

Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen =
Bulletin suisse de minéralogie et pétrographie

Band: 83 (2003)

Heft: 3

Artikel: Strontium isotope systematics in two glaciated crystalline catchments :
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DOI: <https://doi.org/10.5169/seals-63149>

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Strontium isotope systematics in two glaciated crystalline catchments: Rhone and Oberaar Glaciers (Swiss Alps)

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Abstract

We studied the strontium (Sr) isotope composition of runoff and particulate material in two glaciated catchments, the Oberaar (OA) and the Rhone (RH) in the Swiss Alps. Both areas are contained within the crystalline rocks of the Aar Massif, but a zone of highly deformed Variscan basement gneisses and schists that may contain up to 9 wt% calcite is present in the Oberaar catchment.

We analysed meltwaters and precipitation as well as bulk suspended sediment and local bedrock. Ca/Na ratios of 5.0–13.3 and 1.8–2.4 in Oberaar and Rhone meltwaters, respectively, indicate that meltwaters in both catchments are enriched in Ca relative to Na, compared to suspended sediments.

⁸⁷Sr/⁸⁶Sr ratios of Rhone meltwaters (0.7251–0.7258) are lower than those of Rhone bulk suspended sediment (0.7279–0.7306). The Rhone suspended sediment composition is interpreted as a mixture of Grimsel Granodiorite (0.7106–0.7161) and Central Aar Granite (0.7449). We explain the lower meltwater Sr ratio by the preferential dissolution of disseminated calcite, which has a relatively low ⁸⁷Sr/⁸⁶Sr ratio (estimated 0.720–0.730). This interpretation is supported by the enrichment of Ca in the meltwater compared to the suspended sediment. Early and nonstoichiometric cation release exerts another impact on the meltwater signal.

Oberaar meltwaters have a higher ⁸⁷Sr/⁸⁶Sr isotopic ratio (0.7137–0.7174) than the Oberaar suspended sediment (0.7130–0.7148) which reflects the preferential dissolution of the calcite contained within the Variscan gneisses (estimated 0.7160 ± 0.001).

The ⁸⁷Sr/⁸⁶Sr ratio measured in rain is 0.7104 (n = 4). An influence of atmospheric precipitation on Rhone meltwater ⁸⁷Sr/⁸⁶Sr ratio is not excluded. The high Sr isotopic signature of Oberaar meltwaters compared to that of the corresponding suspended sediment and also to the low Sr isotopic ratio of rainwater, however, suggests that the atmospheric contribution is not visible in the Oberaar meltwaters.

The results discussed here suggest that the presence of disseminated calcite within the crystalline rocks of the Aar massif exerts a major impact not only on the meltwater major ion composition but also on its Sr isotope systematics.

Keywords: Subglacial chemical weathering, Swiss Alps, glacial meltwaters, suspended sediment, disseminated calcite, strontium isotopes.

Introduction

Fluxes and isotopic ratios of Sr have been analysed in stream waters in order to trace mineral weathering reactions and the weathering rates of individual silicate minerals and to compare them with the isotopic characteristics of catchment bedrocks (e.g., Blum et al., 1993; Blum and Erel, 1995; Taylor and Blum, 1995; Clow et al., 1997). The chemical weathering of Sr from minerals is not necessarily stoichiometric, as it is dominated by the rapid dissolution of Sr-rich, or highly reactive minerals or mineral inclusions, such as dis-

seminated calcite (Clow et al., 1997; Blum et al., 1998; Jacobson and Blum, 2000; Jacobson et al., 2002) or apatite (Aubert et al., 2001). Biotite releases considerable amounts of highly radiogenic Sr during the initial stages of weathering and initial weathering rates may exceed those of feldspar (Blum and Erel, 1995, 1997; Arn, 2002). In laboratory dissolution experiments, Brantley et al. (1998) show that early Sr release from feldspars is nonstoichiometric and not isotopically identical to the starting material. The nonstoichiometric release is attributed to secondary phases present in minute proportions, and/or to leaching of cations

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from damaged sites. They propose that glacially abraded feldspar particles will exhibit this initial nonstoichiometric release.

