Pyrite-pyrrhotite intergrowths in calcite marble from Bistriški Vintgar, Slovenia

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Abstract. Roman marble quarry in Bistrica gorge in southern Pohorje Mt. (north-eastern Slovenia) is situated in a 20 m thick lens of layered marble, at the contact zone between granodiorite and metamorphites. Grey and yellowish non-homogenous calcite marble is heavily included by mica, quartz, feldspars, zoisite, pyrite and amphiboles. In the present research, we have studied numerous pyrite (FeS₂) crystals associated with yellowish-bronze non-stoichiometric pyrrhotite (Fe₁₋ₓS), not previously reported from this locality. SEM investigation revealed unusual sequence of crystallisation: primary skeletal pyrrhotite matrix is sparsely overgrown by well-crystalline pyrite, both being overgrown by smaller, well-developed hexagonal pyrrhotite crystals of the second generation. With TEM we identify the pyrrhotite as 5T-Fe₁₋ₓS phase, where x is about 0.1 and is equivalent to Fe₉S₁₀. The pyrite-pyrrhotite coexistence allows us a construction of fO₂-pH diagram of stability fields, which reflects geochemical conditions at the time of marble re-crystallisation.

1. Introduction
Calcite marble from old Roman quarry in southern Pohorje Mt. (north-eastern Slovenia) was popular sculpturing material at the time of Trajan and Severi dynasty (96-235 AD) [1]. Due to limited resources of quality material and complicated extraction and transport methods it was only used in near vicinity; some of the tombs and statues are still preserved in archaeological parks near Celje, Šempeter and Ptuj. The original source of the marble was determined by similarity in grain size, chemical composition and characteristic assemblages of the accessory minerals [2, 3]. Marble, investigated in this research, originated from small, partially underground quarry which is still visible in Bistrica gorge (figure 1a). Pohorje metamorphic complex represent SE margin of Eastern Alps. It has complex metamorphic history with at least two stages of progressive and one stage of retrograde metamorphism [4]. Tectonic model proposes that oceanic lithosphere broke off from continental lithosphere during continental collision, explaining syn- to post-collisional magmatic and metamorphic episodes around the Periadriatic Fault and large granodiorite intrusion into central part of massif [5] (figure 1b). The majority of marble outcrops are found in E and S in medium-grade metamorphic rocks, represented by gneiss, mica schists and amphibolites. Up to now Pohorje marbles were investigated in general geological studies of Pohorje massive, where their origin and relation to metamorphic rocks were determined [4, 6, 7]. More recent researches were investigating stable isotopes characterisation focussed on the comparison between Austrian and Slovenian marbles with known ancient quarries in the Mediterranean area [2]. Furthermore the specific Roman quarry was included in extensive cathodoluminescence and petrographical study, in order to detect their local
variability in texture and mineral assemblages in attempt to relate the textures to mineral reactions during the metamorphic process [8]. In latter research mineral inclusions were also identified as mica, quartz, hornblende, feldspars, zoisite, amphiboles and pyrite and from the stability of this mineral assemblage the temperature of marble re-crystallisation was estimated at < 500 °C [2].

Figure 1. a) Partially underground marble quarry. Support pillar with numerous aplite veins is visible in central part of the image. Specimens for analysis were taken from bulk rock in lower part of the pillar. b) General overview of geological settings in Pohorje complex; marble outcrops are concentrated in SE of the region. Investigated outcrop is marked by red x.

During exploitation of marble from considered Roman quarry heavily included layers and pillars were left in its original position, as they were not useful for further processing. While mica, carbonate and amphibole inclusions are inert, oxidation of Fe-sulphide inclusions results in newly released sulphate, which combines with water to produce sulphuric acid, leading to rapid disintegration of the calcite marble. On the other hand preserved Fe-sulphides can be used as a geothermobarometer, which can provide us further information about conditions at the formation of the marble. In order to do so Fe-sulphides and other accessory minerals were investigated with a combination of analytical methods.

2. Materials and methods

Samples with numerous visible inclusions were taken from the central part of quarry, near main support pillar (figure 1a). Chunks of fresh, non-oxidized calcite marble were completely dissolved in 2 M HCl. Remaining insoluble inclusions were selected under stereo-microscope by hand-picking regarding their colour, transparency and crystal habit. Phase composition of the samples was analysed by powder X-ray diffractometer (XRD; Bruker AXS D4 Endeavor, Bruker AXS GmbH) using Ni-filtered Siemens KFL Cu-Kα 50 kV X-ray tube. The spectra were acquired in the range 2θ = 5° - 75° with a step of 0.04° and recording time of 1 s/step. Raw data were interpreted by Philips X’Pert HighScore Software Suite using WebPDF-4+ 2014 database (The International Centre for Diffraction Data).

