

Sr-content and Sr-isotopic composition in contact-metamorphosed argillaceous sediments (Orciatice, Tuscany, Central Italy): relation to fluid circulation

GIORGIO FERRARA

Depart. of Earth Sciences, University of Pisa, via S. Maria 53, 56100 Pisa, Italy
Inst. of Geochronology and Isotopic Geochemistry, C.N.R., Via Maffei 36, 56100 Pisa, Italy

LEONARDO LEONI

Depart. of Earth Sciences, University of Pisa, via S. Maria 53, 56100 Pisa, Italy

FRANCO SARTORI

Depart. of Earth Sciences, University of Pisa, via S. Maria 53, 56100 Pisa, Italy

SONIA TONARINI

Inst. of Geochronology and Isotopic Geochemistry, C.N.R., via Maffei 36, 56100 Pisa, Italy

ABSTRACT. — Sr content and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio distribution along two sections of the Orciatice structure (Tuscany, Central Italy) have been investigated. The Orciatice structure consists of a small mafic alkali-trachyte laccolith, emplaced in marine Pliocene clays, and of a narrow metamorphic aureole all around. The physical, chemical and mineralogical transformations, which affected clays therein, appear to have been enhanced and spread out by an important hydrothermal circulation (LEONI et al., 1986). The present data show that such fluids were essentially connate fluids. For strontium no significant transfer from magma to the host rock occurred; its distribution merely reflects migration of connate fluids in equilibrium with marine carbonates. The Sr isotopic composition of the most intensely metamorphosed clays ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71088$) is in fact very close to the marine carbonate Sr composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70906$; HILDRETH and HENDERSON, 1971) and quite different from magmatic rock ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71586$) and unmetamorphosed «normal» clay ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71160$) values. Mineralogical data rule out the hypothesis that the present Sr isotopic distribution should be due to a mere re-distribution of carbonates following connate fluid circulation; they rather suggest a partial re-equilibration of neo-formed silicate phases with marine Sr. Such process would have been more advanced in the more intensely metamorphosed zones.

The results of the present study are consistent with a model requiring fluid movements along convective cells in an essentially closed system.

RIASSUNTO. — Sono state studiate la distribuzione e la composizione isotopica dello stronzio ($^{87}\text{Sr}/^{86}\text{Sr}$) lungo due sezioni della struttura geologica di Orciatice (Toscana, Italia Centrale). La struttura di Orciatice è costituita da un piccolo laccolite di «selagite» (trachite alcali-femica), intruso in condizioni subvulcaniche in argille marine plioceniche, e dalla sottile aureola metamorfica che lo circonda. Le trasformazioni fisiche, chimiche e mineralogiche subite dalle argille nella zona metamorfosata appaiono in parte conseguenti alla circolazione di fluidi idrotermali (LEONI et al., 1986). I dati raccolti in questo studio mostrano che tali fluidi erano essenzialmente fluidi connati del sedimento e che, almeno per quanto concerne lo stronzio, non vi è stato un significativo apporto dal magma ai sedimenti argillosi incassanti. La composizione isotopica dello stronzio delle argille più intensamente metamorfosate ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71088$) appare molto prossima a quella tipica dei carbonati marini ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70906$; HILDRETH and HENDERSON, 1971) e assai diversa da quella della roccia magmatica ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71586$) e delle argille non metamorfosate ($^{87}\text{Sr}/^{86}\text{Sr} = 0.71160$). I dati mineralogici escludono che l'andamento osservato sia semplicemente conseguente ad una ridistribuzione dei carbonati provocata dalla circolazione dei fluidi idrotermali, ma suggeriscono invece un parziale riequilibrio delle fasi silicatiche di neoformazione con lo stronzio marino. Questo processo appare più avanzato nelle zone più profondamente ricristallizzate, cioè le zone più intensamente metamorfosate prossime al contatto.

I risultati ottenuti nel presente studio implicano un modello di circolazione idrotermale secondo celle convettive in un sistema essenzialmente chiuso.

