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SULFUR-ISOTOPE VARIATION IN VOLCANIC-ASSOCIATED MASSIVE SULFIDES OF THE NORTHERN APENNINE OPHIOLITES (ITALY)

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GEOLOGICAL SETTING

Mesozoic ophiolites exposed in the western Alps and the Northern Apennine of Italy (Fig.1) are fragments of the sub-oceanic lithosphere that floored a marginal basin formed by divergence of the European and the Adriatic plates in the western of the Jurassic Tethys [1]. The ophiolites contain several Fe-Cu-Zn sulfide deposits of the Volcanic-Massive-Sulfide type, originated by hydrothermal processes related with sub-oceanic basaltic volcanism that accompanied the ocean opening [2, 3, 4, 5]. Ophiolites

and VMS deposits in the Northern Apennine differ from those in the Western Alps because of the lack of the high-P, low-T, Alpine-age metamorphism. Mafic and ultramafic rocks (serpentinized peridotite, gabbro, and basalts) only display the effects of low-grade oceanic metamorphism and syn-orogenic deformation caused by north-east thrust onto the Adria continental margin [1, 5]. Sulfides (pyrite, chalcopyrite, sphalerite, pyrrhotite) and gangue minerals (quartz, calcite, chlorite) still display primary depositional textures indicating crystallization under a range of conditions [3, 4]. Results of chlorite geothermometry point to temperatures of about 200°-360°C for deposition of sulfides in the sub-seafloor environment (i.e. stockwork veins) or within accumulating pillow lava (i.e. basalt stratabound ores). Temperatures gradually decrease down to <100°C in stratiform, massive sulfides precipitated on the seafloor, in which syn-sedimentary textures are well preserved [2, 3, 4].

SULFUR ISOTOPE VARIATIONS

The overall range of $\delta^{34}\text{S}$ in hydrothermal deposits of the Northern Apennine is between -2.9‰ and +11.4‰ (av. = +5.9‰), comparable with data from Cretaceous VMS deposits, in Tethyan ophiolites of Cyprus (av. $\delta^{34}\text{S}$ = +4.6‰) and northeastern Turkey (av. $\delta^{34}\text{S}$ = +4.2‰) [6]. Slight differences were detected among sulfide minerals, varying from -0.6‰ to +11.3‰ in pyrite (av. = +5.2‰), -2.9‰ to +11.4‰ in chalcopyrite (av. = +6.7‰), and 0.0‰ to +10.3‰ in sphalerite (av. = +6.1‰). Significant differences are observed among deposits depending on the structural type and host rock lithology (Fig. 2). Stratabound deposits and stockwork veins hosted in basalt and gabbro have similar average $\delta^{34}\text{S}$ of +7.9‰, +8.9‰, and +8.7‰, respectively. Stockwork veins hosted in serpentinite have a significantly lower average $\delta^{34}\text{S}$ = +5.7‰. The stratiform deposits have the lowest $\delta^{34}\text{S}$, showing no difference between deposits hosted in serpentinite (av. = +2.4‰) and basalt breccia (+2.5‰). Isotopic composition of magmatic Fe-Cu-(Ni) sulfides associated with serpentinized peridotite was determined for comparison, yielding an average $\delta^{34}\text{S}$ of +0.8‰ (range -1.7‰...+2.8‰).

INTERPRETATION OF ISOTOPE DATA

Assuming a Jurassic age of 160 Ma for the Northern Apennine VMS deposits, the isotopic ratios of stockwork veins (+3.9‰ to +11.4‰) indicate $\Delta_{\text{H}_2\text{S-SO}_4}$ fractionation factors between -13.14‰ and -5.64‰ with respect to coeval seawater sulfate (~ +17.04 $\delta^{34}\text{S}$ ‰) (Fig. 3). These values are consistent with inorganic reduction of seawater sulfate during convective circulation through the rock substrate [7, 8]. Although, the low $\delta^{34}\text{S}$ values of serpentinite-hosted veins may indicate mixing with light sulfur derived from leaching of magmatic sulfides with near-chondritic composition (av. $\delta^{34}\text{S}$ = +0.8‰).