Chemical composition and morphology of the samples were studied by scanning electron microscope (SEM; JSM-5800, JEOL Inc.) operated at 20 kV and equipped with energy-dispersive X-ray spectrometer (EDS; Oxford Link PentaFet Mod. 6841, Oxford Instruments PLC). Prior to SEM analysis the samples were coated with a conductive carbon layer using a Balzers SCD 050 Sputter Coater (Bal-Tec AG). EDS data were compiled using Link ISIS system (Oxford Instruments) and S/Fe ratio was calculated using the accompanying SEMQuant ZAF-correction software (Z: atomic
number, A: X-ray absorption, F: secondary X-ray fluorescence). Synthetic pure samples with similar S/Fe ratio (mackinawite-FeS$_2$ [10] and pyrite-FeS$_2$ [9]) were used for calibration prior to each session; the standard with known S/Fe ratio was measured and ZAF evaluated.

Structure and chemistry of the Fe-sulphide intergrowths were studied using a 200 kV transmission electron microscope (TEM; JEM-2100, JEOL Ltd.), equipped with an energy-dispersive X-ray spectrometer (EDS; JED-2300 analyser, JEOL Inc.) suited for semi-quantitative chemical analysis. Samples for TEM analyses were mounted in 3 mm Ti-ring, thinned to 100 µm, dimpled at the disc centre down to 10 µm and further ion-milled (Bal-Tec RES 010 Rapid etching system, Bal-Tec AG) at 4 kV by Ar$^+$ ions until perforation.

3. Results and discussion

XRD analysis of the yellowish golden and bronze fragments (less than 2 mm in size), shows that they corresponded to a mixture of pyrite and pyrrhotite, which cannot be further mechanically separated (figure 2a). Thin brownish semi-transparent plate-like hexagonal crystals corresponded to illite (figure 2b), while white opaque, up to 4 mm big irregular chunks corresponded to a mixture of dolomite and quartz (figure 2c). Residual green up to 2 mm big elongated semi-transparent crystals corresponded to the amphibole pargasite (figure 2d). The coexistence of pyrite and pyrrhotite allows us a determination of the possible stability field and the geochemical conditions at the time of marble re-crystallisation.

![Figure 2. XRD spectra of insoluble residues. The sulphide agglomerations correspond to pyrite (py) (JCPDS card # 04-1003) and pyrrhotite (po) (# 29-0724) mixture, mica sheets to illite (il) (# 58-2017), white irregular chunks to dolomite (do) (# 75-1759) and quartz (q) (# 15-7199) mixture and d) to amphibole pargasite (pa) (# 23-1406).](image-url)

Due to small size of the pyrite-pyrrotite intergrowths their relationship was investigated in SEM. EDS analyses, collected in Table 1, show significant difference between both Fe-sulphide phases: (SEM) data were acquired in SEM on the surface of the crystals, (SEM2) data were collected on polished and Ar$^+$ etched cross-sections from the central part of the samples and (TEM) data were acquired in TEM on conventionally prepared sample. EDS analyses of primary pyrrhotite and pyrite surface shows slight sulphur deficiency. We attribute this inconsistency to partial surface decomposition, as thin needle-like crystals of gypsum are often found attached on and near pyrite crystals. As gypsum was not detected by XRD analysis, it was most probably formed during air
exposure or due to instability of Fe-sulphides in HCl. On the other hand, EDS analyses made on the polished central part of the both Fe-sulphides constantly indicate iron deficiency. Since (at least) pyrite shows no visible alterations, we can expect near-stoichiometric composition and we attribute this Fe-depletion to the near-surface structural damage, induced during Ar⁺ etching. EDS analyses of the exact same samples, made in TEM, further confirmed our assumptions, as they showed almost stoichiometric composition for pyrite and pyrrhotite.