Detailed studies of meltwater chemistry have been performed in glaciated catchments draining a variety of subglacial rock (e.g., Fairchild et al., 1994, 1999a, 1999b; Anderson et al., 2000; Sharp et al., 2002; Tranter et al., 2002). These studies show that carbonate weathering dominates bulk meltwater chemistry, even in crystalline catchments (Clow et al., 1997; Blum et al., 1998; White et al., 1999; Anderson et al., 2000; Jacobson and Blum, 2000; Jacobson et al., 2002; Tranter et al., 2002).

Strontium fluxes and isotopic ratios in stream waters also reflect the weathering intensity. Elevated Sr isotopic budgets for Himalayan rivers reflect the increased erosion rates in this mountain range (Galy et al., 1999; Galy and France-Lanord, 2001). They also indicate silicate weathering rates and the relative importance of carbonate and silicate weathering in different Himalayan settings (Harris, 1995; English et al., 2000).

The Sr isotopic ratios in continental riverine runoff are used as a proxy for the rate of chemical weathering on continents. They in turn influence the Sr isotopic signature of deposited marine carbonates, together with other Sr sources such as submarine hydrothermal sources and deep-sea sediment pore waters (Blum and Erel, 1995; Palmer and Edmond, 1989; Hodell et al., 1990; Hodell and Woodruff, 1994). The sharp rise in radiogenic Sr in marine carbonates in the late Eocene–Holocene is influenced by the intensified weathering of continental source rocks associated with the uplift of the Tibetan plateau and Himalayan mountain range (e.g. Raymo et al., 1988; Raymo and Ruddiman, 1992; Edmond, 1992).

Subglacial and proglacial weathering processes increase the chemical weathering rates of some primary minerals (Sharp et al., 1995; Hallet et al., 1996; Anderson et al., 1997; Tranter et al., 2002; Hosein et al., 2004). Glacial weathering also enhances the release of Sr by: (1) grinding and abrasion of rock, generating ultrafine particles ($< 63 \mu\text{m}$) with increased total reactive surface area;