Key words: $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, contact metamorphic aureole, argillaceous sediments, fluid circulation, Orciatice, Tuscany, Italy.

Parole chiave: rapporto $^{87}\text{Sr}/^{86}\text{Sr}$, metamorfismo di contatto, sedimenti argillosi, circolazione di fluidi, Orciatice, Toscana, Italia.

Introduction

As a contribution to the characterization of clay formations as possible sites for nuclear-waste storage, the metamorphic effects induced on plastic argillaceous sediments by the small subvolcanic body of Orciatice (Tuscany, Central Italy) have recently been investigated (LEONI et al., 1984 and 1986).

The Orciatice structure consists in a small mafic alkali-trachyte laccolith, emplaced in Pliocene clays, and in a narrow metamorphic aureole all around; a detailed evaluation of physical, chemical and mineralogical transformations, which affected clays therein, was performed on samples collected both in boreholes and in outcrops (LEONI et al., 1986).

Physical transformations mainly consist of a sharp loss of plasticity and formation of extremely compact and hard rocks, with a typical hornfels texture, in a narrow zone, 0.5 to 1.5 m thick, closest to the contact, and of indurated, fissile shales farther away (up to a distance of 15 m). Mineralogical transformations are a K-feldspar + (Na-Ca)-plagioclase + fassaitic pyroxene + biotite assemblage crystallization in the hornfels zone and a smectite + feldspars assemblage crystallization farther out.

Chemical transformations are mainly represented by an important migration of highly mobile elements such as alkalis ($\text{Na} > \text{K} = \text{Rb}$) and alkaline earths ($\text{Ca} > \text{Ba} > \text{Sr}$), which produced distinct enrichments (commonly more conspicuous close to the contact) within the metamorphic aureole; average contents of «normal» clays appear to be gradually reached at distances varying according to the profile location. LEONI et al. (1986) pointed out that such chemical transfer was mainly linked to a hydrothermal fluid circulation; however available data did not allow to reach definite conclusions whether the elements were at least partly of magmatic origin or the observed enrichments merely reflect mobilization and local concentration of elements entirely coming from the original sediment.

The aim of the present paper is to obtain some informations about the origin of mobilized material; this subject is of great interest for a better understanding of contact

metamorphism processes.

Thus Orciatice metamorphic aureole rocks have been further investigated through the environmental isotope abundance analysis. Among the mobilized elements herein strontium has been considered the best suited for an isotopic composition study; then the $^{87}\text{Sr}/^{86}\text{Sr}$ distribution along two sections of the metamorphic aureole (sections A and S12; LEONI et al., 1986) has been determined.

Geological setting

Location of the studied profiles is reported in Fig. 1, showing a simplified geological sketch of Orciatice structure. Herein columns showing the metamorphic zonation suggested by LEONI et al. (1986) for the S12 and A sections are also reported.

S12 is a full profile from «normal» clays through metamorphosed material to the underlying magmatic rock; it has been located and sampled through a borehole. Within the metamorphic aureole, here relatively thick (7–8 m), the following zones can be distinguished: the first zone (0.5 m thick) is characterized by the mineral assemblage: K-feldspar + (Na-Ca) - plagioclase + pyroxene + biotite (scarce) + smectite (scarce); in the second zone (~ 2 m thick) upward the profile the mineral assemblage is: K-feldspar + smectite + pyroxene + mica (illite + detrital muscovite); calcite, restricted to secondary veins, may be locally very abundant. The third zone, about 4 m thick, is characterized by the presence of quartz, Na-plagioclase (albite), K-feldspar, calcite, illite and smectite. In the fourth zone (~ 2 m thick) the mineralogy is dominated by residual minerals from the original sediment; only smectite, in small amounts, represents a neo-formed phase. This is a transition zone to the overlying «normal» clays, about 7 m thick, which terminate the profile.