Most isotopic values obtained from stratiform sulfides show variable enrichment in the light ^{32}S isotope, up to reach negative $\delta^{34}\text{S}$ ratios. The stratiform sulfides are characterized by distinctive textures indicative of the replacement of microfossils and bacterial reworking suggesting that lightening of sulfur isotope ratios might have resulted from mixing between hydrothermal and biogenic sulfur with $\Delta_{\text{H}_2\text{S-SO}_4}$ as negative as -45‰ [8]. At temperatures up to 110°C, thermophilic bacteria can oxidize the internal organic coat of microfossil shells by reduction of seawater sulfate. The metabolic byproduct of this process is S^{2-} that precipitates metal sulfides resulting in the pseudomorphic replacement of the original shell structure (Fig. 4A). Furthermore, bacterial colonies played a passive role in mineralizing reactions

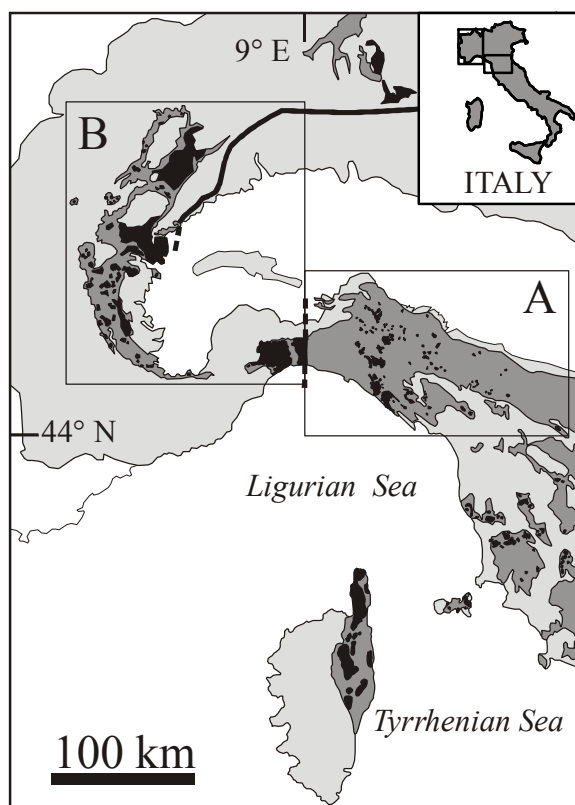


Fig. 1. Structural map of ophiolite complexes (black) in the Northern Apennine and the Western Alps (B) domains, Italy.

