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Fluid advection in shear zones: evidence from geological and geochemical relationships in the Aiguilles Rouges Massif (Western Alps, Switzerland)

by *Didier Marquer*[1], *Eleonora Petrucci*[2] and *Paola Iacumin*[3]

Abstract

At the Southeastern margin of the Aiguilles Rouges Massif, Western Alps, the development of a ductile shear zone has occurred during the Alpine Tertiary events. The feldspathic gneisses of the crystalline basement are transformed into highly-deformed dark mylonites.

This study describes mass-transfer and stable isotope behaviour related to the transformation of gneiss to mylonite. Mass balance calculations using major element data show that the deformation of the gneiss occurred without significant changes in volume and under essentially isochemical conditions, except for calcium. The calcium mobility is probably associated to the shift from a ductile towards a more brittle behaviour of the shear zone in the latest stage of the deformative process. This resulted from opening of the system to fluids of an external origin.

$\delta^{18}O$ quartz values measured in mylonites and gneisses range from +10.2 to +12.6‰ and from +10.9 to 12.4‰ respectively, while whole rock samples have $\delta^{18}O$ values ranging from +8.2 to +9.9‰ from least to most deformed mylonites and from +9.8 to +11‰ for the gneisses, which were only weakly deformed, with the exception of two samples showing peculiar conditions. In agreement with the chemical data, the measured $^{18}O/^{16}O$ ratios suggest a limited participation of external fluids during the mylonitic deformation, while the calcium mobility may be explained in terms of a contamination of a localized Ca-bearing fluid which moved through the system during a later stage of deformation.

Keywords: shear zones, chemical mass-balance, stable isotopes, fluid-rock interaction, mylonite, Aiguilles Rouges Massif, Western Alps.

Introduction

In large scale shear zones it has been observed (Beach, 1976; Mitra, 1978) that changes in both bulk rock chemistry and mineralogical composition of the deformed rocks can occur with respect to the undeformed wall rocks. The widest variations are expected where an aqueous fluid is available: besides mineralogical changes, the presence of such a fluid phase may have an influence on the deformation processes. The modification of the original rock composition in a shear zone, therefore, is essentially the result of chemical exchange processes between the deformed rocks and the fluids (Beach, 1976; Kerrich et al., 1980; see for review Marquer, 1989). Conversely, when the amount of fluid interacting with the system is not significant, the deformation might take place under isochemical conditions (Kerrich et al., 1980).

The mineralogical and chemical changes accompanying deformation in shear zones have already been investigated by several authors (for a review see Marquer, 1989): in most of these studies the transformations observed are the results of hydrothermal fluid solute transport of

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chemical components. However, on the basis of previous studies carried out on the crystalline massifs of the Alps (Hoernes and Friedrichsen, 1978; Fourcade et al., 1989 and references therein) no large amounts of fluids migrated pervasively through the rocks of the crystalline basement during the Alpine deformation, but a channelized flow, which favours chemical heterogeneity in major shear zones is rather advocated by Fourcade et al. (1989).

The Aiguilles Rouges Massif is a pre-Alpine crystalline basement made up mainly of massive quartzo-feldspatic rocks that have undergone deformation with metamorphic conditions of low to medium greenschist facies during the Alpine Tertiary events (Bellière, 1958; von Raumer, 1974, 1984, 1987). A thin cover of autochthonous Mesozoic sediments on the crystalline massif is overlain by the inverted limb of the large recumbent fold of the Morcles nappe, which is rooted in the Chamonix Syncline and on the external part of the Mont Blanc Massif (Trümpy, 1963; Masson et al., 1980; Ayrton, 1980; Dietrich et al., 1989; Ramsay, 1981, 1989; Epard, 1990).

The aim of the present study is to describe the relationships between deformation and whole-rock composition in a well exposed Alpine shear zone at the contact between basement and cover in the southern part of the Aiguilles Rouges Massif (Valais, Switzerland). The approach we have adopted is to perform stable isotope ($\delta^{18}O$) and major element analyses on samples of both deformed and undeformed rocks trying to evaluate: (i) their behaviour throughout the system and (ii) the nature and amount of fluid that may have interacted with the rock during the deformation.

Microstructural and mineralogical modifications

Towards its southeastern margin, at the contact with the cover sediments, the crystalline rocks of the Aiguilles Rouges Massif are constituted mainly of feldspathic gneisses. These become highly deformed into dark mylonites formed in a large shear zone, under condition of greenschist facies metamorphism. This mylonitization is thought to be of Alpine age because of its parallelism with the cleavage of the overlying sediments. Ductile heterogeneous deformation is very strong at the contact between the Aiguilles Rouges Massif and the cover, but finite deformation progressively decreases towards the North. The shear zone is well exposed for more than 300 m along road no. 9 from Vernayaz to Martigny, immediately before Martigny (Fig. 1).

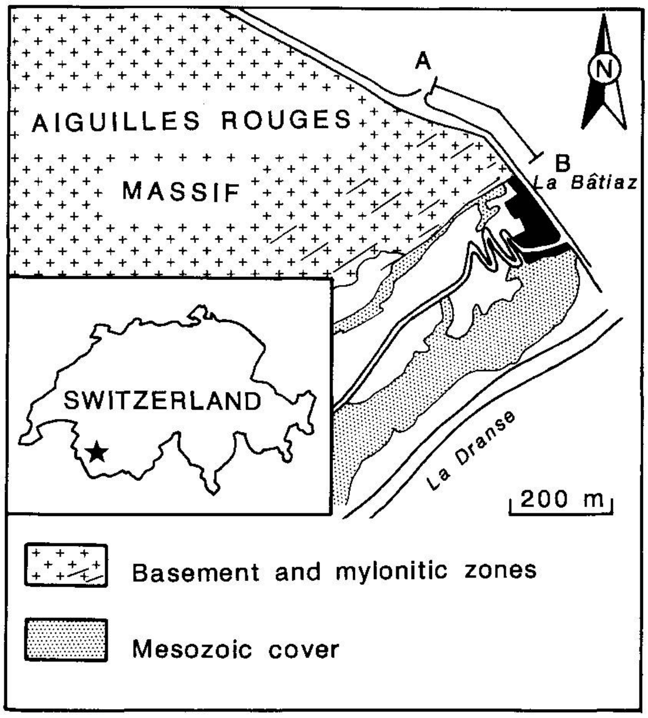

Fig. 1 Schematic geological map showing the location of the studied mylonites in the southeastern part of the Aiguilles Rouges Massif (La Bâtiaz, Martigny, Western Switzerland). Modified from Ayrton (1980). A–B: location of the sampled cross-section.