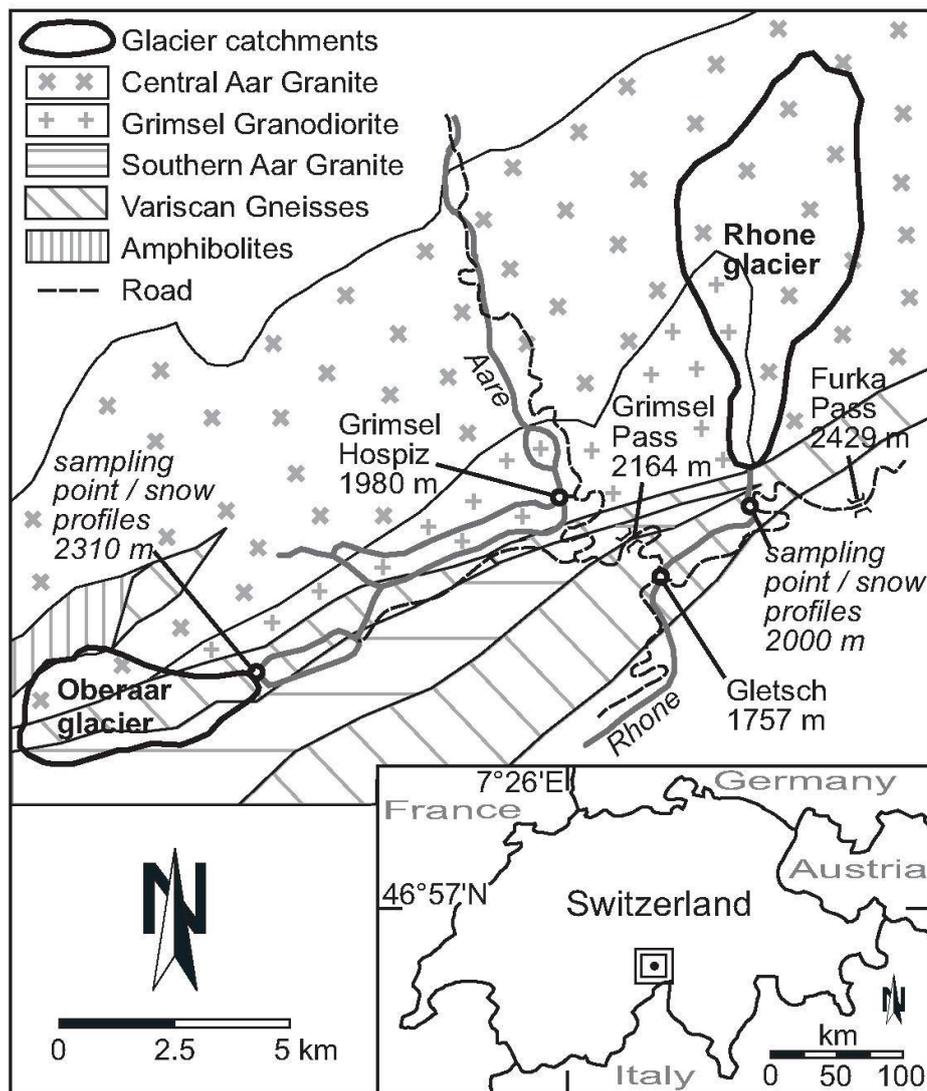


Fig. 1 Location of the catchment together with the main geology.

(2) selective weathering of minerals with relatively high Sr isotopic ratios; (3) providing a continuous supply of these minerals and thereby increased flushing of glacial sediments and soils; (4) producing mechanically damaged surfaces which enhance nonstoichiometric dissolution; and (5) producing large volumes of dilute meltwaters.

We studied subglacial chemical weathering processes and the Sr isotope composition of bedrock, runoff and particulate material in the glaciated catchments of the Oberaar (OA) and Rhone (RH) Glaciers (Swiss Alps), which are both located in the crystalline rocks of the Aar massif. Our goal was to estimate the influence of preferential dissolution of major and trace minerals on the bulk meltwater signal. We suggest that lithological differences between the two areas exert a major influence on bulk meltwater chemistry, meltwater Sr isotope ratios, and the mineralogy of the particulate flux. We show that the dissolution of disseminated calcite and the nonstoichiometric release of Sr from silicates are important sources of Sr and that they strongly influence the Sr isotopic ratios in runoff. A novel aspect of this work is that the glaciated terrains are purely crystalline. Such terrains have not previously been studied in the same detail as mixed crystalline-sedimentary or sedimentary terrains.

Field areas

The Rhone and Oberaar Glaciers are located in the central Swiss Alps, to the east and west of the Grimselpass (2100 m above sea level), respectively (Fig. 1 and Table 1). Climatic conditions are

therefore comparable (Schwab et al., 2001). Both glaciers are presently retreating. Both areas are contained within the crystalline rocks of the Aar Massif (Stalder, 1964; Abrecht, 1994; Fig. 1), and the lithologies are comparable, except for the presence of a zone of highly deformed Variscan basement gneisses and schists in the Oberaar area (Oberhänsli et al., 1988).

The Central Aar Granite and the Southern Aar Granite contain quartz, K-feldspar (microcline), plagioclase (oligoclase), and micas (mainly biotite). The Grimsel Granodiorite is richer in mica (biotite) and contains several meter- to decameter-sized basic lenses in the higher parts of the Oberaar catchment.

The Variscan Gneisses consist of recrystallized quartz, plagioclase (20–50 vol%; albite), and 8–20% biotite, and may contain some K-feldspar (microcline). They are heterogeneous on a small scale and contain up to 9 wt% calcite (compare also Stalder (1964), who found up to 5 vol% calcite). Sulfide mineralization is evident in these rocks, as there are many rusty stains on weathered surfaces and the SO₄ flux is 3.8 to 4.5 times higher in the Oberaar catchment compared to the Rhone (Hosein et al., 2004).

