites is generally related to changes in As/S ratios in crystallising solutions (Yund, 1962; Rosner, 1970).

Bismuthinite, bismutite and *bismite* occur as alterations of bismuth. Microprobe analyses of bismuthinite give the composition Bi_2S_3. Bismu-

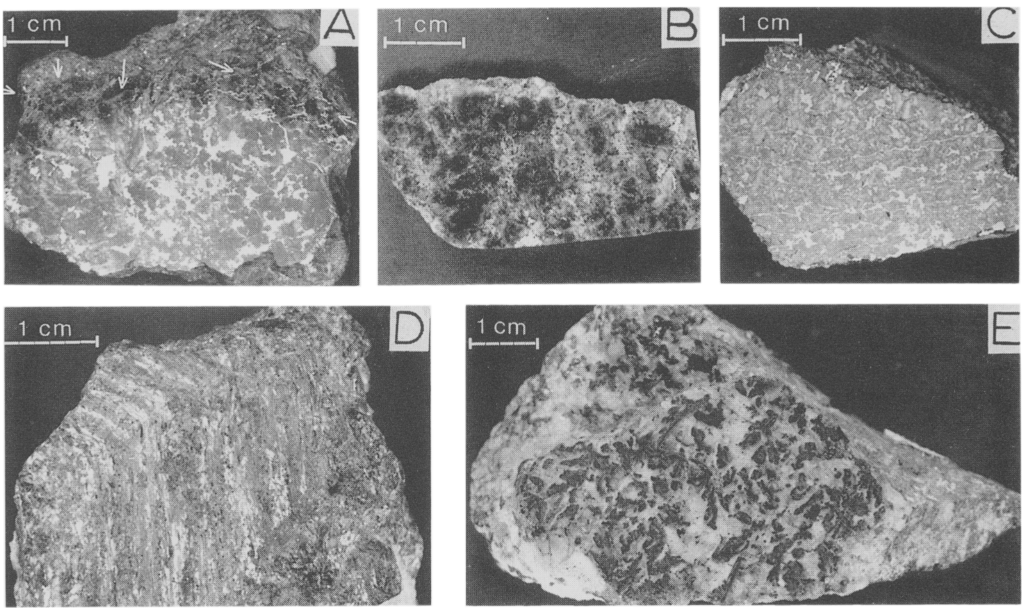

FIG. 2. Bi-rich zone: (A,B) Cells of dark quartz (black, grey) and intercellular bismuth (white) and white quartz (grey, white) show polygonal shrinkage crack pattern (arrows); (C) Stringers of dark quartz (grey) and bismuth (white); (D) Hexagonal skeleton of platy bismuth (white) on fracture plane. Transition zone: (E) Black-stained tree-like bismuth-gersdorffite dendrites in coarse white quartz.

tite, $(BiO)_2CO_3$, and bismite, Bi_2O_3, were identified by X-ray powder diffraction analysis.

The wall zones

The 1–3 mm thin, sharply bounded wall zones consist of columnar quartz orientated normal to vein walls and wall rock inclusions.

The Bi-rich zones

The Bi-rich zones show a cellular matrix of dark quartz and intercellular crack-fillings of white quartz, dendritic bismuth, gersdorffite and late Bi-minerals.

The dark quartz is characterised by rosettes, chain-rosettes and stringer-combs of fibrous-spherulitic quartz spherocrystals radiating from globular, chain- and stringer-like centres of fine-granular (0.01–0.07 mm) allotriomorphic quartz aggregates (Fig. 3). Between the 1–2 mm large quartz rosettes, bending and branching chain-rosettes, and straight stringer-combs are interstitial fillings of granular diffusely spherulitic quartz and bismuth. The dark quartz in rosettes and combs is clouded with dusty particles; the interstitial quartz is clear. The textures indicate three steps in the crystallisation of the quartz matrix: (1) formation of a globular chain and stringer network of fine-granular allotriomorphic quartz; (2) crystallisation of dust-clouded fibrous-spherulitic quartz around the fine-granular allotriomorphic quartz; (3) crystallisation of granular diffusely spherulitic quartz and bismuth in interstices.