The weakly deformed gneisses consist of approximately equal amounts of orthoclase and oligoclase, quartz, biotite and muscovite as essential minerals. Chlorite, epidote and amphibole are accessory minerals. In response to deformation, the feldspars are deformed to small grains of the parent composition or are recrystallized to small albite and white micas. Biotite reacts to secondary biotite and locally to chlorite. Locally, some rare calcite fibres are found in pressure shadows around feldspar porphyroclasts. Calcite fibres occur preferentially in the late tectonic veins which cross-cut the Alpine schistosity. These latter veins are present only in a narrow decimetric zone localized at the basement-cover contact. The mylonite-ultramylonite sequence is therefore composed of ultrafine-grained feldspar, biotite, quartz, chlorite and white micas, with calcite as a minor and local phase.

The structural and grain-size changes that accompany the increasing intensity of deformation through the studied area are shown in figure 2: the most undeformed sample is a gneiss collected at 160 m from the contact with the sedimentary cover, whose grain-size (Fig. 2A) becomes gradually smaller passing to a mylonite (Fig. 2 B–C) and fine-grained ultramylonite at the basement-cover contact (Fig. 2 D). The general direction of the

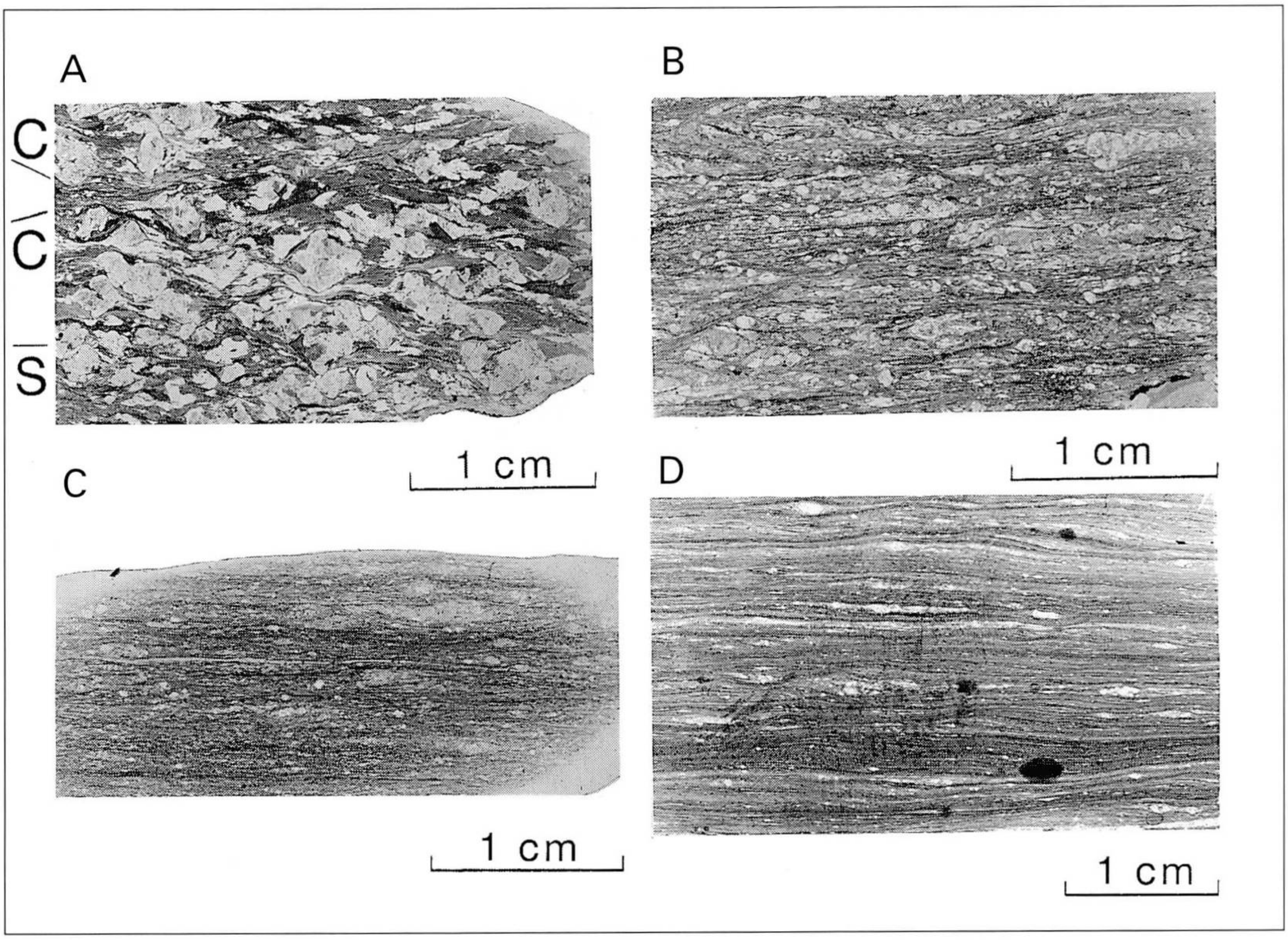

Fig. 2 Photomicrographs illustrating the progressive deformation of crystalline rocks of the Aiguilles Rouges Massif. A) sample E11 gneiss at low stage of deformation; B) sample E5, mylonite. Notice the shear band system cross-cutting the mylonitic foliation. C) sample E0, mylonite. The shear bands are gradually curved into foliation. D) sample E16, ultramylonite, very fine-grained, representing the highest degree of deformation in the studied section.

mylonitic foliation (S), defined by compositional banding of quartz and asymmetric feldspar porphyroclast tails is also shown.