Sampling and analytical methods

Weekly (summer) to monthly (winter) bulk meltwater samples (1000 ml) were taken at both glaciers between 6 July 1999 and 1 October 2001 and a representative collection was used for Sr-analyses. The samples were immediately filtered in the field using 0.45 µm cellulose nitrate filters, acidi-

Table 1 Comparison of the field areas.

	Oberaar		Rhone	
Geogr. Position	46° 32' N 8° 14' E		46° 35' N 8° 23' E	
Surface of catchment	11.2 km ²		23 km ²	
Altitude	2310 – 3631 m a.s.l.		1750 – 3630 m a.s.l.	
Glacier cover today (%)	57%		73%	
Annual mean temperature †	– 1 °C §		+ 1.2 °C §	
Annual mean precipitation †	2100 mm		2200 mm	
Geology of catchments:	total*	ice covered**	total*	ice covered‡
Central Aar Granite	38%	26%	90%	76 ± 1%
Grimsel Granodiorite	7%	3%	10%	24 ± 1%
Variscan gneisses	42%	60%	–	–
Ultramafic Inclusions	1%	–	–	–
Southern Aar Granite	12%	11%	–	–

† Schwab (2001)

§ within proglacial area; 2300 m at Oberaar, 1757 m at Rhone

* from geological maps of areas, see text for references

Ultramafic inclusions neglected, see text for explanations

‡ calculated in this work, see text for explanations

Table 2 Results of the different bedrock and suspended sediment analyses.

Sample			Sr μmol g ⁻¹	⁸⁷ Sr/ ⁸⁶ Sr	2σ error	Calcite* wt%	Ca μmol g ⁻¹	Ca/(1000×Sr)	Na μmol g ⁻¹	Ca/Na
Bedrock										
Central Aar Granite										
R17	TD	SB	0.422	0.7449	± 0.000026	0.11	52	0.122	526	0.098
CAGr		¥	1.050	0.7471	± 0.000109		159	0.151	660	0.240
Aar10		#	0.902	0.7319	± 0.000028					
		<i>Bio</i>	1.142	0.7413	± 0.000167					
		<i>Kfs</i>	0.711	0.7338	± 0.000058					
Aar12		#	0.799	0.7371	± 0.000032					
		<i>Bio</i>	0.652	0.7391	± 0.000043					
Aar17		#	0.811	0.7441	± 0.000056					
		<i>Bio</i>	0.148	0.7486	± 0.000098					
		<i>Plagio</i>	0.822	0.7434	± 0.000079					
Grimsel Granodiorite										
R6	TD	SB	1.941	0.7115	± 0.000024	0.27	185	0.096	874	0.212
R1		SB	3.139	0.7161	± 0.000024		285	0.091	597	0.478
R9		SB	3.630	0.7106	± 0.000026		503	0.138	911	0.552
Aar31		#	0.594	0.7164	± 0.000046					
		<i>Kfs</i>	3.311	0.7101	± 0.000085					
AD20		#	2.686	0.7101	± 0.000029					
		<i>Plagio</i>	1.498	0.7105	± 0.000075					
ACIIh		#	2.573	0.7114	± 0.000053					
		<i>Bio</i>	0.726	0.7154	± 0.000074					
Variscan gneisses										
R8	TD	SB	1.792	0.7121	± 0.000024	0.15	1818	1.014	450	4.040
R15	TD	SB	4.121	0.7078	± 0.000022	9.01	1230	0.298	321	3.832
Suspended sediment										
Oberaarglacier										
OAP6	TD	SB	1.838	0.7148	± 0.000013		241	0.131	569	0.423
OA1	SA	BE	2.717	0.7130	± 0.000014		355	0.131	453	0.783
OA2	SA	BE	2.705	0.7138	± 0.000008		351	0.130	500	0.702
Rhoneglacier										
RH3.8.	TD	SB	1.164	0.7302	± 0.000015		141	0.121	639	0.220
RH1	SA	BE	1.142	0.7306	± 0.000021		162	0.142	621	0.261
RH2	SA	BE	1.176	0.7279	± 0.000029		168	0.143	597	0.281
Carbonate crusts (subglacially precipitated)										
OK1		BE	1.725	0.7164	± 0.000013					
RH1		BE	0.160	0.7192	± 0.000024					