Table 1. EDS analyses of sulphide crystals, normalized [at%].

| Pyrite | ref. [11] | SEM | SEM2 | TEM | Pyrrhotite | ref. [12] | SEM | SEM2 | TEM |
|--------|-----------|-----|------|-----|------------|-----------|-----|------|-----|
| S      | 66.7      | 61.3| 69.1 | 65.5| S          | 52.6      | 41.5| 54.9 | 49.1|
| Fe     | 33.3      | 38.7| 30.9 | 34.0| Fe         | 47.4      | 58.5| 45.1 | 50.9|
| Total  | 100.0     | 100.0| 100.0| 100.0| Total      | 100.0     | 100.0| 100.0|100.0|

SEM observation of Fe-sulphide intergrowths revealed unusual sequence of crystallisation: primary skeletal pyrrhotite (po1) is overgrown by well crystallized first-generation pyrite (py1), both being sparsely covered by small hexagonal pyrrhotite of second generation (po2). Almost all pyrite cubes of first generation are modified by (111) faces, while pyrite cubes of second generation (py2), modified by (110) and (111) faces, are rare and are overgrowing second generation of pyrrhotite (figure 3). According to literature [13, 14], the {100} faces attain the lowest energy at sulphur-poor and iron-rich conditions and with increasing amounts of available sulphur the {210}, {110} and {111} faces prevail [9]. Based on sequence of crystallisation and our observations in SEM, sulphide crystallisation begins with fast, irregular and skeletal pyrrhotite growth in sulphur-poor conditions. Subsequent exsolution of pyrite from pyrrhotite begins as a result of cooling, forming typical euhedral cubes rather than exsolution lamellae, in a process known as non-coherent exsolution [15]. Second generations of both Fe-sulphides are result of local variations in S- and Fe-availability or small temperature fluctuations.

To further identify possible structure variations in pyrite and pyrrhotite we investigated the Fe-sulphide intergrowths by TEM. TEM analysis of pyrrhotite was made on single pyrrhotite crystal of first generation, partially overgrown by pyrite. Pyrite showed no deviations from the normal pyrite structure and corresponds to JCPDS pattern # 04-1003. The electron diffraction (ED) pattern of pyrrhotite shows spacings of 2.04, 1.72 and 2.63 Å due to (200), (220), and (205) planes, respectively. The d(220) spots in ED pattern show splitting due to superstructure of Fe₁₋ₓS. The Fe-S system has a complex phase diagram, with hexagonal Fe₇S₈ as most defined and stable phase. Our sample, based on HR-TEM images and ED pattern (figure 4), does not correspond to hcp lattice, but it does correspond with 5T-Fe₁₋ₓS phase (card # 29-0724) (Table 2). Pyrrhotite 5T, for the formula Fe₁₋ₓS where x is about 0.1 and is equivalent to Fe₇S₈ with Z = 4, is characteristic for low-temperature systems [12]. The crystal system's true symmetry is orthorhombic [12] and sulphur atoms are arranged in an approximately hexagonal close-packed array, with iron atoms occupying octahedral interstices between the layers, where one in 8 of the octahedral interstices is vacant. Consequently this can be regarded as a "defect structure", with many options for disordering of the vacancies.

Table 2. Experimental and reference (JCPDS # 29-0724) d-values for pyrrhotite.

| Pyrrhotite | exp.[Å] | ref.[Å] |
|------------|---------|---------|
| 220        | 1.7     | 1.723   |
| 205        | 2.6     | 2.647   |
| 200        | 2.9     | 2.98    |
Figure 3. SEM micrographs of pyrite-pyrrhotite intergrowths. Primary pyrrhotite (po₁) is overgrown by first generation of pyrite (py₁), followed by second generation of pyrrhotite (po₂). Second generation of pyrite (py₂) crystallized last.

Figure 4. a) HR-TEM image of pyrrhotite (Fe₁₋ₓS) single crystal; insets are showing FFT and experimental ED patterns. b) Log fO₂-pH diagram showing stability fields for minerals found in investigated marble [16]. Grey area represents most possible conditions of mineralising fluids.
4. Conclusions
Our research of the accessory mineral associations in unaltered marble from Bistriški Vintgar Roman quarry showed that re-crystallisation temperature was as low as < 500 °C. Newly discovered pyrrhotite improved resolution of possible stability fields at the time of marble re-crystallisation, since pyrite-pyrrhotite coexistence is possible in a very narrow window. The main conclusions can be summarized as follows:

- Non-sulphide inclusions are illite, dolomite, quartz and amphibole.
- Primary sulphides are a mixture of pyrite and pyrrhotite.
- Pyrite exsolved from pyrrhotite as a result of cooling.
- Pyrite morphology indicate S-poor and Fe-rich conditions at the time of crystallisation.
- Investigated pyrrhotite correspond to 5T-Fe$_{1-x}$S variety.

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