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A NOTE ON THE OCCURRENCE, CHEMISTRY AND K/Ar DATA OF STILPNOMELANE FROM MT. CONTRARIO (APUAN ALPS, NORTHERN TUSCANY)

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RIASSUNTO. — Vengono riportate le caratteristiche chimiche, mineralogiche, petrografiche e l'età radiometrica (metodo K/Ar) dello stilpnomelano rinvenuto nei marmi della formazione dei « Calcari Selciferi ad Entrochi » del M. Contrario (Alpi Apuane, Toscana). Il minerale si ritrova in vene, in noduli e disperso nella matrice del marmo. La composizione chimica e la distanza basale d_{001} indicano trattarsi di un ferristilpnomelano; l'età radiometrica varia tra 6,8 e 1,8 milioni d'anni.

I valori di età radiometrica vengono discussi e confrontati con l'età di formazione dello stilpnomelano quale risulta dalle caratteristiche tessiturali e microstrutturali del minerale e della roccia che lo contiene. Le variazioni di età radiometrica vengono discusse in rapporto alle caratteristiche chimiche (rapporto Fe^{+2}/Fe^{+3}) e strutturali del minerale.

ABSTRACT. — Occurrence, chemistry and K/Ar age of stilpnomelane from Mt. Contrario (Apuan Alps) have been reported. The stilpnomelane has been observed in three modes of occurrence: in veinlets, in nodules and dispersed in the matrix of the marble. On the basis of textural data it seems originated in the time interval between the first and the late phases of deformation that affected the Apuan Alps.

Chemical and X-ray data reveal that the stilpnomelane is a ferric iron-rich term. The K/Ar age of the mineral varies from 6.8 to 1.8 m.y. and does not seem to date the time of its genesis. The spread of K/Ar age in relation to the Fe^{+2}/Fe^{+3} ratio and crystal structure of the mineral is discussed.

Introduction

This paper deals with the occurrence, chemistry and K/Ar age of stilpnomelane encountered (for the first time) in the marbles outcropping about 250 m northwards from Mt. Contrario (Apuan Alps, Tuscany).

The marbles belong to the « Calcari Selciferi ad Entrochi » Formation which is a lithologically heterogeneous Formation composed mainly of pure and impure marbles including nodules or lenses of metachert and minor phyllite and calco-phyllite rocks. Details on stratigraphy, geology and tectonics of the Mt. Contrario area can be found in NOTINI (1982). Fig. 1 shows the geological structural sketch map of the area together with the sampled locality.

In the Mt. Contrario area two generations of folds may be distinguished, each of them displaying different orientation and different style in the deformation. Direction and plunge of the two fold systems together with the orientation of their axial plane schistosity, are presented in fig. 1. The first phase of deformation is synchronous with the regional metamorphism realized in the low greenschist facies while the second one (corresponding to the late folding phase of CARMIGNANI and GIGLIA (1979)) took place after the peak of the metamorphism, producing a new locally penetrative schistosity (S_2) coupled with mineralogical growth.

On the basis of the K/Ar and Ar^{40}/Ar^{39} age of K-white mica related to the first and second generation of microstructures, both these phases of deformation could have occurred between 26 and 10 m.y. (KLIGFIELD et al., 1980).

Occurrence of stilpnomelane

Stilpnomelane of Mt. Contrario has been encountered in three modes of occurrence: in veinlets, in nodules and dispersed in the matrix of the marbles.