In the previous studies (LEONI et al., 1984 and 1986) it has been regarded as «normal», i.e. not metamorphic, all the sediments not affected by evident physical, chemical and mineralogical changes with respect to the average characteristics of Pliocene sediments. This definition has been here maintained,

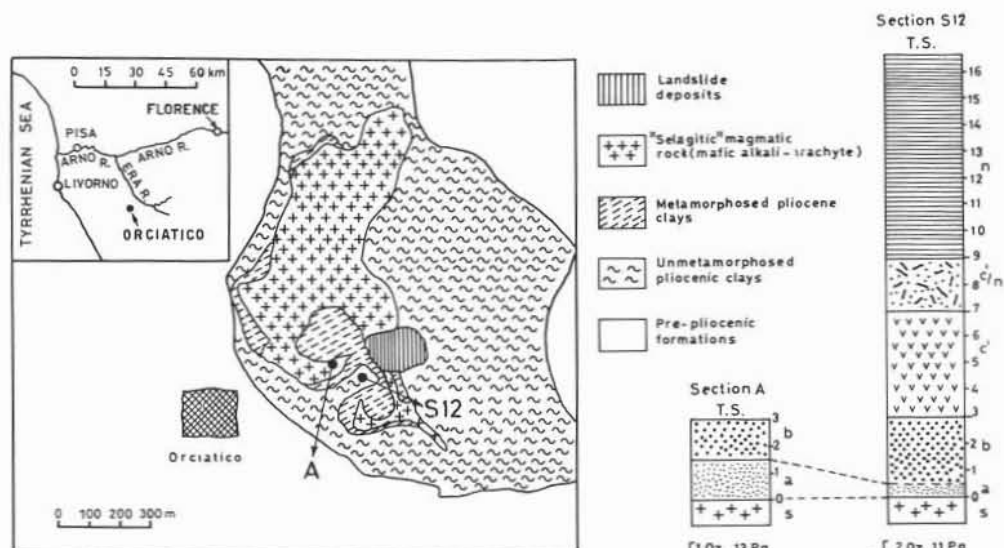


Fig. 1. — Geological sketch of Orciatico structure and metamorphic zonation (modified after LEONI et al., 1986) in S12 and A sections. Distances (in meters) from the contact «magmatic rock - sediments» are shown on the right side of the columns (Symbols: T.S. = topographic surface; S = «selagite» magmatic rock; Qz = quartz; Pg = plagioclase; K-f = K-feldspar (orthoclase or microcline); Cc = calcite; Mi = mica-like minerals (illite, detrital muscovite or neo-formed biotite); Ch = chlorite; I/Sm = illite-smectite mixed-layer minerals; Vm = vermiculite; In = chloritic intergrades; Sm = smectite; Analc. = analcime; Py = pyroxene).

notwithstanding isotopic data show that at least the lower zone of «normal» clay covering (S12 profile) has been affected by some fluid migration too.

Section A represents an outcropping profile, 3 m thick, where metamorphosed clays are in contact with the main magmatic body. Due to erosion it lacks upper zones showing lower metamorphic overprint and «normal» clays covering; samples from A section then represent the materials most intensely affected by metamorphism. Herein two main zones may be distinguished. The first zone, 1.5 m thick, exhibits a typical hornfels texture and is characterized by the following mineral assemblage: K - feldspar + (Na - Ca) - plagioclase + pyroxene + smectite (scarce) + biotite (scarce) + analcime. Petrographic data show that in this zone smectite and analcime represent secondary minerals from a late stage hydrothermal circulation following

thermal metamorphism s.s. The second zone (~ 1.5 m thick) farther from the contact has a mineralogy dominated by K-feldspar and smectite (together the two phases make up more than 90% of the whole rock), associated with minor amounts of quartz and analcime.