A system of conjugate shear bands (C) is present in the most deformed part of the area studied. As the intensity of deformation increases, the angle between foliation and conjugate shear bands system diminishes progressively and the C and S surfaces become subparallel at the higher deformation stage (Fig. 2 D).

Analytical methods

In order to investigate chemical and isotopic variations accompanying the transition from gneiss to mylonite, samples were collected along the outcrop from the contact with the sedimentary cover in the SE to the NW over a distance of 350 m (Fig. 1). Major elements were determined by X-ray fluorescence spectrometry. Stable isotope analyses have been carried out on whole rock and mineral phases such as quartz and calcite: oxygen was extracted from quartz and whole rock samples by reaction with BrF_5 (CLAYTON and MAYEDA, 1963) and converted to CO_2 by cycling over hot graphite heated inductively and by using platinum as catalyst. Carbonates were reacted with 100% H_3PO_4. The isotopic measurements were carried out on a Finnigan Delta E mass spectrometer and the results are reported as $\delta^{18}O$ values in per mil relative to V-SMOW for silicates and carbonates and as $\delta^{13}C$ values relative to PDB-1 for carbon. Repeated measurements of the $\delta^{18}O$ value of NBS-28 quartz standard yielded a mean of +9.60‰ ± 0.1‰. The standard deviation of our oxygen and carbon isotope measurements on carbonates is, on average, ± 0.05 to ± 0.1‰ (1σ). A standard deviation of ± 0.1 to 0.2‰ (1σ) affects our whole-rock sample measurements.

Tab. 1 Chemical analyses of ultramylonitic-mylonitic rocks and gneisses from the Southeastern margin of the Aiguilles Rouges Massif. Distance is expressed in m from ultramylonites (E0) at the contact with Mesozoic limestones.

	Ultramylonites			Mylonites					Gneiss			
	E16	E0	E1	E4	E5	E6	E7	E9	T9	E11	E12	E13
Distance	0 m	12 m	17 m	28 m	35 m	52 m	63 m	84 m	150 m	165 m	350 m	550 m
SiO_2	67.79	58.97	62.73	66.26	67.63	70.26	73.49	73.54	71.10	66.57	63.80	67.38
TiO_2	0.41	0.87	0.75	0.62	0.45	0.16	0.14	0.16	0.21	0.52	0.69	0.48
Al_2O_3	14.92	15.08	15.72	14.13	14.25	13.79	13.45	14.11	14.39	15.07	15.85	15.41
Fe_2O_3	3.23	5.82	4.75	5.33	3.30	1.02	1.32	1.22	1.58	3.61	4.87	4.20
MnO	0.04	0.09	0.08	0.06	0.04	0.05	0.02	0.02	0.00	0.04	0.05	0.06
MgO	1.18	2.67	2.00	2.33	1.24	0.63	0.37	0.41	0.49	1.54	2.78	1.61
CaO	1.31	3.52	1.72	0.75	1.36	2.44	0.90	0.64	0.77	1.16	2.11	1.19
Na_2O	2.56	4.03	4.63	2.22	2.89	2.83	3.15	2.99	3.17	2.63	3.21	2.83
K_2O	5.41	1.95	2.04	3.32	4.08	4.22	4.57	5.09	4.91	4.57	2.26	3.21
P_2O_5	0.20	0.32	0.32	0.26	0.22	0.27	0.28	0.30	0.31	0.26	0.20	0.21
L.O.I.	1.40	4.51	2.98	2.74	2.68	2.64	0.86	0.87	1.24	1.64	2.15	1.17
Total	98.45	97.83	97.72	98.03	98.14	98.31	98.55	99.35	98.17	97.81	97.98	97.76

Experimental results

CHEMICAL VARIATIONS

Chemical variations due to deformation processes occurring throughout the transition basement-cover can be studied by means of chemical variation profiles when the following conditions are accomplished: (i) the absolute gains and losses of different oxides are estimated by comparison of chemical compositions of each mylonite with the weakly deformed rocks, and if (ii) the ranges of initial compositional variations were below those associated with deformation.

Mass balance calculations cannot be expressed directly by comparing whole-rock chemical composition of the initial non-modified rock, expressed in weight percent and chosen as the chemical reference frame, with that of the deformed rock (FONTEILLES, 1978; MARQUER, 1987). Estimates of absolute chemical variations require the knowledge of volume changes, density changes or identification of non-mobile elements. To compare the chemical composition of two different rocks, the method developed by GRESENS (1967) and modified by POTDEVIN et al. (1987) has been applied to the studied samples, whose abundances of major elements are given in table 1 and 2. The resulting diagrams are reported in figure 3. GRESENS (1967) gave a general linear equation to calculate the variation of a given oxide mass content in the modified rock with respect to its initial mass content in the initial rock:

$$Xn = fv \cdot (d_{II}/d_I) \cdot Cn_{II} - Cn_I$$

where Cn_I and Cn_{II} are the weight percent of the oxide in the initial and the modified rocks respectively, d_{II} and d_I are densities of these rocks, and fv the volume factor given by the volume ratio between the transformed and the initial rocks. In granitic and gneissic rocks, the d_{II}/d_I ratios remains usually uniform when the mylonites are compared to the weakly deformed rocks (MARQUER, 1987). In the studied rocks, the d_{II}/d_I ratio is assumed to be close to 1, permitting calculation of absolute chemical mass changes versus possible volume changes for each oxide. The graphical resolution of GRESEN'S equation allows estimation of the absolute mass-transfer between two rocks.

