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APPLICATION OF CHLORITE AND FLUID-INCLUSION GEOTHERMOMETRY TO VEIN AND STRATIFORM Fe-Cu-Zn SULFIDE DEPOSITS OF THE NORTHERN APPENNINE OPHIOLITES (EMILIA-ROMAGNA AND LIGURIA, ITALY)

APPLICAZIONE DELLA GEOTERMOMETRIA, BASATA SU CLORITE ED INCLUSIONI FLUIDE, AI DEPOSITI DI SOLFURI DI Fe-Cu-Zn STRATIFORMI ED IN VENE DELLE OFIOLITI DELL'APPENNINO SETTENTRIONALE (EMILIA-ROMAGNA E LIGURIA, ITALIA)

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KEY-WORDS: Chlorite, fluid-inclusion, sulfide deposits, ophiolites, Northern Appennine, Italy.

PAROLE CHIAVE: Clorite, inclusioni fluide, depositi di solfuri, ofioliti, Appennini settentrionali, Italia.

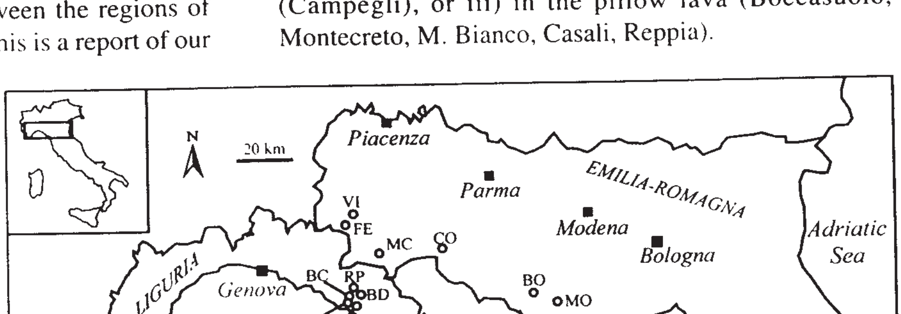
1. INTRODUCTION

Compositional variations of trioctahedral chlorites are believed to reflect physic-chemical conditions of crystallization. In particular, the amount of Al^{IV} substituting for Si in the tetrahedral site is temperature dependent, increasing with depth in hydrothermal, diagenetic or metamorphic systems. Temperature information can also be obtained from the study of fluid inclusions in solid crystals, provided that they were not disturbed by secondary processes. In general, the temperature at which the components of a fluid inclusion (i.e. vapor + liquid ± solid) can be homogenized by heating indicates the minimum temperature at which the inclusion was trapped in the mineral host. Basing on these experimental assumptions, we have applied the chlorite and fluid inclusions geothermometry to the historical Fe-Cu-Zn sulfide deposits located in the Mesozoic ophiolites of Northern Appennine, between the regions of Liguria and Emilia Romagna (Fig. 1). This is a report of our preliminary results.

2. GEOLOGICAL SETTING

The Northern Appennine ophiolites do not display the typical stratigraphy of the Tethyan ophiolites in the Eastern Mediterranean basin. Field evidence indicates that a well developed cumulus sequence and a true "sheeted-dike" complex are absent. Instead, the mantle tectonite contains large, intrusive bodies of cumulus gabbro, and is commonly covered by thick layers of ophiolitic breccias, indicating that the plutonic basement was exposed at the ocean floor and eroded, prior to the outflow of pillow-lava and deposition of pelagic sediments. Basing on morphology and structural relationships with the host rocks, the Fe-Cu-Zn sulfide deposits of the Northern Apennine ophiolites can be divided into the following main groups (Ferrario & Garuti, 1980):

1. The stratiform mineralization laying concordant with lithostratigraphic joints: i) at the top of the pillow lava unit, in contact with the sedimentary cover (Corchia), ii) at the base of the pillow lavas, inside the ophiolitic breccia, covering the plutonic basement (M. Bardeneto, M. Bianco, Reppia), and iii) inside the pillow lava unit (Libiola).
2. The stockwork-vein mineralization consists of a network of quartz + carbonate veins, from one centimeter to some decimeters in thickness, containing low-grade disseminated sulfides. The stockwork-veins cut across different units of the ophiolite sequence: i) in the mantle tectonite (Vigonzano, M. Castello), ii) in the massive gabbro (Campegli), or iii) in the pillow lava (Boccasuolo, Montecreto, M. Bianco, Casali, Reppia).