The intercellular crack-fillings consist mainly of bismuth and granular diffusely spherulitic quartz. Thin bismuth crack-fillings grade laterally into irregularly thickening (up to 2 mm) and bifurcating branches of crack-filling bismuth dendrites.

The quartz rosettes and combs show faceted surfaces and asymmetric growth towards the crack-filling bismuth, suggesting unimpeded growth of quartz in crack openings before crystallisation of bismuth (Figs. 3, 4A). The later crystallisation of bismuth is indicated by veining with bismuth of the quartz and dispersion of quartz fragments as inclusions in the bismuth (Figs. 3, 4C,D). Space for the bismuth was afforded by widening of cracks (Fig. 4A). Quartz rosettes and combs show adaptation of grain size to the spacing of bismuth-filled cracks, suggesting that the cracks formed in a precursor matrix before crystallisation of quartz rosettes and combs was completed (Fig. 3B). These textures reflect the opening of shrinkage cracks in the crystallising quartz matrix. Granular diffusely spherulitic quartz crystallised in the opening cracks, while the crack-filling fluids evolved into bismuth-depositing solutions. Crystallisation of bismuth in widened cracks is clearly shown where the bismuth encloses gersdorffite microveinlets.

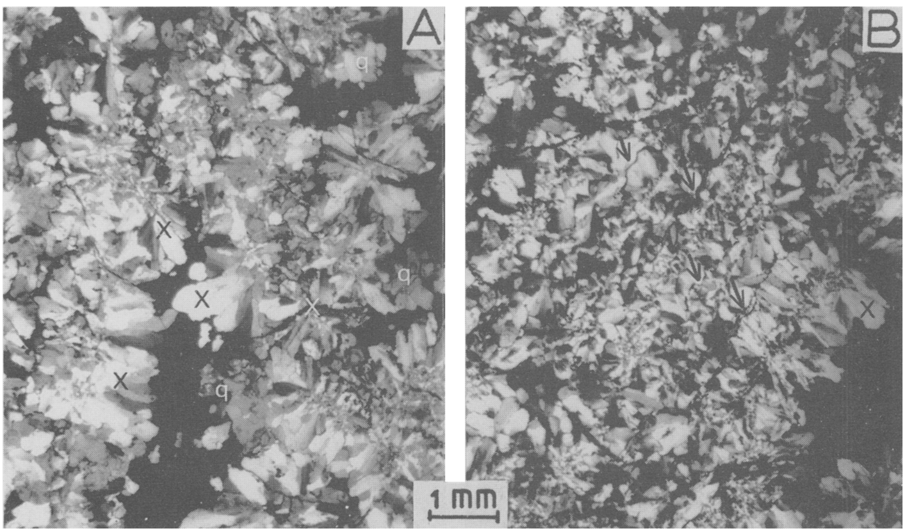

FIG. 3. (A,B) Quartz rosettes, chain rosettes and stringer combs enclosing globules, chains and stringers of fine-granular allotriomorphic quartz. Granular quartz (q) and bismuth (black) fill interstices and cracks. Rosettes show asymmetric growth (black X) towards former crack openings. Grain size of stringer-combs adapted to spacing of thin bismuth crack-fillings (arrows). Thin bismuth veinlet (white X) across quartz rosette connects bismuth crack-fillings. Transmitted light, oblique nicols.