The identification of mobile and non-mobile oxides is facilitated by the use of relative mobility diagrams (POTDEVIN et al., 1987). Where the mass variation of each oxide is normalized with respect to the content of the same oxide in the initial rocks:

$$\Delta Xn = fv \cdot (d_{II}/d_I) \cdot (Cn_{II} / Cn_I) - 1$$

These diagrams are particularly useful for comparing the behaviour of major and trace elements between two chemical analysis of rocks (MARQUER, 1989). Comparisons of oxides with pronounced differences of absolute abundance in the whole-rock analysis (e.g. SiO_2 and TiO_2) are easier: elements with the same behaviour have the same slope in the graphical solution of this equation. With these mass-balance calculations, two ways can be used to deduce oxide behaviour (mobile or non-mobile) and to calculate absolute mass transfers: (i) fixed volume factor, or (ii) fixed immobile element.

Tab. 2 Average and standard deviation of chemical compositions of four weakly deformed rocks (gneiss) during Alpine deformation.

	E13	E11	E12	T9	Average	Std dev.
SiO_2	67.38	66.57	63.80	71.10	67.21	3.01
TiO_2	0.48	0.52	0.69	0.21	0.48	0.20
Al_2O_3	15.41	15.07	15.85	14.39	15.18	0.62
Fe_2O_3	4.20	3.61	4.87	1.58	3.57	1.42
MnO	0.06	0.04	0.05	0.00	0.04	0.03
MgO	1.61	1.54	2.78	0.49	1.61	0.94
CaO	1.19	1.16	2.11	0.77	1.31	0.57
Na_2O	2.83	2.83	3.21	3.17	3.01	0.21
K_2O	3.21	4.57	2.26	4.91	3.74	1.23
P_2O_5	0.21	0.26	0.20	0.31	0.25	0.05
L.O.I.	1.17	1.64	2.15	1.24	1.55	0.45
Total	97.75	97.81	97.97	98.17	97.93	0.19

In some studies, a very low mobility of Al_2O_3 in rocks deformed in greenschist facies conditions is suspected (Carmichael, 1969; Ferry, 1979, 1982; Kerrich et al., 1977, 1980; Marquer, 1989). This low mobility of Al_2O_3 is consistent with the metamorphic reactions observed in metagranites deformed in the conditions of the greenschist facies (Marquer, 1987). In this study, if the assumption of constant aluminium content is taken, the comparisons between weakly deformed rocks or between mylonites and weakly deformed rocks reveal volume changes less than ± 10% of the initial volume (Fig. 3). On this basis, the relative mass variation of each constituent (ΔX) is calculated assuming a constant volume factor (fv) for each comparison among the deformed rocks. This assumption, that deformation took place under isovolumetric conditions, does not introduce large errors in further calculations.

Samples E11 and E12 (gneiss collected at a distance of 165 and 350 m respectively from the contact) represent the pre-Alpine gneisses which have not experienced a strong Alpine deformation and have been chosen as the chemical reference. Their chemical compositions give evidence

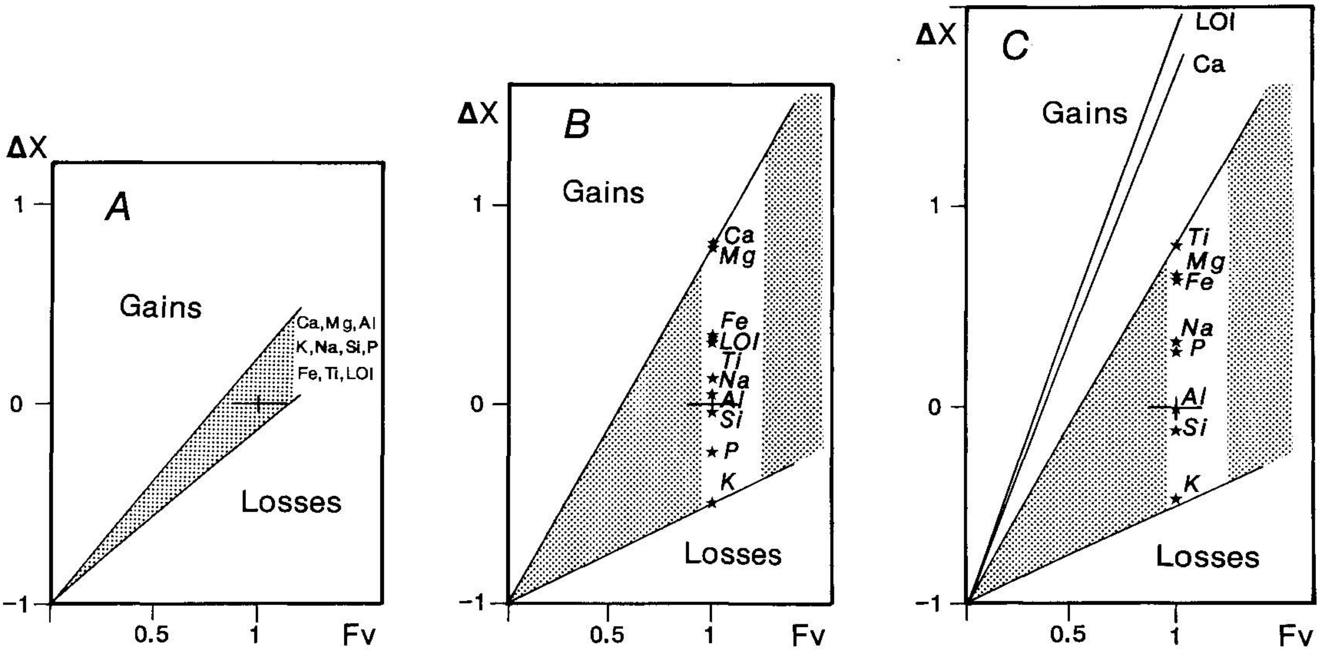

Fig. 3 Composition-volume relationships (see text for explanation). A: comparison between chemical analysis of sample E11 and average of chemical analysis from four weakly deformed rocks during Alpine deformation (see Tab. 2); B: comparison between the weakly deformed samples E11 and E12; C: comparison of ultramylonite E0 and the average chemical analysis of weakly deformed samples (close to the reference sample E11, see Tab. II). Dashed area: domain of non-mobile elements (initial chemical heterogeneities).