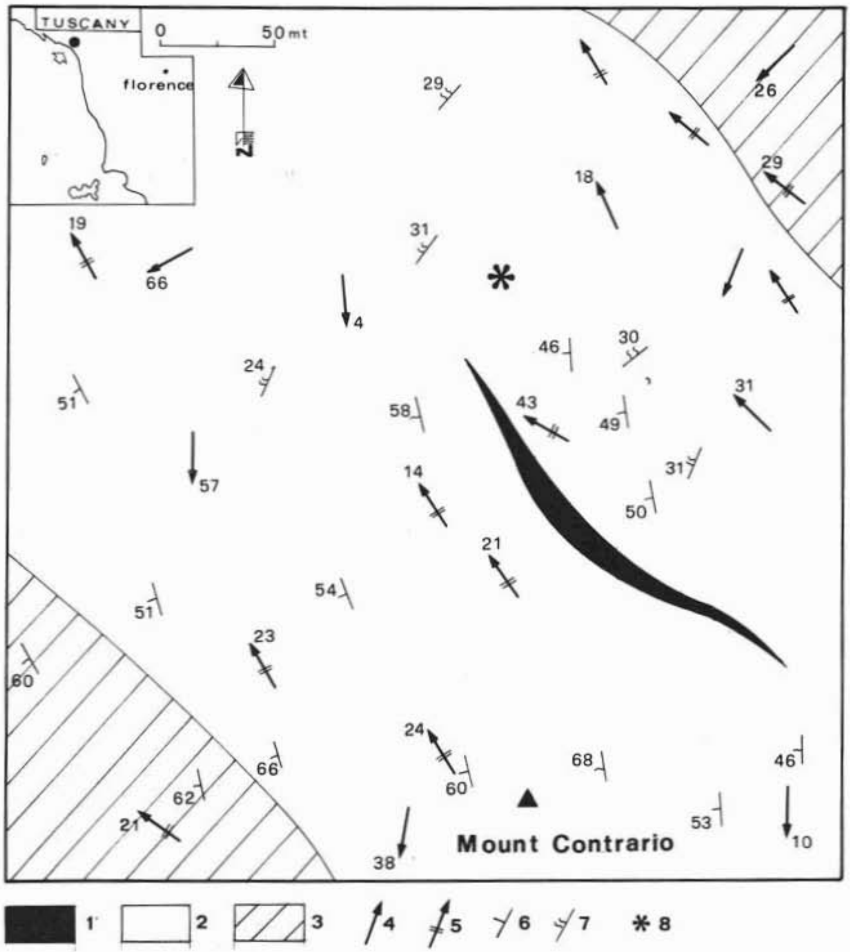

Fig. 1. — Schematic structural map of the Mt. Contrario area. - 1 = metaradiolarites; 2 = « Calcari Selciferi ad Entrochi » Formation; 3 = scaglia phyllites and calco-phyllites; 4-5 = strike and dip of F_1 and F_2 fold axis; 6-7 = strike and dip of S_1 and S_2 axial plane schistosity; 8 = sampled locality.

Stilpnomelane-rich veinlets - A selected stilpnomelane-rich veinlets is shown in fig. 2. The veinlets trace tight folds (4-5 mm thick at the most), whose thickness decreases from the hinge to the limb region of the folds. In the hinge region the mineral appears bent and slightly deformed and shows a distinct orientation with its lengthening direction parallel to the hinge curvature of the folds. The orientation sharply decreases in the limb region where a sheaf-like structure prevails. Stilpnomelane is associated to calcite, chlorite, sphene, magnetite and rare white mica; its modal proportion varies widely from the hinge to the limb of the fold, reaching a maximum value in proximity to the limb-hinge transition zone. The mineral grains (about 0.1-0.2 mm long and 0.05 wide) always exhibit a wavy extinction and frequently appear to be cracked. The chlorite occurs as green pleochroic, very fine-grained crystals; this mineral, which seem to be oriented as the S_2 schistosity, appears disomogeneously distribuited in the

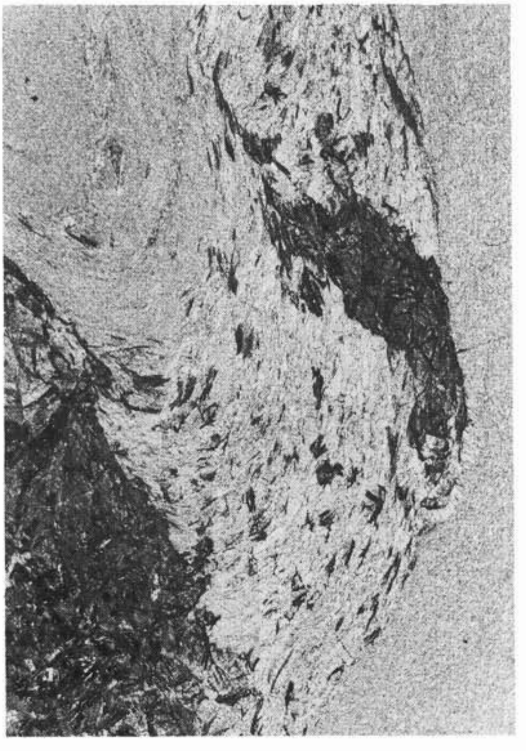

Fig. 2. — Stilpnomelane-rich veinlets. The stilpnomelane-rich nodule is also shown in the hinge-limb transition zone of the fold. Photomicrograph, Nicols //, x 10.