«Normal» clays are plastic marly silty clays of pliocene age, sedimented in a prevalently marine environment. Their average grain size is: sand 5%, silt 41%, clay 54%; their average mineralogical composition is: quartz 25%, plagioclase 6%, K-feldspar 2%, calcite 14%; illite and detrital micas 37%, illite/smectite interstratified 5%, vermiculite 5%, chloritic intergrades 6% (LEONI et al., 1984). The samples assumed as representing «normal» clays in the present study were selected from S3 and S4 profiles studied by LEONI et al. (1984); such profiles were sampled through wells drilled down to 13 m and 17 m depths, respectively, through sequences absolutely not

TABLE 1
 $^{87}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Rb}/^{86}\text{Sr}$, Rb and Sr contents within Orciatice metamorphic aureole

Sample	Distance from the contact (meters)	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma$	Rb (ppm)	Sr (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$
S12 Section					
S12/4.90	11.8	0.71378 ± 6	178	165	3.12
S12/7.00	9.7	0.71360 ± 9	162	161	2.92
S12/9.50	7.1	0.71250 ± 12	163	238	1.98
S12/12.10	4.6	0.71182 ± 6	211	287	2.13
S12/14.60	2.1	0.71152 ± 6	932	368	7.53
S12/15.70	1.0	0.71101 ± 6	464	464	0.39
S12/16.70a	0	0.71087 ± 6	546	338	4.67
A Section					
1	0	0.71066 ± 6	387	607	1.84
2	0.5	0.71077 ± 16	466	536	2.15
3	1.0	0.71060 ± 6	407	605	1.95
4	1.5	0.71116 ± 6	844	623	3.92
5	2.0	0.71082 ± 4	674	536	3.64
6	2.5	0.71109 ± 4	765	838	2.64
7	3.0	0.71104 ± 5	823	1724	1.38
Unmetamorphosed clays					
S3/1.60	-	0.71185 ± 7	150	240	1.81
S3/6.30	-	0.71144 ± 21	122	260	1.36
S4/17.00	-	0.71152 ± 21	165	313	1.53
S4/17.00 (carbonate fraction)	-	0.70900 ± 5	5	1775	0.008
S4/17.00 (silicate fraction)	-	0.71932 ± 6	190	91	6.04
"Selagite" magmatic rock					
S2/15.90	1.2	0.71600 ± 6	621	645	2.79
S12/20.30	3.6	0.71572 ± 6	582	562	3.00

affected by metamorphism.

The Orciatice magmatic rock is a mafic alkali-trachyte called «selagite» by the first petrographers (WASHINGTON, 1900); its features are fully described by BARBERI and INNOCENTI (1967). Two samples were selected from S2 and S12 profiles to represent the magmatic rock. Such samples, as well as the others from S12, S3 and S4 profiles, are labelled with the number of the boring well followed by figures showing the depth (in m) below ground surface (e.g. S4/17.00).

Analytical methods

Sr and Rb concentrations have been determined by the isotope dilution method. Analytical error for the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio is

estimated to be $\pm 1.5\%$. Sr isotopic compositions were determined using a Varian® MAT TH5 mass-spectrometer, on line with a computer for data collecting and processing.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Determinations of «Strontium carbonate SRM 987» standard sample gave $^{87}\text{Sr}/^{86}\text{Sr} = 0.71031 \pm 0.00003$. For the Orciatice samples the errors of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are reported at 2σ level in Table 1. In most cases only whole rock samples were analyzed. For S4/17.00 sample analytical determinations on separated carbonate and silicate fractions have also been performed; the carbonate fraction was dissolved by 2.5 N acetic acid and the solution separated by filtering.