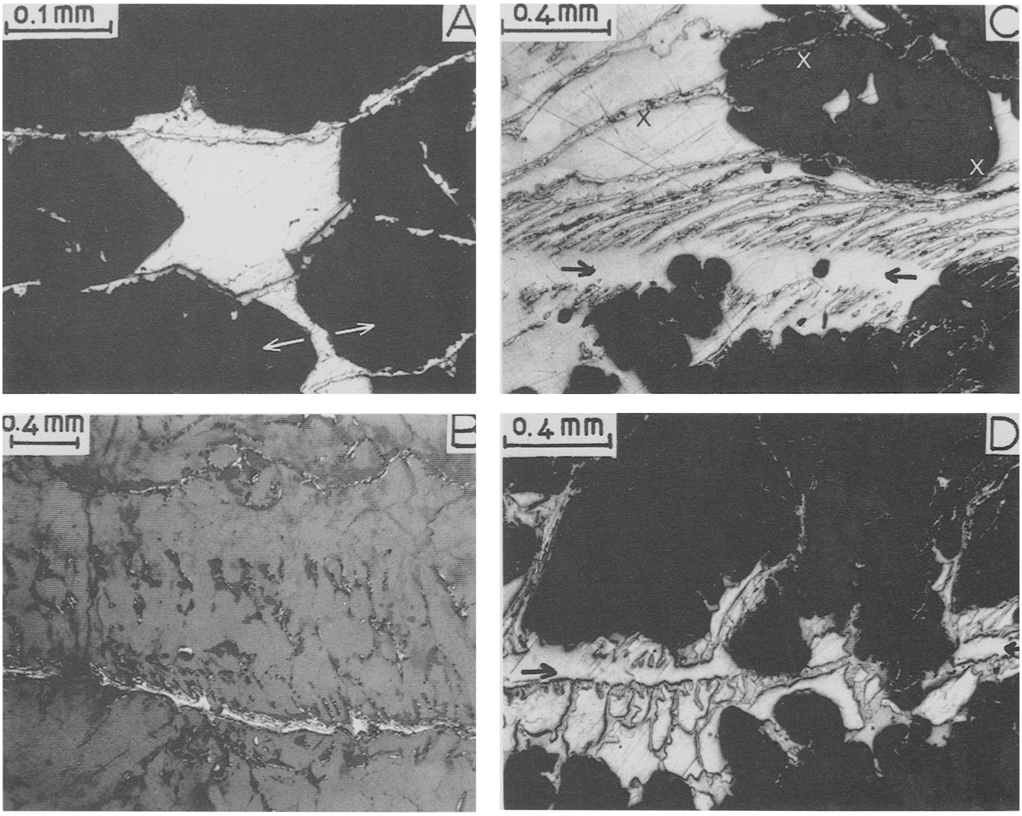

FIG. 4 (A) Intergranular gersdorffite microveinlets in quartz rosettes (black) show one-sided dentate growth boundaries; bismuth (white) fills openings afforded by pulling apart of rosettes (arrows) and encloses gersdorffite microveinlets. (B) Thin bismuth veinlet (white) fringed by gersdorffite festoons resembling rhythmic diffusion bands. (C,D) Bismuth (white) crack-fillings enclose fragments of quartz walls (black) and gersdorffite festoons fringing bismuth-filled feeder cracks (arrows); split gersdorffite microveinlets (X) in quartz and bismuth. Reflected light.

Gersdorffite is associated with microfracturing. Inclusions of microfractured quartz in unfractured bismuth indicate that microfracturing occurred after the deposition of quartz, but before that of bismuth. Microfractures along grain boundaries and across grains in the quartz matrix are marked by thin, long and smooth or short and curling gersdorffite microveinlets forming festoons and bundles (Fig. 4). Bismuth crack-fillings fringed by gersdorffite festoons that resemble rhythmic diffusion bands (Fig. 4B) suggest diffusion of gersdorffite-depositing solutions from a feeder crack into intergranular microcracks in the crack walls. Gersdorffite festoons in the crackled quartz matrix are partially enclosed in the bismuth. The textures indicate crack-opening and quartz-filling, microfracturing and gersdorffite microcrack-filling, crack-widening and bismuth crack-filling.

The gersdorffite microveinlets in crackled zones bifurcate and join, enclosing blocky fragments and thin screens of quartz. The microveinlets often show a smooth nucleation boundary at one side and a dentate growth boundary with faceted gersdorffite at the other side (Fig. 4). Split gersdorffite microveinlets show dentate growth boundaries against an enclosed thin quartz screen, which appears partially replaced by the gersdorffite and infilling bismuth. Many gersdorffite microveinlets grade laterally into split veinlets of gersdorffite with bismuth infillings, and into thin bismuth veinlets.