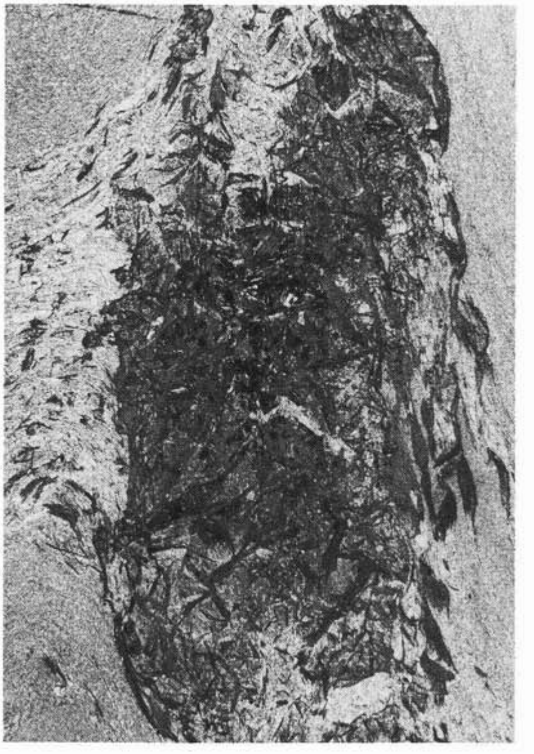

Fig. 3. — Typical occurrence of stilpnomelane in nodules, with two weak high-angle flake orientations. The first and the third type of calcite associated to the stilpnomelane are also shown. Photomicrograph, Nicols //, x 10.

veinlets and its modal proportional decreases from the margin to the interior of the veinlets.

Three types of calcite occur in veinlets. A first type, located prevalently at the margin of the veinlets occurs as medium-grained crystals which, in the limb region, appear to be strongly bent, while they form a typical palisade texture in the limb region. A second type of calcite, characterized by a relatively smaller grain size, forms a mosaic-type structure. The third type always occurs associated to the stilpnomelane aggregate and is characterized by a very fine grain size, just resolvable under the optical microscope.

Stilpnomelane-rich nodules - A representative stilpnomelane-rich nodule is shown in fig. 3. The nodules generally exhibit an elliptical shape and are found as isolated bodies in the matrix of the marbles or in the hinge-limb transition zone of the veinlets. Macroscopically the nodules do not present an evident orientation of the stilpnomelane crystals, while under the microscope they display two high-angle stilpnomelane flakes orientations. The older orientation is defined by bent crystals which are arranged approximately in the same way as the crystals occurred in the hinge folds of the veinlets, the younger orientation by the axial plane of the meso-folds. The mineralogical association of the nodules, except for the absence of chlorite and the different modal proportion of several components, is the same as that of the veinlets.

Stilpnomelane dispersed in the matrix of the marble - Stilpnomelane in the matrix of the marble occurs as single elongate flakes or aggregate of interlocking laths forming a sheaf-like structure. Both the single flakes and the crystalline aggregate are oriented as the calcite crystals of the marble matrix (S_2 schistosity). The most relevant feature of

TABLE 1

Chemical composition of stilpnomelane

	(1)	(2)*	(3)*	(4)*
SiO_2	45.16	45.20	44.88	43.76
TiO_2	0.35	0.26	0.24	0.19
Al_2O_3	8.16	7.24	6.21	7.05
Fe_2O_3	23.92	30.33	29.92	31.46
FeO	5.92	-	-	-
MnO	0.09	0.07	0.04	0.04
MgO	6.11	6.19	6.52	6.32
CaO	0.63	0.50	0.70	0.40
Na_2O	0.1	0.11	0.11	0.09
K_2O	1.59	1.25	1.16	1.44
L.O.I.	8.07	-	-	-
Total	100.00	91.15	89.78	90.75

* Microprobe data; total Fe as Fe_2O_3. (1) and (2) stilpnomelane from the matrix of the marble; (3) stilpnomelane from nodules; (4) stilpnomelane from veinlets.

stilpnomelane is a mantle of microcrystalline calcite which looks like the third type of calcite in the veinlets. Microcrystalline calcite always occurs among and around the network of the interlocking laths.