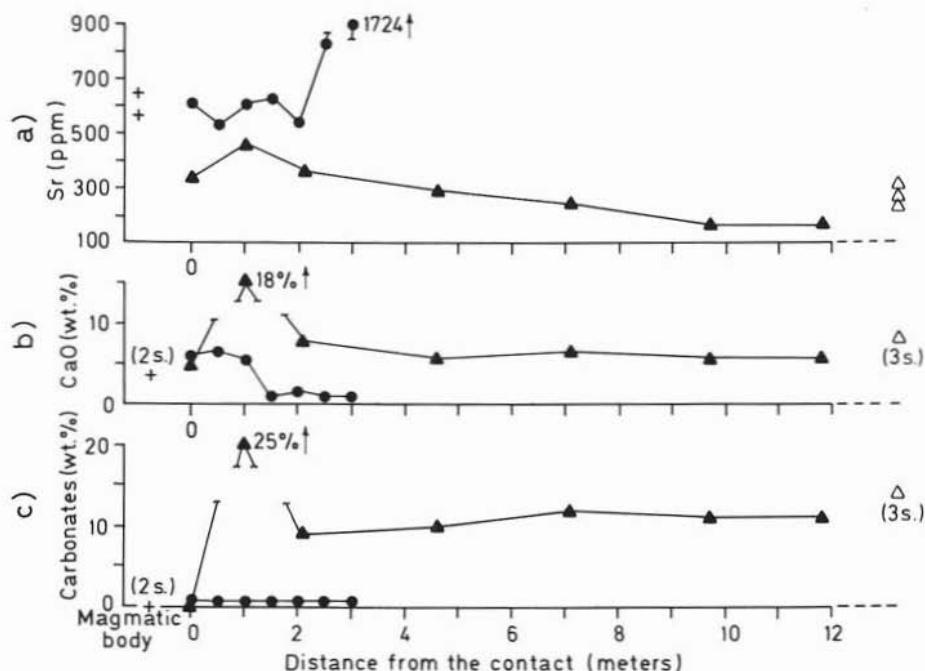


Fig. 2. — Sr, CaO¹ and carbonate^{1,2} distributions within Orciatice metamorphic aureole (+ «selagite» magmatic rock samples; ● A section samples; ▲ S12 section samples; △ unmetamorphosed «normal» clay samples; s. = samples; (1) data from LEONI et al., 1984 & LEONI et al., 1986; (2) carbonates in A section samples are below detection limits (2‰)).

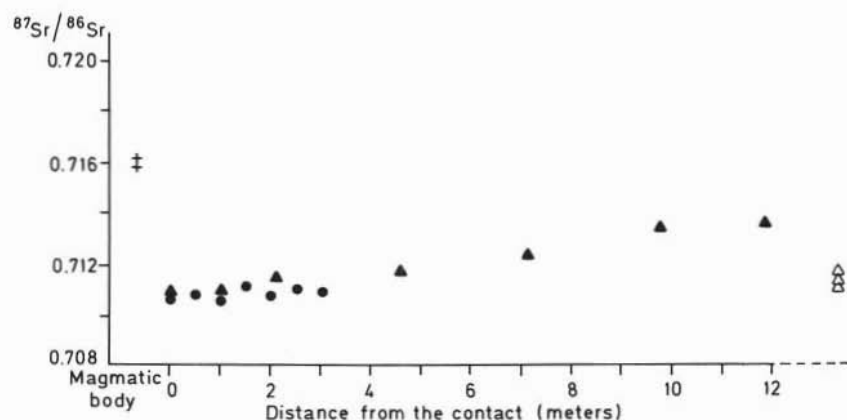


Fig. 3. — $^{87}\text{Sr}/^{86}\text{Sr}$ vs. distance from the contact «magmatic rock-sediments» within Orciatice metamorphic aureole (symbols as in Fig. 2).

Discussion

The analytical data are presented in Table 1. The Orciatice magmatic rock shows a Sr isotopic composition quite different from clays both «normal» and metamorphic; its $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.71600 - 0.71572) appear

significantly higher than the values for unmetamorphosed (0.71144 - 0.71185) and metamorphosed (0.71060 - 0.71380) sediments.

In Fig. 2a Sr contents along S12 and A profiles are plotted against distance from the

contact «selagite» - sediments; «selagite» and «normal» clay samples are also reported. Compared with «normal» clays the zone next to the laccolith is Sr-enriched in both profiles (LEONI et al., 1986). The enrichment is more marked in A section; here the highest Sr contents are observed in a zone about 3 m off set from the contact, where maximum recrystallization of K-feldspar occurred. In S12 profile first zone, up to 2 m from the contact, Sr is only slightly enriched; then its contents gradually decrease until the upper zone becomes slightly Sr-depleted.