MO = Montecreto, BO = Boccasuolo, CO = Corchia, MC = M. Castello, FE = Ferriere, VI = Vigonzano, BD = M. Bardeneto, CS = Casali, CP = Campegli, LB = Libiola, BC = M. Bianco, RP = Reppia

Fig. 1 - Geographical location of relevant sulfide deposits of the Northern Appennine ophiolites.

Localizzazione geografica dei principali depositi di solfuri delle ofioliti negli Appennini settentrionali.

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3. CHLORITE CHEMISTRY AND THERMOMETRY

Electron microprobe analyses of chlorite are plotted in terms of variations of Fe/(Fe+Mg) versus the Si content (Fig. 2), and compared with the conventional nomenclature after HEY (1954). Compositions split into two groups: one corresponds to chlorites from stockwork-veins characterized by relatively low Si contents (5.4-6.8 at% Si), most values being lower than 7.0 Si at% (Fig. 2A), the other consists of chlorites from stratiform deposits, showing enrichment in Si (6.5-7.74 at%) with more than a half of the values over 7.0 Si at% (Fig. 2B). Microprobe analysis also reveals that Mn is relatively enriched (0.85 wt% MnO) in Si-poor chlorites from stockwork-veins in basalt, whereas Cr is higher in chlorites associated with ultramafic breccias (3.45 wt% Cr_2O_3). This has been interpreted as due to different geochemical environments of chlorite crystallization. Thermometric significance of the investigated chlorites was not affected by alkalis contamination (FRIMMEL, 1997) that was usually less than 0.1 at% Ca+Na+K. Treatment of chlorite data with the equation of KRANIDIOTIS and MACLEAN (1987) yielded the most reliable results, well consistent with the geological constraint of the investigated sulfide ores. In general, chlorites from stockwork-veins gave temperatures higher than those from stratiform deposits (Fig. 3), although data for single ore deposits (Table 1) indicate that a small group of chlorites in quartz veins crystallized at relatively low temperature (<200°C).

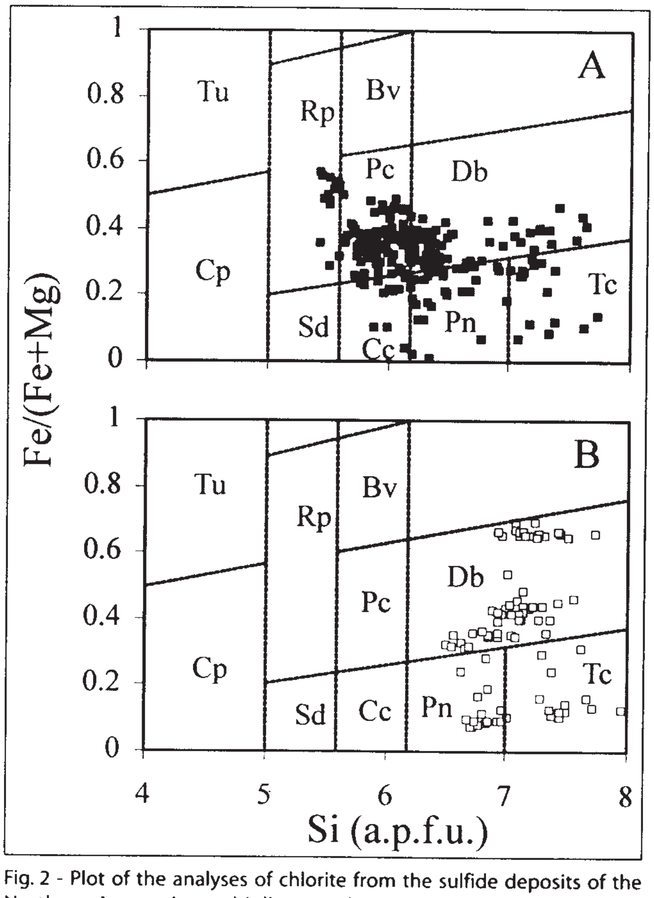

Fig. 2 - Plot of the analyses of chlorite from the sulfide deposits of the Northern Appennine ophiolites on the Hey diagram (Hey, 1954). A) stockwork-veins; B) stratiform ores. Abbreviations: Cp = corundophillite, Tu = pseudothuringite, Sd = sheridanite, Rp = Ripidolite, Cc = clinochlore, Pc = pycnochlorite, Bv = brunsvigite, Pn = penninite, Db = diabanite, Tc = Talc-chlorite.