SB measured at Centre de Géochimie de la Surface in Strasbourg; TD bulk samples

BE measured at Geologisches Institut, University of Berne; SA strong acid leachates

NE measured at GEA Lab, University of Neuchâtel

¥ Schaltegger et al. (1990)

Challandes et al. (2001)

* From RockEval analyses, GEA Lab, University of Neuchâtel

fied using suprapure HNO₃, and stored in pre-washed (10% HNO₃) polypropylene bottles at 4 °C. Suspended sediment was collected from both glaciers during the ablation seasons (1999 to 2001) by filtering meltwater in the field. The sediment samples were oven-dried at 40 °C. Rain samples were taken during the 2000 and 2001 ablation seasons: A polypropylene bottle was connected to a plastic funnel via a polypropylene tube (all equipment was prewashed with 10% HNO₃). The bottle was left for a maximum of 24

hours before the rainwater was filtered and stored like the meltwater samples. 17 samples of bedrock were taken randomly within the proglacial areas and on the valley walls beside the glaciers. The bedrock samples include the major lithologies of the two catchment areas. Subglacially precipitated carbonate deposits were also sampled in both catchments, they appear quite widespread in front of the retreating glaciers. Whole-rock and carbonate samples were crushed and ground to a fine powder using an agate mill.

Table 3 Results of the different meltwater and rain water analyses.

Sample		Sr* μmol l ⁻¹	⁸⁷ Sr/ ⁸⁶ Sr	2σ error	Ca μmol l ⁻¹	Ca/(1000×Sr)	Na# μmol l ⁻¹	Ca/Na
Meltwater								
Oberaar glacier								
O51	BE	0.403	0.7156 ± 0.000024		203.74	0.51	23.04	8.84
O65	BE	0.197	0.7137 ± 0.000023		86.78	0.44	6.52	13.31
O75	BE	0.146	0.7154 ± 0.000020		90.27	0.62	9.57	9.44
O80	BE	0.109	0.7174 ± 0.000046		67.48	0.56	16.96	3.97
P6	SB	0.125	0.7160 ± 0.000013		69.98	0.56	14.00	5.00
P4	NE	0.218			136.90	0.63	–	–
P7	NE	0.079			83.40	1.05	–	–
K8	NE	0.301			136.77	0.45	14.35	9.53
P8	NE	0.240			108.87	0.45	–	–
P9	NE	0.479			231.07	0.48	–	–
K25	NE	0.238			99.52	0.42	6.52	15.26
Rhone glacier								
A111	BE	0.013	0.7256 ± 0.000159		9.48	0.75	3.91	2.42
A142	BE	0.018	0.7258 ± 0.000192		12.22	0.67	6.09	2.01
RH3.8.	SB	0.011	0.7251 ± 0.000014		9.00	0.84	5.00	1.80
P046	NE	0.008			23.65	2.82	10.00	2.37
A067	NE	0.007			20.18	2.77	7.83	2.58
P093	NE	0.006			9.10	1.51	4.35	2.09
P071	NE	0.009			19.31	2.09	8.26	2.34
P142	NE	0.010			27.77	2.87	6.09	4.56
A169	NE	0.027			45.06	1.69	15.65	2.88
Rain								
RR1	BE	n.a.	0.7100 ± 0.000108		2.49	–	2.17	1.15
RR2	BE	n.a.	0.7097 ± 0.000024		11.72	–	3.91	3.00
RR3	BE	n.a.	0.7098 ± 0.000013		n.a.	–	n.a.	–
RR4	BE	n.a.	0.7100 ± 0.000033		n.a.	–	n.a.	–