for the presence of initial large chemical heterogeneities (Fig. 3 B). In this case, the gains and losses of oxides (ΔXn) for a volume factor equal to 1 is up to 80% for Ca and Mg and to –50% for K. On the other hand, the average of chemical compositions of weakly deformed rocks is close to the chemical composition of sample E11 (Tab. 1, Fig. 3 A). This E11 sample is taken as a reference composition for the chemical variation profile (Fig. 4). These two facts underline the locally great initial whole-rock chemical heterogeneities but nevertheless, show the representativity of sample E11 in terms of average analysis of the analyzed initial rocks.

With respect to the large chemical variability of the weakly deformed rocks, comparisons of deformed rocks with the E11 reference sample permit the definition of which oxides could be considered as mobile or immobile during Alpine deformation processes. The great initial chemical heterogeneities of the gneisses infers that the chemical differences could be pre-deformational or/and that the mobility of the elements during Alpine deformation could stay in the range of the initial heterogeneities. Nevertheless, CaO and L.O.I. seem to behave as mobile oxides and increase in the deformed rocks by 160% ($\Delta Xn = 1.6$) and 190% ($\Delta Xn = 1.9$) respectively (Fig. 3 C). The other oxides show no chemical variations greater than present in the range of initial chemical compositions (compare Figs 3 B and C). In other words, their possible mobility does not exceed the amplitude of the initial variations. During Alpine deformation, these oxides could be considered as immobile or weakly mobile, staying in the range of the pre-Alpine chemical heterogeneities. A chemical variation profile for CaO, established with respect to initial rock E11 and to initial chemical fluctuations (dashed zone: Fig. 4) show an increase of the calcium mobility towards the contact with the Mesozoic sedimentary cover.

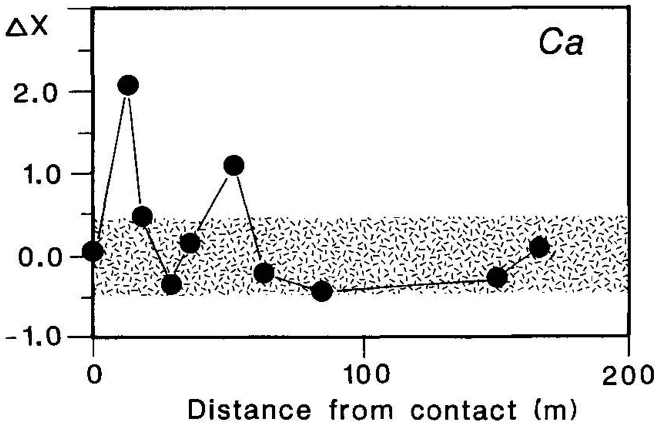

Fig. 4 Calcium concentration variation (ΔX Ca) versus distance from the contact (m). The dashed area represents an estimate of the initial chemical variations (cf. values taken from Tab. 2: Δ Ca = ± std dev./average = ± 0.43).

STABLE ISOTOPE DATA

The oxygen isotopic composition of a rock may be a sensitive indicator of fluid-rock interactions in the sense that it provides useful information concerning the source and the amount of the fluids with which it interacted (Dipple and Ferry, 1992).

Oxygen isotope exchange between a rock and an aqueous reservoir is generally the cause of a shift in the rock $\delta^{18}O$ from its initial value by an amount which depends on the temperature, water-rock ratios and the $\delta^{18}O$ of the external fluid (Taylor, 1974). Conversely, the oxygen isotopic composition of rocks and minerals may be used in estimating fluid temperatures and/or fluid $\delta^{18}O$ values when equilibrium conditions are reached and maintained (Urey, 1947).

In order to discuss (i) the variation of the oxygen isotope composition as a function of the intensity of deformation across the shear zone, and (ii) to define the boundary conditions of the system, whole rock and mineral samples from the gneiss-mylonite transition and limestone samples from the autochthonous cover have been analyzed. All the data obtained are reported in table 3. The $\delta^{18}O$ of quartz in the weakly deformed gneisses and in the mylonites is relatively uniform (from +10.9 to +12.4‰ and +10.2 to +12.6‰ respectively), as well as the $\delta^{18}O$ values obtained from whole rock analyses (from +8.2 to + 9.9‰ for the ultramylonites-mylonites and from +9.8 to +11‰ for the gneisses). No discernable shifts in isotopic composition accompanying deformation are evident for the transformation gneiss-mylonites, with the exceptions of two samples: E16 (+7.4‰) which is an ultramylonite collected at the contact with the sedimentary cover (this value will be discussed below) and E13 (+7.6‰ gneiss, contain chlorite and a smaller amount of quartz) which have the lowest $\delta^{18}O$ values. Apart from these samples, the rather homogeneous $^{18}O/^{16}O$ ratios obtained for the transition gneiss-mylonite may likely represent the isotopic composition of the starting material (Fourcade et al., 1989) and may suggest relatively low water/rock ratios under which the deformation took place. Thus, large oxygen isotope exchange processes between the starting material and interacting fluids are not likely to have occurred.