Composizione delle cloriti dei depositi a solfuri delle ofioliti negli Appennini settentrionali nel diagramma di Hey (Hey, 1954). A) stockwork-vene; B) depositi stratiformi. Abbreviazioni: Cp = corundophillite, Tu = pseudothuringite, Sd = sheridanite, Rp = Ripidolite, Cc = clinochlore, Pc = pycnochlorite, Bv = brunsvigite, Pn = penninite, Db = diabanite, Tc = Talc-chlorite.

4. FLUID INCLUSIONS

Primary fluid inclusions, consisting of *liquid* or *liquid+vapor*, were observed in quartz and calcite of the stockwork and stratiform ores. Eutectic temperatures of less than – 40°C were found, corresponding to a fluid system of the type H_2O-NaCl-$CaCl_2$. The melting temperature of the hydrohalite could be determined only in a few cases, giving values consistent with Na/Ca < 1. The melting temperature of the last ice crystal suggests low salinity, between 1.1 and 4.0 wt% NaCl equivalents. The homogenization temperatures vary 64°-360°C for inclusions in quartz, and 86°-256°C those in calcite (Fig. 4). Most data from the stockwork-veins concentrate below 150°C, being generally higher in calcite (146°C on average) than in quartz (< 150°C). In contrast, quartz from stratiform ores gave temperatures up to 360°C, with a good half of the values falling in the range 240°-360°C.

5. PRELIMINARY CONCLUSIONS

The preliminary geothermometric results indicate that the stratiform sulfide deposits in the Northern Appennine

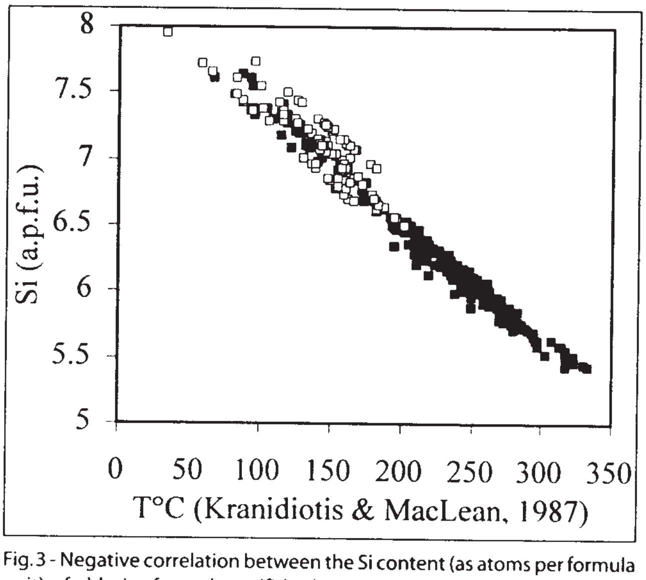

Fig. 3 - Negative correlation between the Si content (as atoms per formula unit) of chlorite from the sulfide deposits of the Northern Appennine ophiolites and temperature calculated according to the equation of Kranidiotis & Mac Lean (1987), black square = stockwork-veins; open square = stratiform ores.

Correlazione negativa tra il contenuto di Si (atomi per unità di formula) della clorite dei depositi a solfuri delle ofioliti negli Appennini settentrionali e le temperature calcolate con l'equazione di KRANIDIOTIS & MAC LEAN (1987), quadrati neri = stockwork-vene; quadrati bianchi = depositi stratiformi.

Locality	*Host Rock*	*Sulfides*	*Gangue*	*T°C*	*N°*
Stockwork-Vein Ore					
Boccassuolo (MO)	basalt	Py-Ccp-Sph	Qz-Cal-Ep	204-317	24
M. Bianco (GE)	basalt	Py-Ccp	Qz-Al	307-332	12
Casali (GE)	basalt	Py-Ccp-(Sph)	Qz-Al	218-271	38
Campegli (GE)	gabbro	Py-Ccp-(Sph)	Qz-Al	212-294	28
Ferriere (PC)	basalt	Py-Po-Ccp	Qz-Cal-Sid	181-295	20
Montecreto (MO)	idraulic breccia	Py-Ccp-(Po-Sph)	Qz-(Cal)	136-302	42
Reppia (GE)	basalt	Py-Ccp-Sph	Qz	87-177	20
Vigonzano (PC)	serpentinite	Py-Po-Chp-Mar-(Mil)	Qz-(Srp)	202-294	30
M. Castello (PR)	mantle-peridotite	Po-Ccp-Py	Srp-Gnt	66-250	15
Stratiform Ore					
Corchia (PR)	basalt-sediments	Py-Ccp-Sph	Qz-Cal	100-181	34
Libiola (GE)	basalt	Py-Ccp-Sph	Qz	158-200	15
M. Bardeneto (GE)	serpentine breccia-basalt	Py-Po-Ccp-Sph	Qz-Cal-Sid	25-182	26
M. Bianco (GE)	serpentine breccia-basalt	Py-Ccp-(Sph)	Qz-Cal-Sid	<50	18
Reppia (GE)	serpentine breccia-basalt	Py-Po-Ccp-(Sph)	Qz-Cal-Sid	115-202	28