BE measured at Geologisches Institut, University of Berne

SB measured at Centre de Géochimie de la Surface in Strasbourg

NE measured at GEA Lab, University of Neuchâtel

* measured using quadrupole ICP-MS at GEA Lab, University of Neuchâtel

measured using ion chromatography at GEA Lab, University of Neuchâtel

A first series of samples was analysed at the Geological Institute of the University of Berne. Approximately 100 ml of water were evaporated and the residue dissolved in 1 ml of 3M HNO₃. The evaporated samples were taken into solution with 6M HCl and H₂O (ultra-pure deionized), evaporated again and subsequently dissolved in 1 ml of 3M HNO₃. 4 suspended sediment samples (approx. 0.06 g each) containing the sediment of several subsequent samplings and a carbonate deposit sample were digested for 72 hours at 120 °C in closed Savilex vessels with 14M HNO₃ (strong acid samples, SA). The supernatant was centrifuged, evaporated and subsequently dissolved in 1 ml of 3M HNO₃.

All samples were spiked with approximately 0.05–0.06 mg of an ⁸⁴Sr spike. All acids used were purified by double distillation. All samples were centrifuged prior to analysis using columns with

Sr spec-pure resin. Strontium samples were stored in 0.01M HNO₃ and some of them were diluted with 0.35M HNO₃ prior to analyses. The samples were analysed on a Nu Instruments® Multiple Collector Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) in static mode. Mass fractionation corrections were applied by normalising the average ⁸⁷Sr/⁸⁶Sr ratios to the ⁸⁶Sr/⁸⁸Sr ratio of 0.1194. A total of 19 standards (NBS 987) were measured with an average ⁸⁷Sr/⁸⁶Sr of 0.71030 (2 s.d. = 0.00002).

A second series of samples was analysed in the Centre de Géochimie de la Surface in Strasbourg. Representative bedrock samples, two suspended sediment samples, and meltwater samples were analysed for their Sr isotopic composition and chemistry. The chemistry, including Sr, was measured on an ICP-MS. For the analyses of the Sr isotopic composition, powders of the samples were