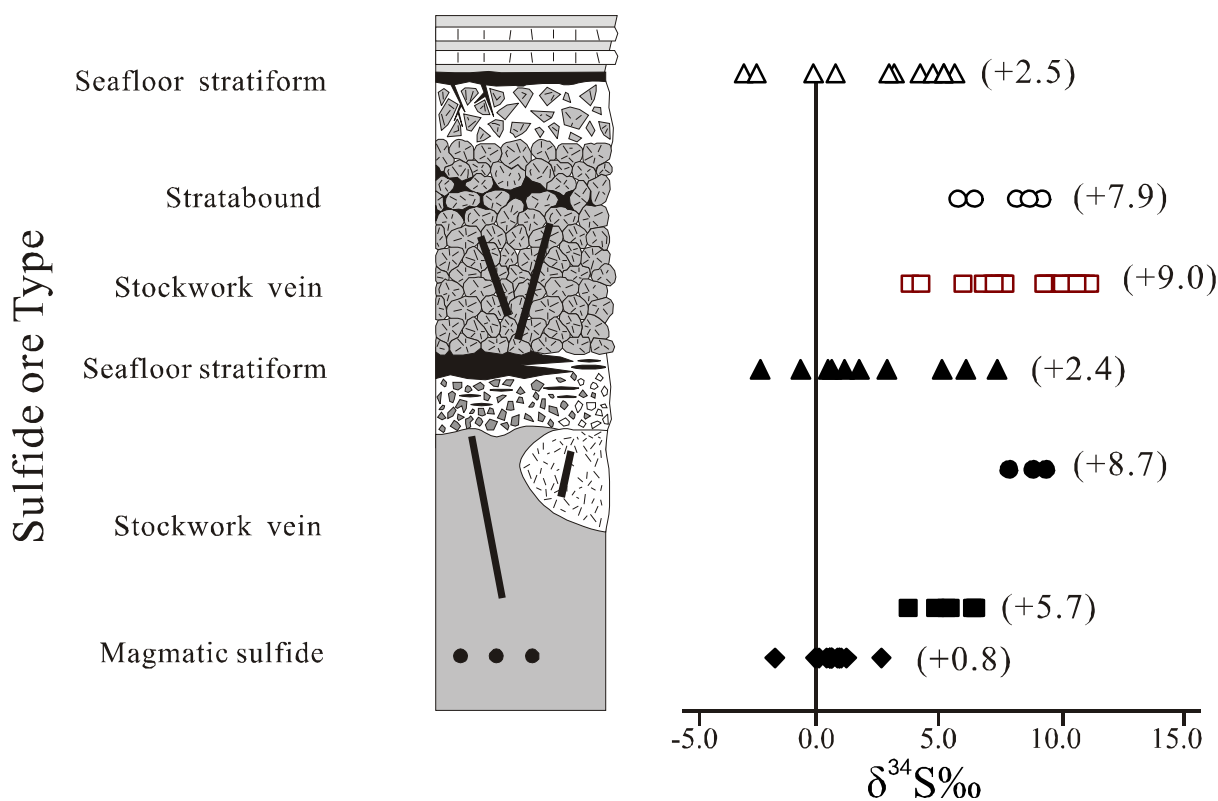


Fig. 2. Variation of $\delta^{34}\text{S}$ ratios as function of the stratigraphic position of the Northern Apennine VMS deposits.

Black squares = hydrothermal veins in serpentinite; black dots = hydrothermal veins in gabbro; black triangles = seafloor stratiform ore in serpentinite breccia; open squares = hydrothermal veins in pillow basalt; open circles = stratabound ore in pillow basalt; open triangles = stratiform ore in basalt breccia; black diamond = magmatic sulfides in serpentinite.

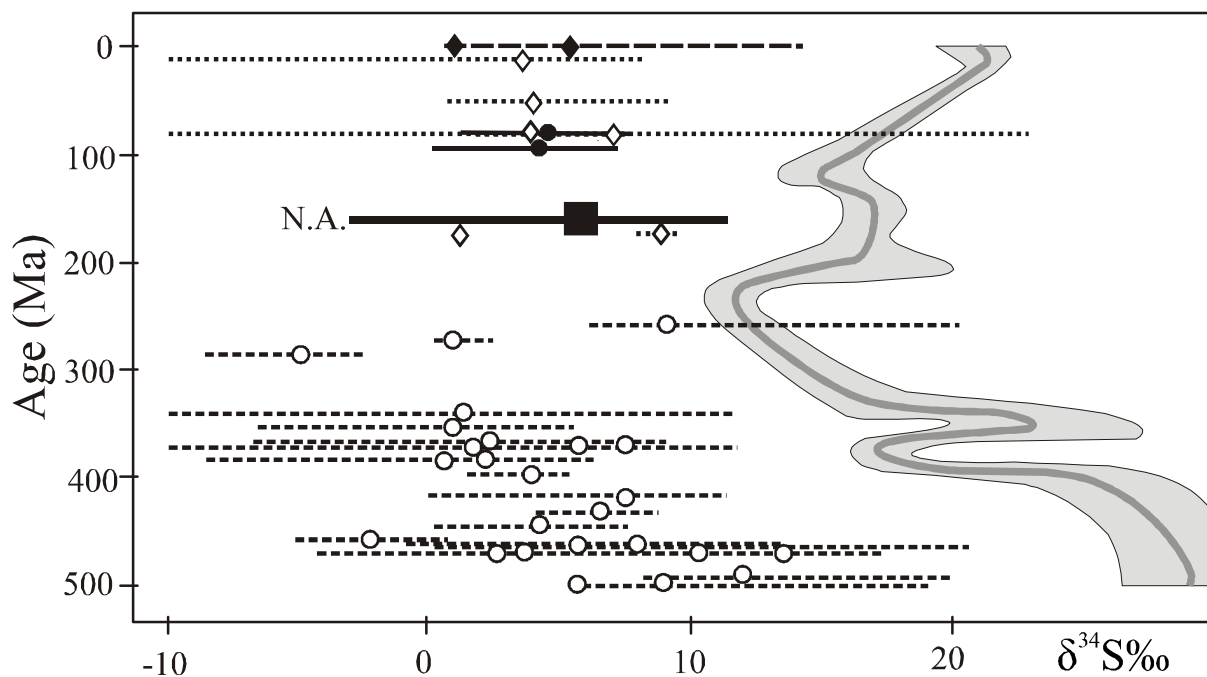


Fig. 3. Evolution of $\delta^{34}\text{S}$ in Phanerozoic VMS deposits and coeval seawater sulfate.