Sr isotopic composition vs. distance from the contact is plotted in Fig. 3. This diagram clearly shows that A section samples have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios significantly lower than

respectively) the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are distinctly higher than «normal» clays values.

In Fig. 4 the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is plotted against $1/\text{Sr}$; in this diagram the data relative to «selagite», «normal» clays and carbonate and silicate fractions from one «normal» clay sample (S4/17.00) are also presented. From Fig. 4 it is evident that the two parameters are strictly correlated. Only samples 4, 6 and 7 show significant displacements from the regression line; these are caused by their unusually high Sr contents (which obviously affect $1/\text{Sr}$ values), presumably related to a very important K-feldspar neo-crystallization (amounts of K-feldspar up to 65% of the whole rock samples).

It is evident from the comparison of the

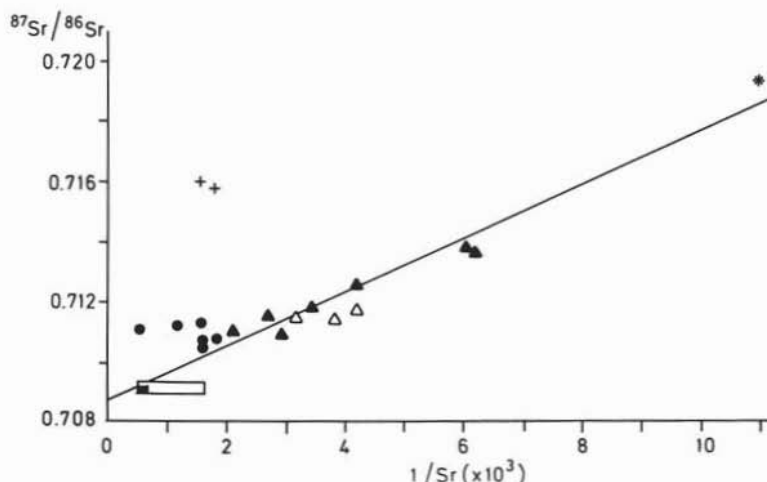


Fig. 4. — $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ within Orciatico metamorphic aureole (+ «selagite» magmatic rock samples; • A section samples; ▲ S12 section samples; △ unmetamorphosed «normal» clay samples; ■ «normal» clay carbonate fraction; * «normal» clay silicate fraction; □ marine carbonates (after VEIZER, 1983)).

«normal» clay values; such ratios appear practically constant all along the profile. In S12 section a linear correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with distance from the contact is apparent; the first two samples (belonging to the hornfels zone) have a Sr isotopic composition close to that of A section rocks; for the next two samples, collected at ~ 2 m and ~ 4.5 m from the contact, respectively, a Sr isotopic composition within the «normal» clays range is observed; in the following three samples farther from the contact (collected at ~ 7, ~ 10 and ~ 12 m from the latter,

selagite $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with the corresponding values of metamorphosed and «normal» clays that the strong trends exhibited by the Sr content and Sr isotopic composition distributions (Figs. 2, 3 and 4) cannot be interpreted as the result of significant Sr-transfer from magma to the metamorphosed sediments.

On the contrary there are strong evidences suggesting that such trends result from circulation of connate fluids having the marine carbonate Sr isotopic composition. In fact the diagram of Fig. 4 shows that the linear plot

of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $1/\text{Sr}$ intercepts the ordinate axis just close to the marine carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ value. Since in S12 profile the carbonate contents are, on the whole, close to «normal» clay values (S12/15.70 sample excepted) (Fig. 2c) and A profile samples are carbonate-free, a mere re-distribution of carbonates following connate fluid circulation cannot be proposed. It is then necessary to assume that silicate phases neo-formed during contact metamorphism processes achieved at least partial equilibration with marine Sr. In the more intensely metamorphosed zone, where re-crystallization has been more advanced, a more close approach to such equilibration was achieved; the process would have been supported by a continuous inward flow of connate water (and dissolved carbonates) from the cooler, outer zones to the hot front.