The values of $\delta^{18}O_{\text{whole rock}}$ are plotted against the distance from the contact which can also be

Tab. 3 Isotope composition of minerals (quartz and calcite) and whole rocks (W.R.) from the Aiguilles Rouges Massif. $\delta^{18}O_{water}$ calculated from the mineral-water fractionation equations reported by BOTTINGA and JAVOY (1973, 1975).

Sample		δ^{18}Ow.r.	δ^{18}O quartz	δ^{13}C	δ^{18}O water	
					350 °C	500 °C
E17	limestone	+24.7		+2.3		
E18	"	+25.2		+2.2		
E22	"	+25.4		+2.0		
E23	"	+25.1		+2.3		
E16	ultramylonite	+7.4			+3.0	+5.9
E0	"	+9.3			+4.9	+7.8
E0	calcite vein	+9.8		-6.3		
E1	ultramylonite	+9.4			+5.0	+7.9
E1	calcite vein	+9.7		-6.3		
E4	mylonite	+9.0			+4.6	+7.5
E5	"	+9.9			+5.5	+8.4
E6	"	+9.9			+5.5	+8.4
E7	"	+9.9			+5.5	+8.4
E7	"		+12.6		+5.7	+9.4
E9	"	+9.1			+4.7	+7.6
E9	"		+11.4		+4.5	+8.2
E21	"	+9.0			+4.6	+7.5
E26	"	+8.4			+4.0	+6.9
E26	"		+10.2		+3.3	+7.0
E27	"	+9.6			+5.5	+8.1
E28	"	+8.2			+3.8	+6.7
E30	"	+8.5			+4.1	+7.0
E30	"		+11.8		+4.9	+8.6
T9	gneiss	+9.8			+5.4	+8.3
T9	"		+11.2		+4.3	+8.0
E11	"	+11.0			+6.6	+9.5
E11	"		+12.4		+5.5	+9.3
E12	"	+10.1			+5.7	+8.6
E12	"		+12.2		+5.3	+9.0
E13	"	+7.6			+3.2	+6.1
E13	"		+10.9		+4.0	+7.7

interpreted in terms of decrease of deformation (Fig. 5). If a large transport of external fluid occurred across the deformation profile studied, this would have resulted not only in mineralogical and chemical changes, but also in isotopic gradients larger than those observed (KERRICH et al., 1980).

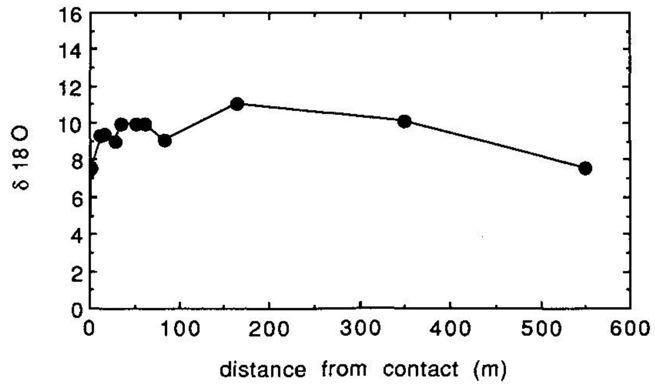

Fig. 5 Diagram illustrating the Variation of $\delta^{18}O_{whole\ rock}$ versus distance from the basement-cover contact (scale in m).

Independent chemical evolution of cover and basement during ductile Alpine tectonics, with relatively low fluid/rock ratios, seems to be confirmed also by the isotopic data obtained from the carbonate rocks of the autochthonous Malm limestone sampled at the contact cover-ultramylonites. $\delta^{18}O$ and $\delta^{13}C$ values measured on these limestones range respectively from +24.66 to +25.40‰ (versus V-SMOW) and from +2.01 to +2.30‰ (versus PDB-1) (Tab. 3). These results are in good agreement with previous data obtained by BURKHARD and KERRICH (1988) for marine carbonates of Mesozoic age coming from nearby areas. According to these authors, the isotopic data obtained from the carbonates indicate that they underwent moderate exchange processes suggesting, as their primary isotopic sedimentary values did not change drastically during the deformation, the lack of pervasive isotope exchange with external fluids.

Discussion

Assuming an ambient temperature of deformation in the range of greenschist facies metamorphic conditions (350–500 °C; FREY, 1986), the isotopic compositions of water in equilibrium with the gneiss-mylonite system may be estimated by using the experimental quartz-water and theoretical feldspar-water fractionation curves proposed by BOTTINGA and JAVOY (1973, 1975). This latter theoretical equation is in good agreement with recent laboratory measurement of equilibrium oxygen fractionation in quartz, albite and anorthite (CLAYTON et al., 1989):

$$10^3 \ln \alpha_{(qtz.\text{-}water)} = 4.10\,(10^6/T^2) - 3.70 \qquad (1)$$

$$10^3 \ln \alpha_{(feld.\text{-}water)} = (3.13 - 1.04\beta)(10^6/T^2) - 3.7 \qquad (2)$$

where α is the isotope fractionation factor between the two phases (mineral-water), β is the mole fraction of anorthite and T is the temperature of equilibrium in °K.

Assuming that the rocks are close to an internal isotopic equilibrium, the isotopic composition of water in the gneiss and the mylonitic rocks is evaluated by considering that the whole rock compositions are close to the composition of an albite phase ($\beta = 0$). This approximation does not introduce a substantial error in the evaluation of the $\delta^{18}O_{water}$: in fact, using equation (2) for a plagioclase of oligoclase composition ($\beta = 0.2$), the calculated values of $\delta^{18}O_{water}$ would be only shifted of +0.5‰. The $\delta^{18}O_{water}$ values obtained from the relationships above range between +3.0 to +5.5‰ at 350 °C and +5.9 to +8.4‰ at 500 °C for the mylonites and +3.2 to +6.6‰ at 350 °C and +6.1 to +9.5‰ at 500 °C for the gneisses.