Symbols and lines indicate mean and ranges of variation (data from [6]). black square = Northern Apennine (N.A.); black diamonds = Red sea and western Pacific; black dots = Tethyan VMS of Cyprus and northeastern Turkey; open diamonds = Mesozoic VMS; open circles = Paleozoic VMS. The heavy line and grey area indicate the evolution with age of the seawater-sulfate [7].

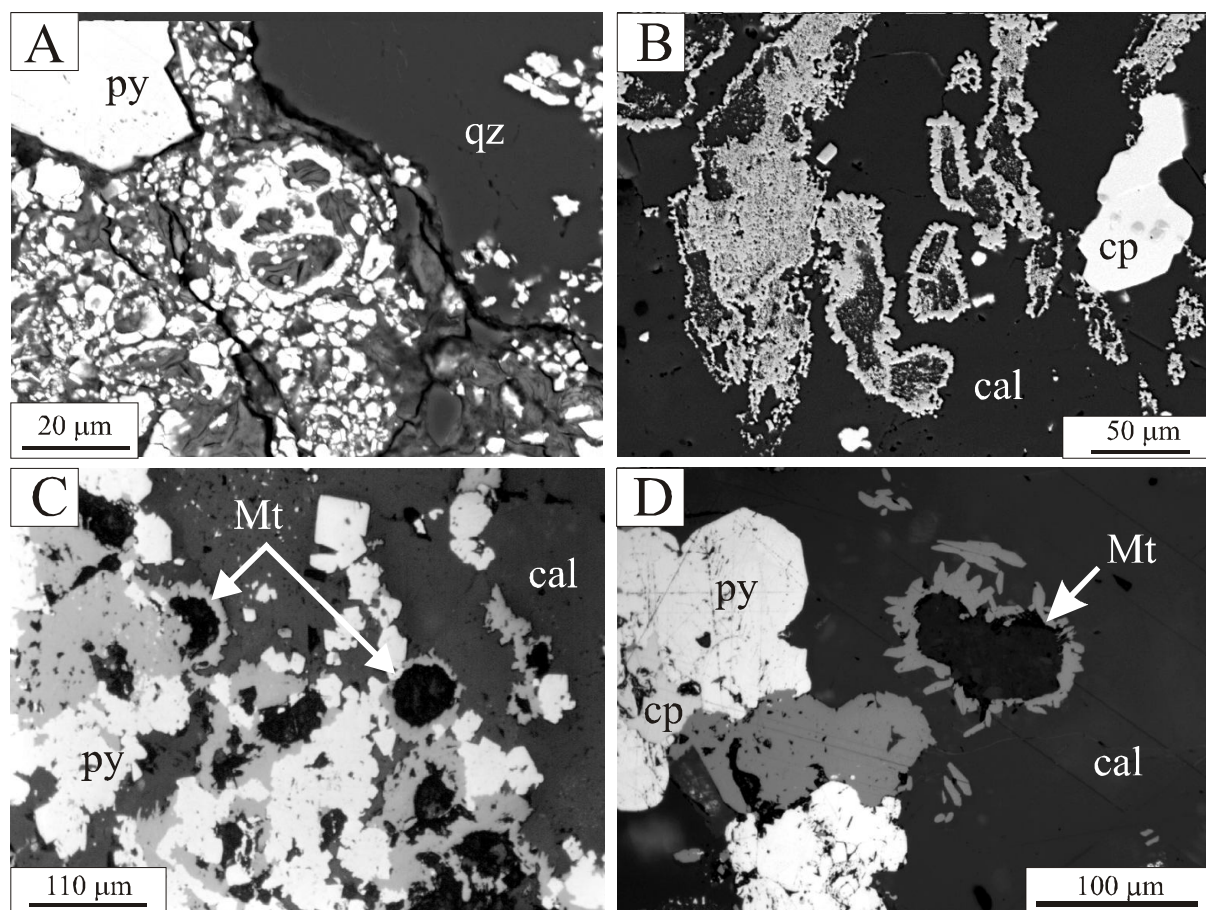


Fig. 4. Biogenic sulfide textures in seafloor stratiform VMS deposits of the Northern Apennine.