The host rocks

The host rocks are primarily pure and impure limestones with subordinate pelitic layers. The fissility is moderate and the rocks reveal a weak variation in the degree of schistosity, in relation to the abundance of phyllosilicates. Microscopic folds of the second generation occur in the marbles and pelitic layers with different style. In the marbles the folds are open ones while the folds observed in pelitic layers are tighter and associated everywhere to the new axial plane schistosity.

The marbles consist of calcite (up to 80-90%), chlorite (0-10%), white mica (0-5%) and minor amounts of quartz, tourmaline, apatite, sphene and magnetite. The pelitic layers mainly consist of white mica and chlorite (up to 80-90 %) and quartz; tourmaline and sphene represent the more common accessories; in these layers the S_2 schistosity is defined either by a reorientation of phyllosilicates or by a new growth of white mica.

Chemistry of stilpnomelane and associated minerals

Stilpnomelane

Microprobe analyses of stilpnomelane from the three modes of occurrence are presented in table 1. Microprobe analyses were performed using a fully automated ARL/SEMQ instrument at the University of Modena. A complete characterization of the mineral was obtained by analyzing a small quantity of pure material separated from the matrix of the marbles. In this case Na_2O, Al_2O_3, SiO_2, CaO, MnO and total Fe as Fe_2O_3 were determined by X-ray fluorescence analysis according to the method of FRANZINI and LEONI (1972) modified by LEONI and SAITTA (1974); MgO was determined by atomic absorption spectrometry, FeO by titration method and H_2O as loss to ignition at 850° C. The results of this analysis are reported in table 1 (column 1).

Microprobe analysis of different crystals from nodules, veinlets and matrix of the marbles do not show significant variation in any of the major elements. The average microprobe data of stilpnomelane from different occurrences (table 1) reveal only small variation in Al_2O_3 and total Fe_2O_3 content, while comparison between microprobe and X-ray fluorescence data reveals some differences, chiefly in the Al_2O_3 content.

On the basis of the chemical data of column (1) in table 1, a chemical formula was derived:

$$(Al_{3.47}, Fe^{+3}_{24.81}, Ti_{0.24})_{28.52}$$

$$(Fe^{+2}_{6.82}, Mg_{12.55}, Mn_{0.11})_{19.48}\,(OH)_{19.24}\,O_{76.76}$$

$$(Si_{31.11}, Al_{4.89}, O_{60.00})_2$$

$$(K_{2.79}, Ca_{0.37}, H^{+}_{6.25}, H_2O_{24.32}).$$

The structural formula was calculated assuming that the unit cell contains 48 octahedral cations, 72 tetrahedral cation and 216 anions (EGGLETON, 1972).

According to the definition given by several writers (KATADA and SUMI, 1966; BROWN, 1967; HASCHIMOTO, 1969; EGGLETON, 1972), stilpnomelane from Mt. Contrario should be regarded as a ferristilpnomelane, that is, a ferric iron-rich term. In fact our mineral contains about 25 Fe^{+3} cations and about 29 R^{+3} as whole on the

TABLE 2
K-Ar age, $d_{[001]}$ spacing and Fe^{+2}/Fe^{+3} weight ratio of stilpnomelane from different occurrences

Sample	occurr.	K (wt.%)	$^{40}Ar_{rad.}$ (10^{-7}ml STPg^{-1})	($^{40}Ar_{rad.}$/$^{40}Ar_{tot.}$)	Age (m.y.)	d(001) (A)	FeO (wt.%)	Fe^{+2}/Fe^{+3}
Stilpn.I	matrix	1.37	2.17	0.30	4.1 ± 0.2	12.30	5.57	0.26
Stilpn.II	matrix	1.25	1.06	0.18	2.2 ± 0.3	12.27	6.51	0.30
Stilpn.III	veinl.	1.51	1.08	0.23	1.8 ± 0.2	12.22	7.84	0.41
Stilpn.IV	veinl.	1.33	3.50	0.33	6.8 ± 0.2	12.32	5.11	0.22
Stilpn.V	nodul.	1.24	1.97	0.11	4.1 ± 0.2	12.29	n.d	-

octahedral sheet. The hydroxyls [(OH) = $(48 - R^{+3})$] and the H_2O content (19.24 and 24.3 respectively) also seem roughly consistent with a ferric iron-rich term (EGGLETON, 1972).