The isotopic compositions of water in equilibrium with the quartz samples in the mylonites and gneisses obtained from relationship (1) range from +3.3 to +5.7‰ at 350 °C and from +7.0 to +9.4‰ at 500 °C and from +4.0 to +5.5‰ at 350 °C and +7.7 to 9.3‰ at 500 °C respectively. The $\delta^{18}O_{water}$ in equilibrium with the whole rocks and the quartz in the gneisses and mylonites falls in the same range of values (Tab. 3). The results are consistent with the $\delta^{18}O$ field of metamorphic fluids as reported by SHEPPARD (1986). Though, these values are also possible to obtain by shifting the isotopic composition of meteoric water by interaction with the wall rocks at high temperature with small water/rock ratios. Anyway, the homogeneity of $^{18}O/^{16}O$ ratios obtained for both quartz and whole rock samples in the transition gneiss-mylonites, along with the low permeabilities associated with these rocks are good evidences that the amount of an external (meteoric) water interacting with the rocks was not sufficiently abundant to act as an isotopic reservoir during the main ductile Alpine deformation. An interpretation in terms of metamorphic fluids (internal to the system) is also consistent with weak variations of major elements through the transition studied.

Fluid infiltration seems to have occurred after the main ductile deformation event (mylonitization) as evidenced by the presence of late calcite veining in the most deformed rocks, corresponding to the basement-cover contact: together with chemical mass balance across the shear zone, this suggests local open system conditions to an external Ca-rich fluid. The veins, whose grains show moderate to intense twinning, are very thin (1 to few mm width) and have well-defined boundaries. They crosscut the Alpine schistosity and, according to BURKHARD and KERRICH (1988), probably formed in the later period of deformation, corresponding to a shift from ductile towards a more brittle behaviour, when fluid circulation was mostly confined to the fractures. The stable isotope composition of these veins is reported in table 3 (samples E0–E1).

Ambient temperatures of veining are not well defined, but on the basis of mineralogical observations and previous data obtained by BURKHARD and KERRICH (1988) from the cover units of the Helvetic zone, a range of isotopic equilibration temperatures between 200 and 350 °C may be assumed. The $\delta^{18}O$ of the fluid from which the calcite precipitated (calculated by using the calcite-H_2O equation of O'NEIL et al., 1969) would then have been +0.2‰ at 200 °C and +5.5‰ at 350 °C. According to BURKHARD and KERRICH (1988) these temperatures represent the limits for formation of calcite veins.

The calculated $\delta^{18}O$ of interacting water at 200 °C is considerably lower than that obtained from the isotopic composition of mylonites at the greenschist facies temperatures (350–500 °C, Tab. 3). These relatively low $\delta^{18}O$ fluids may result from a variable mixture of ^{18}O-rich metamorphic fluid with an ^{18}O-depleted meteoric water component, which probably entered the system after the main ductile deformation event. Deep penetration of this surface-derived, low ^{18}O meteoric water could easily occur along the most deformed part of the shear zone and into the late fractures formed at the basement-cover contact. The isotope exchange processes occurring between this late fluid and ^{18}O-rich host rocks allowed the development of the $\delta^{18}O$ pattern observed in the ultramylonites. It is in fact in the most deformed and fractured part of this sequence that the lowest $\delta^{18}O$ value, corresponding to sample E16, has been measured.

A possible interpretation of the $\delta^{13}C$ values (–6.3‰) refers to a hydrothermal decarbonation model of preexisting limestones in terms of a Rayleigh distillation with a continuous CO_2 removal process. A late fraction of CO_2 could be related to the genesis of the calcite veins.

Progressive mass-transfer and fluid advection

The results obtained in this study are summarized on figure 6. In this sketch, we propose a three-stage model to explain the chemical and isotopic results:

1) Mass balance calculations using major elements lead to the conclusion that the Alpine mylonitization of the Aiguilles Rouges gneiss corresponds to a main ductile deformation event and was essentially an isochemical and isovolumetric process. Quartz and whole rock $\delta^{18}O$ values are relatively uniform across the transition gneiss-mylonite. Both features imply limited participation of external fluids, at least in the first stage of deformation. During this first stage, therefore, mylonites acted basically as a closed system with respect to large circulations of external fluids.

2) When the deformation proceeds and becomes more localized, the system became open to fluid infiltration in its most deformed part, corresponding to the contact with the sedimentary cover. The deformation likely shifted from a ductile towards a more brittle behaviour, as can be inferred from a system of calcite veins found in the ultramylonites sampled at the contact with the cover. These veins, that cross-cut the main Alpine schistosity might also represent the evidence of a Ca-rich fluid migration from the sedimentary units of the cover. Calcium is, in fact, the only element showing a concentration variation nearby the contact. This variation could, therefore, be explained in terms of a contamination of a Ca-bearing fluid moving from the carbonates towards the mylonites under an hydraulic pressure gradient.

3) At a very late stage, at the interface between the deformed crystalline massif and the autochthonous cover, (Fig. 6c) ^{18}O-depleted fluids (meteoric waters?) may have interacted with the fine-grained ultramylonites, shifting their isotopic composition to the lowest values recorded for these rocks across the section studied (sample E16).

The data obtained for sample E16 is not aberrant and it should be carefully evaluated: because of its extremely fine grain size, this sample probably recorded the interaction processes more intensely than the other mylonites analyzed. Such fluid-rock interactions, that seemed to act just on a very narrow strongly deformed mylonitic zone, can account for a channelized fluid regime, as also reported in ETHERIDGE et al. (1983) and FOURCADE et al. (1989).