A. Shells of foraminifera replaced by pyrite. B. Pyrite spherules, coronas, filaments and capsular aggregates with silicate infilling. C. and D. magnetite spherules with silicate infilling. Qz = quartz, cal = calcite, py = pyrite, Mt = magnetite spherules.

by acting as the template for deposition of metals [9]. The sulfide spherules, coronas, filaments and other irregular capsular aggregates strongly recall bacteria cells encrusted with sulfide crystallites and filled with Fe-Al hydrous silicates associated with dusty Fe-sulfide particles (Fig. 4B). Similar structures were produced in bacterial cultures generated by microorganisms able to flock Fe-Al silicates around their bodies with retention of considerable amounts of heavy metals [9].

Magnetite spherules (Fig. 4C, 4D) can be a byproduct of the oxidation of organic matter by ferric iron reducing bacteria, involving a change in redox conditions from anoxic-suboxic to oxic due to progressive recession from the venting site toward a more marginal zone. Interestingly, it has been observed in nature that one single bacterium can produce Fe-sulfide or Fe-oxide under anoxic or oxic conditions, respectively, suggesting that the local variation in O^{2-} to HS^- activity was the factor controlling the type of excreted iron species [10].

The results of this investigation provide evidence that the sulfur isotopic composition of hydrothermal VMS deposits of the Northern Apennine was determined by initial reduction of seawater sulfates during convective circulation in the rock substrate followed by: 1) mixing with magmatic sulfur derived by leaching of ultramafic rocks, with a possible, but not observed contribution from a juvenile source; 2) mixing with biogenic sulfur during and soon after deposition of sulfides on the seafloor. Preservation of biogenic textures in the Northern Apennine VMS deposits support this hypothesis.

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MAGMA MIXING IN MAFIC ROCKS OF URALIAN-ALASKAN-TYPE MAFIC-ULTRAMAFIC COMPLEXES IN THE URAL MOUNTAINS, RUSSIA: EVIDENCE FOR COEVAL MELTS FROM DIFFERENT SOURCES

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RESULTS AND DISCUSSION

The distinctive geologic and petrographic feature of classical Uralian-Alaskan-type zoned mafic-ultramafic complexes is a zonal distribution of mafic and ultramafic rocks, with a central dunite body that grades outward into wehrlite, clinopyroxenite and gabbroic lithologies (tilaite). This rock association is considered to represent cumulates of a single parental melt feeding a magma chamber system [1]. In this study we discuss the results of in-situ trace element analyses (LA-ICPMS) of clinopyroxene from mafic rocks of the Nizhny Tagil and Kytlym complexes in the Ural Mountains in Russia.

The tilaite have clinopyroxene phenocrysts in a matrix of olivine, clinopyroxene, feldspar ± phlogopite ± amphibole + minerals of the spinel group. Based on additional minerals and their spatial distribution three types of tilaite can be distinguished. The nepheline tilaite are silica undersaturated and contain in the matrix plagioclase_{An28-48}, K-feldspar_{Or47-98} and nepheline. They are only observed in Nizhny Tagil and the south western part of the Kytlym Complex. The second type, the bytownite tilaite are silica saturated, contain up to 15% plagioclase_{An56-89} and in places orthopyroxene as matrix phases. They coexist with the nepheline tilaite in Nizhny Tagil and south west Kytlym. The third group of tilaite at the Tilaysky Kamen Mountain massif in the central part of the Kytlym complex also consists of bytownite tilaite, but they do not coexist with nepheline tilaite and have distinct mineral and trace element compositions.

Gabbronorites, olivine- and hornblende gabbros in the eastern part of the Kytlym complex contain 15-35% plagioclase_{An85-97} and a significant amount of orthopyroxene and amphibole. The large mass of