Associated minerals

Microprobe analyses of about 30 calcite grains have shown small chemical variation; calcites have low MgO and FeO contents (< 0.5 and < 0.9 respectively). In the stilpnomelane veinlets no significant differences in composition were observed among calcites. In some cases the microcrystalline calcite associated to the stilpnomelane of veinlets has a relatively higher FeO content (up to 2 % by weight).

Microprobe analyses of five chlorite grains show the chemical composition of this mineral to be substantially constant; the FeO/MgO weight ratio calculated assuming all the iron in the ferrous state ranges from 0.18 to 0.20. Microprobe analyses of magnetite and sphene reveal these mineral to be substantially pure phases.

Conventional K/Ar age and Fe^{+2}/Fe^{+3} ratio of stilpnomelane

In order to determine the isotopic age of stilpnomelane, five samples from veinlets, nodules and matrix of the marbles were carefully separated to be analyzed by K/Ar method. The technique used for the argon extraction has already been described by DEL MORO et al. (1982); potassium contents were determined with 303 Mod. Perkin Elmer Absorption spectrophotometer. The results of these determinations are reported in table 2.

The isotopic age covers a range from 6.8 to 1.8 m.y. Some of the data were duplicated and the results also appear to be scattered among stilpnomelanes from a same occurrence, the variations covering, in this case, a range similar to that observed for stilpnomelanes from different occurrences.

With the aim of finding a possible explanation to the spread of stilpnomelane K/Ar apparent age table 2 reports, for each analyzed sample, the FeO content and the Fe^{+2}/Fe^{+3} weight ratio, obtained by combining the FeO contents, determined by titration method, and the total Fe contents (as Fe_2O_3) resulting from microprobe data. Table 2 also reports the d_{001} basal spacing which according to EGGLETON (1972) is sensitive to the Fe^{+2}/Fe^{+3} atomic ratio; the values of this parameter were determined from the average of $3d_{003}$ and $4d_{004}$ measured using $CuK_{\bar{\alpha}}$ radiation on a Philips PW1730 diffractometer.

From table 2 an inverse relationship between the Fe^{+2}/Fe^{+3} ratio and the radiometric K/Ar age of stilpnomelanes emerges; moreover, no systematic relationship between K/Ag age and mode of occurrence or host rock microstructure has been detected.

Summary and conclusions

Chemical data and d_{001} basal spacing reveal that stilpnomelane from the Mt. Contrario area can be considered a ferric iron-rich term. The composition of the mineral does not seem to show significant variation in relation to its mode of occurrences, small differences in FeO contents and Fe^{+2}/Fe^{+3} ratio proving to be independent of this petrographic characteristic.

In veinlets stilpnomelane appears to be folded by the later folding phase and cut across the S_1 schistosity, which according to CARMIGNANI et al. (1978) must be related to the earlier phase of deformation; furthermore stilpnomelane crystals dispersed in the matrix of the marbles seem to be reoriented as the S_2 schistosity, pointing out that they have undergone some influences of the later episode of deformation.

As regards the presence of the mineral in the « Calcari Selciferi ad Entrochi » Formation, mode of occurrence and textural characters suggest stilpnomelane to be growth after the earlier phase of deformation or early-syn the second one, probably as a consequence of hydrothermal circulation of fluids which seems to affect the Apuan Alps in this period (CARMIGNANI et al., 1976).

The radiometric K/Ar age of the mineral (ranging from 6.8 to 1.8 m.y.) does not seem to date the time of its genesis; in fact textural data and radiometric age determined on K-white mica oriented as S_2 schistosity (KEIGFIELD et al., 1980) indicate that stilpnomelane was originated before 10 m.y. age. Besides K/Ar radiometric age of the stilpnomelane does not seem to have any relevant significance since no regional geological events are known in the metamorphic sequence of the Apuan Alps between 6.8 and 1.8 m.y.

The spread of K/Ar age among adjacent samples in the same outcrop is puzzling. It is conceivable that, owing to its crystal structure (presence of large channels in the tetrahedral sheet where H_2O, K and other large cations are located in the same way as in zeolites (EGGLETON, 1972) stilpnomelane may easily exchange radiogenic argon as a result of small variations of the confining environmental conditions.

The inverse relationships observed between the K/Ar age and the FeO/Fe_2O_3 ratio seem to suggests that small variations in P_{O_2} may be one of the possible factors which control the exchange of radiogenic argon between stilpnomelane and the external environment.

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