Conclusions

The initial, non-deformed rocks are characterized by a pronounced primary chemical variability. For this reason, the chemical modifications that are related to the initial heterogeneous composition in the starting material, and those associated instead with the deformative events are difficult to evaluated quantitatively. Therefore, from mass-balance calculations, all major elements except calcium, seem to be weakly mobile during the main ductile Alpine deformation (e.g. mylonite formation). LOI follows the Ca behaviour. Stable isotope data are in good agreement with the chemical mass-balance calculations along the deformation profile: at the southeastern margin of the Aiguilles Rouges Massif the oxygen isotope composition of both quartz and whole rocks does not vary as a function of increasing degree of deformation. The homogeneity of the values obtained lead us to the conclusions that: (1) the shear zone acted as a closed system in the early stage of its deformation, and (2) the oxygen isotope pattern obtained for the transition gneiss-mylonites is the result of re-equilibration processes occurring under low water/rock ratios and under the same temperature conditions throughout the system. These fluids could possibly be of metamorphic origin, internal to and buffered by the system, mobilized during the main deformative event (BURKHARD and KERRICH, 1988): this would be in agreement with the absence of consistent isotope shifts in the mylonites and ultramylonites.

Therefore a progressive model of the chemical mass-transfer and fluid circulation could be proposed as follows: During the early stage, deformation within the shear zone took place probably under isovolumetric and isochemical conditions in a closed system. The system was progressively opened to external fluid infiltration when larger connections among brittle-ductile deformation zones became possible. The calcium fluctuations, recorded close to the contact with the sediments, can hence be referred to this stage of evolution of

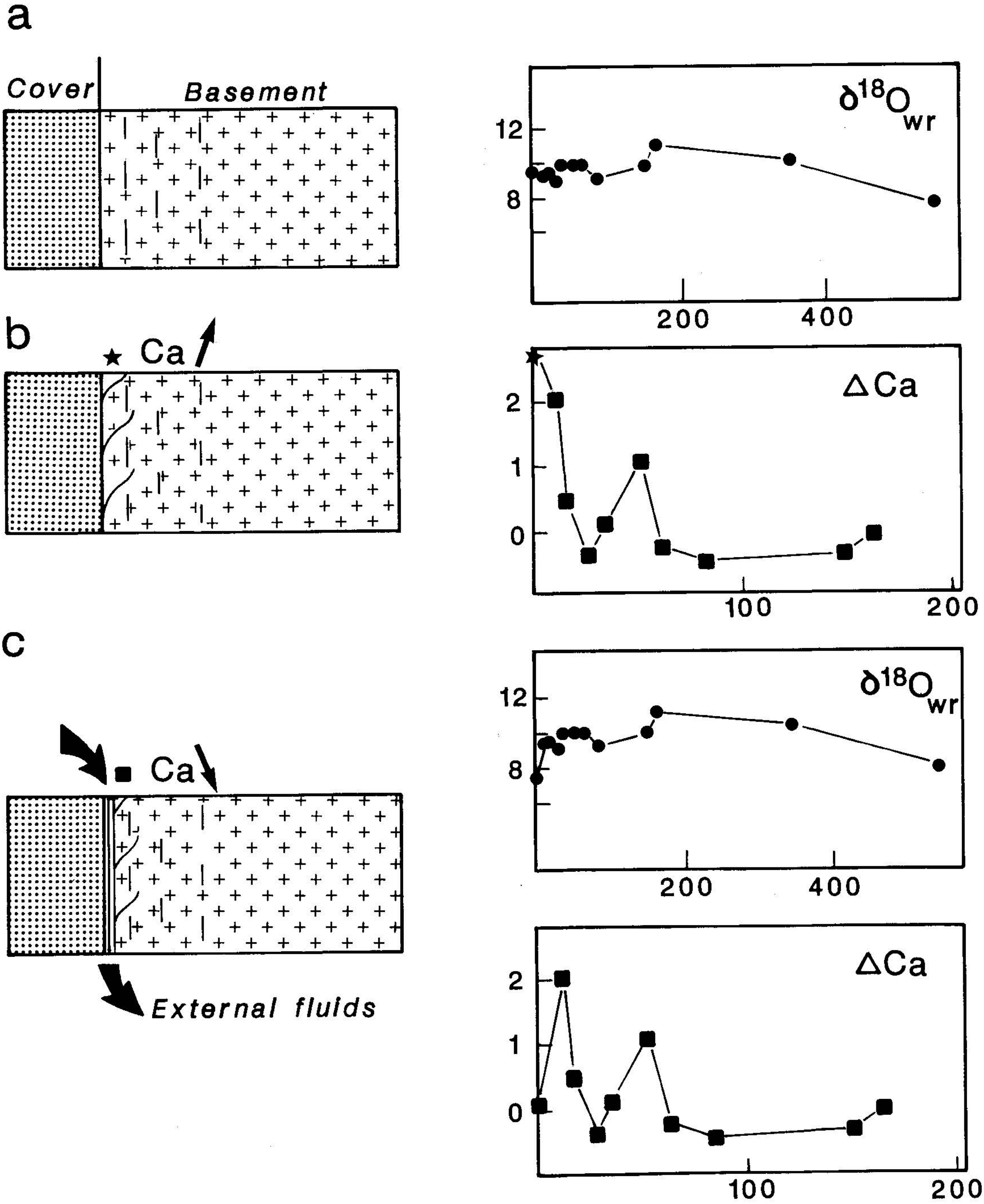

Fig. 6 Three-stage evolution model proposed for the chemical and stable isotopic behaviour at the cover-basement transition (see text for explanations).

the shear zone, contemporaneous to the calcite veinlets formation.

Additional analyses are, nevertheless, required, like Sr-isotope studies and δD determinations on hydrated mineral phases, in order to better identify the precise sources of these fluids. The overall tendency appears to be a result of a transition from an initially closed system that became progressively open in the later stages of deformation, as the whole process shifted from ductile toward brittle behaviour (see also Burkhard and Kerrich, 1988), as independently reported for Alpine ultramylonites in the Aar massif by Fourcade et al. (1989). This ductile-brittle mechanical transition seems to be, therefore, a common feature for a certain stage of the deformation history of the external crystalline massifs of the Alps.

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