Figs. 4C,D shows relics of originally thin cracks fringed by festoons of gersdorffite microveinlets as in Fig. 4B; widening of the cracks by pulling apart of the walls afforded space for infilling bismuth, which also penetrated into the gersdorffite-filled microcracks; the gersdorffite microvein-

FIG. 5. Branch of tree-like bismuth-gersdorffite dendrites showing concentric gersdorffite (g) bands and infilling euhedral quartz (Q) and bsimuth (white); fibrous-spherulitic quartz (q) radiates from dentate growth surface of gersdorffite. Reflected light.

lets were detached from the walls and *in situ* enclosed in the bismuth as textural relics indicating the original morphology of the microcracks, while loosened quartz grains from the walls were dispersed in the bismuth filling of the widened crack. Fig. 4 shows gersdorffite microveinlets and split microveinlets that pass with preservation of typical morphology from the quartz matrix into bismuth fillings of widened cracks. The textures reflect the sequential deposition of gersdorffite–bismuth with skeletal dendritic habit in widening cracks.

Fine-grained bismuthinite, bismutite and bismite occur as replacements of bismuth. Lateral transitions and absence of intersections indicate the broadly coeval formation of crack-filling veinlets of quartz-bismuth, bismuth, and hypogene late Bi-minerals.

The transition and vug zones

The transition zones show coarse-granular (0.3–1.5 mm) quartz enclosing tree-like gersdorffite–bismuth dendrites, which differ in morphology from the crack-filling platy bismuth dendrites in the Bi-rich zones (Fig. 2). Vugs are frequent; shrinkage cracks and wall rock inclusions are absent. Fibrous–spherulitic dust-clouded quartz forms rims around dendrite branches, while diffusely spherulitic clear quartz forms the matrix between the dendrites.

The dendrites show up to three concentric, 0.02–0.1 mm thick gersdorffite bands, filled in with bismuth and euhedral quartz (Fig. 5). The gersdorffite bands show dentate growth boundaries at one side, and resemble diffusion bands resulting from solution differentiation due to different rates of ion diffusion in infiltrating fluids (Garrels *et al.*, 1949). Fibrous–spherulitic dust-clouded quartz radiates outward from the dentate surface of gersdorffite bands. Locally, infilling bismuth transects the outer gersdorffite bands and forms interstitial bismuth associated with bismuthinite, bismutite and bismite, in the quartz matrix between the dendrites.

The dendrites presumably mark fluid infiltration paths in an originally opaline overcrusting on the Bi-rich zone. The infiltrating solutions came from the Bi-rich zone and carried dissolved ions; solution differentiation caused formation of gersdorffite diffusion bands in the opaline matrix, which recrystallised into fibrous–spherulitic dust-clouded quartz. From these centres recrystallisation in coarse-granular clear quartz spread out over the matrix. Precipitation of gersdorffite was followed by that of bismuth, late quartz, and late Bi-minerals. The formation of the composite dendrites involved isothermal sequential, non-equilibrium crystallisation of dendrite-forming mineral phases from infiltrating metastable supersaturated solutions (Oen *et al.*, 1984).

The vug zones show coarse-granular (1–5 mm) diffusely spherulitic quartz with faceted crystals in vugs.

Metacolloidal origin of vein fillings

The formation of metacolloids (i.e. mineral aggregates developed from colloids) generally involves a stage of coagulation of a gel, followed by stages of globulation and crystallisation. Natural and experimental silica gels in various stages of aging and diagenesis have been studied by optical and electron microscopy (Lebedev, 1967). During coagulation silica gels begin to globulate, forming lumpy aggregations of very small (10^{-6}–10^{-4} mm) gelatinous silica globules. Incipient aging is marked by formation of globulites (i.e. spherical aggregates of small globules) and coalescence of small globules into larger ones (10^{-4}–10^{-3} mm). Further aging involves growth and aggregation of globules and globulites to globular chain and network aggregates. Silica gels at this stage vary from liquid dilute gels carrying globules and globular aggregates in suspension, to viscous gels showing networks of branching globular chain aggregates, and to solid powdery gels of dense accumulations of coalescent globules. Diagenesis is marked by precipitation of metastable silica phases or quartz in fine (10^{-3}–10^{-2} mm) collomorphic aggregates with globular morphology reminiscent of the globulation stage. During further diagenesis allotriomorphic–granular, spherulitic-radiating and parallel-columnar quartz form by recrystallisation of the fine-colloidal silica or direct crystallisation from the gel. The gel desiccates and develops fluid-filled shrinkage cracks.