Sulfides: Py=pyrite, Ccp=chalcopyrite, Sph=sphalerite, Po=pyrrhotite, Mar=marcasite, Mil=millerite.
Gangue: Qz=quartz, Cal=calcite, Ep=epidote, Al=albite, Sid=siderite, Srp=serpentine, Gnt=garnet.
T°C according to KRANIDIOTIS & MACLEAN (1987). N° = number of analyzed grains.

Tab. 1 - Results of Chlorite-Geothermometry in selected Fe-Cu-Zn sulfide deposits of the Northern Appennine Ophiolites (Liguria, Emilia Romagna)
Risultati della goetermometria della clorite nei depositi di sulfuri a Fe-Cu-Zn delle ofioliti dell'Appennino Settentrionale (Liguria, Emilia Romagna).

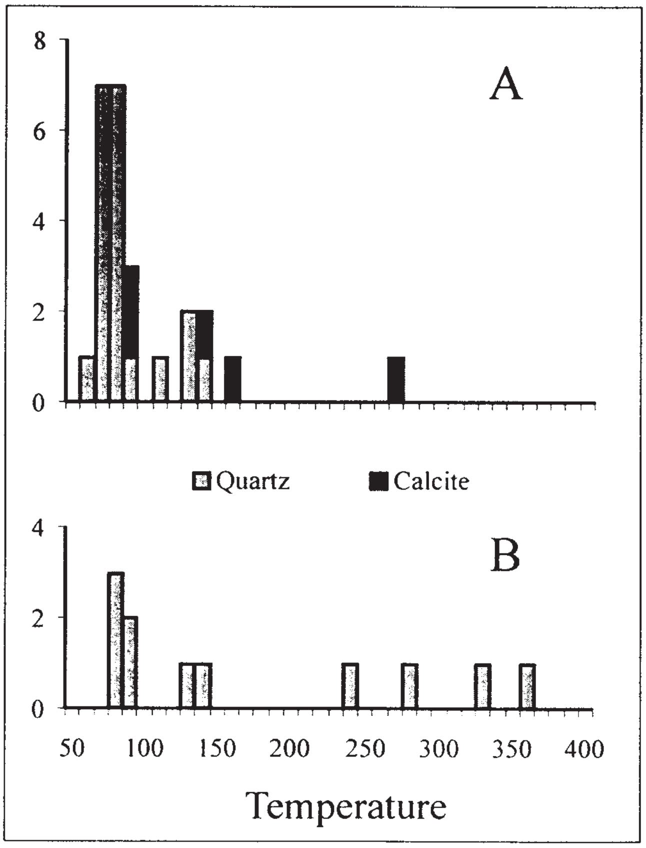

Fig. 4 - Frequency distribution of the homogenization temperature of fluid inclusions from the sulfide deposits of the Northern Appennine ophiolites. A) stockwork-veins; B) stratiform ores.
Distribuzione di frequenza delle temperature di omogeneizzazione delle inclusioni fluide dei depositi a solfuri delle ofioliti negli Appennini settentrionali. A) stockwork-vene; B) depositi stratiformi.

ophiolites formed at the sea floor from submarine hydrothermal vents, of which the stockwork-veins were possible feeders (FERRARIO & GARUTI, 1980). The highest temperatures (200°-360°C) registered by fluid inclusions and chlorite probably reflect the initial temperature of ore deposition. The lowest temperatures registered in the stockwork-veins may indicate that cooling of the hydrothermal system proceeded well below 100°C. The temperatures calculated from chlorite in the stratiform deposits are generally lower than those registered by the fluid inclusions in quartz and calcite. This possibly indicates that quartz and calcite crystallized from the hot hydrothermal brine at relatively high temperature, whereas chlorite formed in situ by alteration of ultramafic detritus during cooling of the ore deposits.

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