In the metamorphic aureole middle zone the milder metamorphic reactions, involving only fine-sized mineral grains (LEONI et al., 1986), would have produced only minor effects on the isotopic composition of the whole rock samples, which consequently don't appear to differ significantly from «normal» clays.

Farther out from the intrusion the cooler metamorphic zones have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than «normal» clays; this feature is interpreted as a consequence of the drainage from these zones of the original marine connate water (with dissolved carbonates) toward the intrusion front and return therefrom of waters slightly depleted in Sr. This is well illustrated by the samples S12/4.90, S12/7.00 and, subordinately, S12/9.50, which appear slightly depleted in Sr (Table 1 and Fig. 2a) compared with «normal» clays. The low whole-rock Sr content can be partially ascribed to a slightly lower carbonate content (11-12%) in comparison with «normal» clays (14%) (Fig. 2c; LEONI et al., 1986), but most of the Sr depletion in the outer zones of the metamorphic aureole can be only explained by inferring a significantly lower Sr content in their carbonate fraction.

The model suggested requires fluid movements along convective cells, which are

in full agreement with the cooling mechanism proposed by LEONI et al. (1986) for the Orciatice subvolcanic body. According to these authors an important convective circulation of hydrothermal fluids in the argillaceous host rock around the laccolith would have been induced by the high thermal gradient and mostly enhanced by the growing of a diffuse micro-cracking as a consequence of clay plasticity loss.

Conclusions

The data presented here suggest that in Orciatice metamorphic aureole no significant transfer of strontium from the magma to the host formation occurred; the present Sr distribution is only resulting from circulation of connate fluids within the metamorphic aureole. Sr isotopic composition indicates that advanced equilibration of neo-formed silicate phases with such fluids occurred in the hottest metamorphic zone next to the laccolith; only Sr contents of carbonate and interstitial water would have been affected in the outer zones of the aureole. Moreover isotope analysis shows that hydrothermal circulation extended farther out from the contact than the distance previously inferred from mineralogical and whole-chemistry changes. Thus our data prove that isotopic composition analysis may be a well suited tool to track mobilization phenomena within metamorphic aureoles, a tool more sensitive than classical mineralogical and geochemical studies.

As for the applied consequences dealing with the development of waste repositories the present study shows that mobilization of elements may be induced even in argillaceous formations by a connate fluids circulation started by a high thermal gradient. However the data would suggest a water circulation in an essentially closed system along convective cells: in the present case these are traced by the flow of connate marine water from the outer zones of the aureole to the heat source and the return therefrom to the same zones of fluids characterized by a lower Sr content.

REFERENCES

- BARBERI F., INNOCENTI F. (1967) - *Le rocce selagitiche di Orciatice e di Montecatini in Val di Cecina*. Atti Soc. Tosc. Sc. Nat., Mem., Ser. A, 74: 139-180.
- HILDRETH R.A., HENDERSON W.T. (1971) - *Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ for sea-water strontium and the Eimer and Amend SrCO_3* . Geochim. Cosmochim. Acta, 35: 235-238.
- LEONI L., POLIZZANO C., SARTORI F., SENSI L. (1984) - *Chemical and mineralogical transformations induced in Pliocene clays by a small subvolcanic body and consequences for the storage of radioactive wastes*. N. Jb. Miner. Mh., Jg. 1984, H.4: 155-168.
- LEONI L., POLIZZANO C., SARTORI F. (1986) - *Nuclear waste repositories in clays: the Orciatice metamorphic aureole analogy*. Appl. Clay Sci., 1: 385-408.
- VEIZER J. (1983) - *Trace elements and isotopes in sedimentary carbonates*. In: Reeder R.J. (Ed). Carbonates: mineralogy and chemistry. M.S.A. Review in Mineralogy. Vol. 11.
- WASHINGTON H.S. (1900) - *Some analyses of Italian volcanic rocks*. Amer. Journ. Sci., 9: 46-48.