The network of fine-granular allotriomorphic quartz forming the cores of rosettes, chain-rosettes and stringer-combs in the quartz matrix of the Bi-rich zones shows strong morphological resemblance to globules and globular chains in viscous silica gels. However, gel globules are smaller than 10^{-3} mm, whereas the quartz grains are about 10^{-2} mm and form chains to 0.3 mm thick. The fine-globular gel structures presumably served as centres for precipitation of fine-colloidal silica precursors that recrystallised into fine-granular allotriomorphic quartz; the recrystallisation involved coarsening of the gel structures with preservation of the overall globular network morphology. This process represents a first step in the formation of a metacolloidal texture showing morphological relics of a globulated gel stage. A second step is represented by crystallisation of fibrous–spherulitic quartz from the gel matrix around nucleation centres of fine-granular allotriomorphic quartz. Radial textures may form in diverse media and are not specific to metacolloids. Nevertheless, a gel is most favourable for mass-formation of rosette textures, which thus afford strong indication for a metacolloidal origin (Lebedev, 1967; Guilbert and Park, 1986). The quartz encloses clouds of colloidal particles derived from the silica gel; the fibrous spherocrystal habit is related to incorporation of such particles in growing crystals (Grigor'ev, 1965; Lebedev, 1967). A viscous gel precursor also explains the unsupported wall rock inclusions in the Bi-rich zones.

The negatively charged dispersed silica phase in silica colloids adsorbs cations, and Bi, Co, Ni may be concentrated in silica gels derived from hydrothermal solution; other colloidal particles may adsorb anions of As and S. Concentrations of adsorbed elements in silica gels may be orders of magnitude higher than those in hydrothermal solution. Crystallisation of the gel liberates the adsorbed elements and water. The desiccating gel develops shrinkage cracks filled with a dilute hydrosol of colloidal dispersions in hydrous solution saturated with metals and other components taken over from the gel. Cooling or drying results in crystallisation of crack-filling minerals.

The thin wall zones are interpreted as quartz fillings of boundary cracks between walls and shrinking gel mass. Drying or cooling of shrinkage crack-filling hydrous sols resulted in crystallisation of quartz followed by bismuth dendrites. Solution differentiation caused deposition of gersdorffite in microcracks in front of growing bismuth dendrites. Enrichment of S, CO_2 and O_2 in rest solutions led to formation of late Bi-minerals. The crystallisation of bismuth dendrites from solutions derived from dewatering Bi-enriched silica gels explains dendrite formation without assuming abnormal Bi-concentration in transporting solutions or long range diffusion processes.

Drying of the silica hydrosols may also result in an opaline crust. The transition and vug zones are interpreted as an opaline crust, now recrystallised into quartz. The bismuth–gersdorffite dendrites in the transition zones crystallised from solutions that infiltrated from the Bi-rich zones into the recrystallising crust. The transition zones are enriched in gersdorffite due to solution differentiation; Ni, Co, As and S have higher diffusion rates in infiltrating solution than Bi.

Bi–Ni–Co veins of metacolloidal type presumably formed where pneumatolytic–hydrothermal fluids of granitic origin were forcefully ejected into fault-gouge-filled fissures and dispersion of material caused formation of an aero- or hydrosol (Lebedev, 1967). Cooling and mixing with solutions from the walls resulted in coagulation of the dispersed phase of the sol and formation of viscous silica gels on fissure walls. Bi, Ni, Co, As, S from the hydrothermal fluids were adsorbed in the silica gels. The Bi–Ni–Co veins may be related to high-temperature hydrothermal fluids, but the mineral paragenesis crystallised at moderate temperature from a silica gel precursor. A temperature above 75 °C is suggested by parquet-twinning in bismuth.

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