

## Mineralogical and ore-petrographic investigation of the iron ore occurrence of Ano Valsamonero, Rethymno (Crete)

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Numerous iron ore occurrences appear within the Phyllite-Quartzite-Series (PQS) of Crete, some of which were occasionally mined. The PQS forms the lower part of the Phyllite nappe, which with Gypsum-Rauwacke-Formation, composes the Phyllite nappe of Crete that includes the metamorphic rocks between the Plattenkalk-Series underneath and the Tripolitza-Series above. The PQS contains mainly phyllites and quartzites, in addition to metaconglomerates, marbles, calcareous phyllites and metabasalts.

The examined occurrence is located about 15 km southwest from Rethymno next to Ano Valsamonero and occurs in the form of lenses within the phyllite and quartzite of the PQS. Sampling took place along a 10 m thick profile, in distances approximately 1 m in vertical arrangement. X-ray diffraction and ore microscopy were used for determination of the mineralogy and structure of the iron ore, while the chemical composition was determined by X-ray fluorescence.

The iron ore consists predominantly of hematite, goethite and quartz, and subordinately of chlorite and muscovite. Hematite occurs in the form of radial, or more rarely in punctate aggregates between the quartz grains of ferruginized quartzite, especially in those samples, which originate from the above layers of the profile. In the samples from the middle and lower parts of the profile, hematite and goethite form a ferruginized front, which replaced the largest part of the groundmass of quartzite. The Fe-rich solutions penetrated quartzite and precipitated as goethite, which forms concentric textures. The goethite changes gradually by dehydroxylation into hematite. The replacement by the Fe-rich solutions takes place from hair-cracks of the existing quartz grains. The composition of the iron ore along the profile varies regarding the Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents within a wide range.

According to the microscopic investigation of the ore, it is concluded that the processes, which have caused the massive replacing ferrugination of the ore occurrence of Ano Valsamonero are of epigenetic origin and can be classified to the continental ones.

## Multiple sulphur isotopes reflecting compositional changes in Earth's early atmosphere

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Pyrite extracted from more than 120 samples collected from Archean and Paleoproterozoic siliciclastic sedimentary units in southern Africa, western Australia, south-central Canada as well as in southwest Greenland and ranging in age from 3.8 to 2.1 Ga display nonzero  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$  values. Based on empirical and experimental data as well as respective modeling results, non mass-dependent sulphur isotope fractionations are considered to result from photochemical reactions of different sulphur-bearing compounds in the atmosphere under low atmospheric oxygen abundances (e.g., Farquhar *et al.*, 2000; Farquhar and Wing, 2003; Pavlov and Kasting, 2002).

The record of newly obtained non mass-dependent sulphur isotope results displays distinct temporal variations in their magnitude. High-magnitude  $\Delta^{33}\text{S}$  values for the Paleoproterozoic are followed by a somewhat attenuated  $\Delta^{33}\text{S}$  signal in the Mesoproterozoic, while the Neoproterozoic and early Paleoproterozoic show extremely variable  $\Delta^{33}\text{S}$  values (total range of 11.5‰). Post-2.3 Ga old sediments do not show a non mass-dependent sulphur isotope signal.

In addition to the temporal change in  $\Delta^{33}\text{S}$ , distinct temporal differences also exist considering relationships between  $\delta^{34}\text{S}$  and  $\Delta^{33}\text{S}$  as well as between  $\Delta^{33}\text{S}$  and  $\Delta^{36}\text{S}$ . This suggests variations in the respective photochemical reactions (e.g., different sulphur-bearing compounds involved) and/or reflect differences in atmospheric composition with respect to effective UV-shielding. However, we clearly rule out transient oxygen abundances as possible cause. Instead, potential alternatives include variations in the atmospheric abundance of methane and/or in the ratio of carbon dioxide to methane.

### References

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