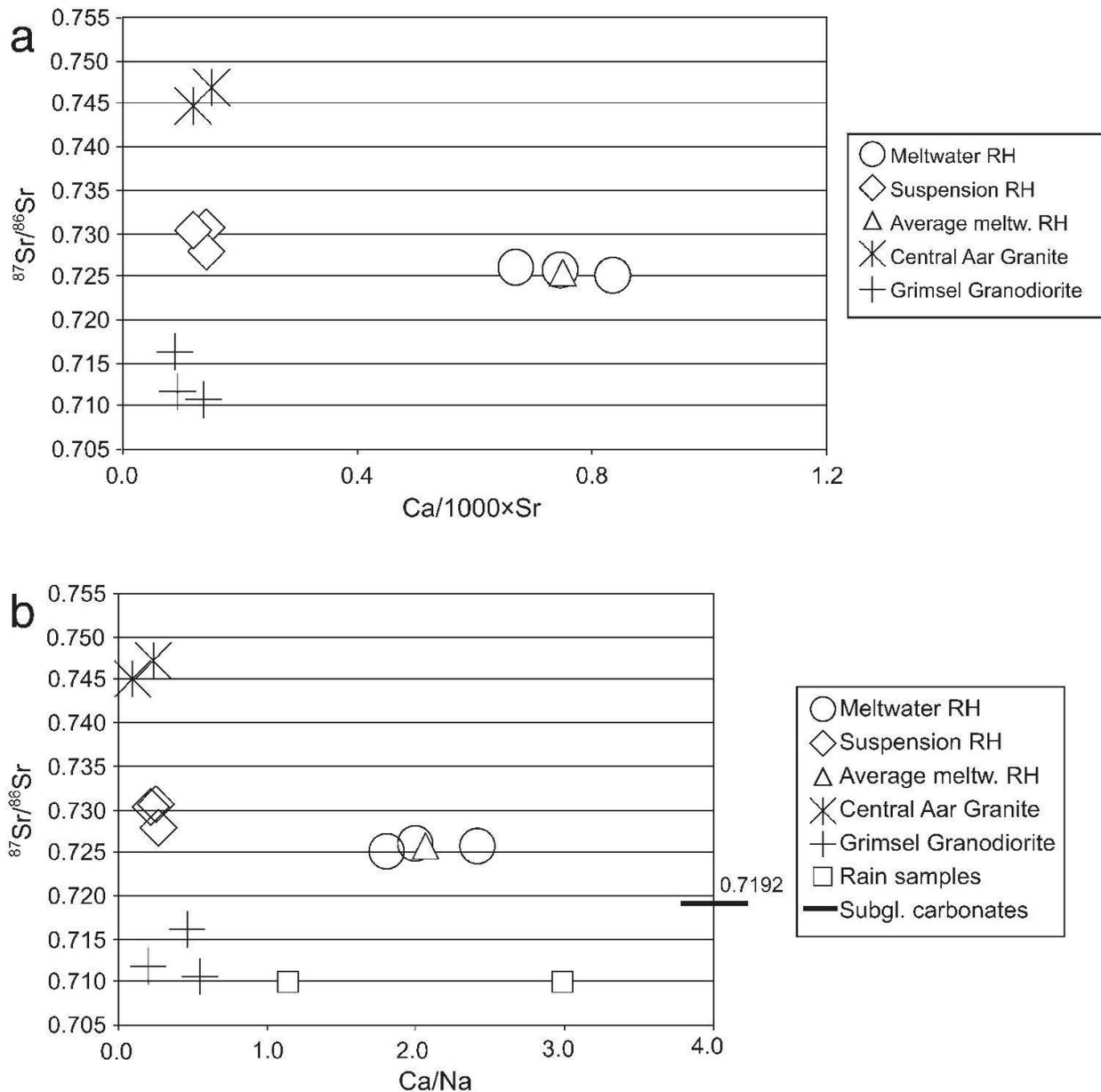


Fig. 2 (a) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\text{Ca}/(1000 \times \text{Sr})$ and (b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Na for water, bedrock and suspended sediment samples from Rhone catchment.

digested for 7 days in closed Savilex vessels containing a mixture of HF , HNO_3 , and HClO_4 (bulk samples, TD). Strontium was separated from the other ions using a cation exchange resin with 1.5 and 4M HCl as eluents. The total procedural blank was < 0.5 ng. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were determined on a VG Sector[®] multicollector thermal ionisation mass spectrometer (TIMS). Strontium was deposited on a W filament with Ta_2O_5 as activator. Corrections for mass fractionation were made as above. The accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ analyses was evaluated by determining the NBS 987 standard. A mean value of $^{87}\text{Sr}/^{86}\text{Sr} = 0.71030$ (2 s.d. = 0.00003, $n = 9$) was obtained.

A third series of samples was analysed at the Geochemical and Environmental Analyses (GEA) Laboratory at the University of Neuchâtel: 10 fur-

ther meltwater samples were measured on a quadrupole ICP-MS. The detection limit of this quantitative method is < 100 ppt for Ca and < 1 ppt for Sr.

Total inorganic carbon was determined on about 100 mg of ground rock powder, using Rock Eval 6 standard bulk rock pyrolysis (Espitalié et al., 1986; Lafargue et al., 1996). The inorganic or mineral carbon contents (MINC) were calibrated with marble standards and expressed as wt% calcite. For low concentrations, the error is 20% (RSD); for higher concentrations (≥ 0.5 wt%), the error is 5% (RSD) or less.

Major cations in the meltwater samples were measured by ion chromatography (Dionex DX 500, Hosein et al., 2004). The error is $\pm 5\%$ for concentrations of < 100 ppb and $\pm 2\%$ for concentrations between 100 ppb and 10 ppm.

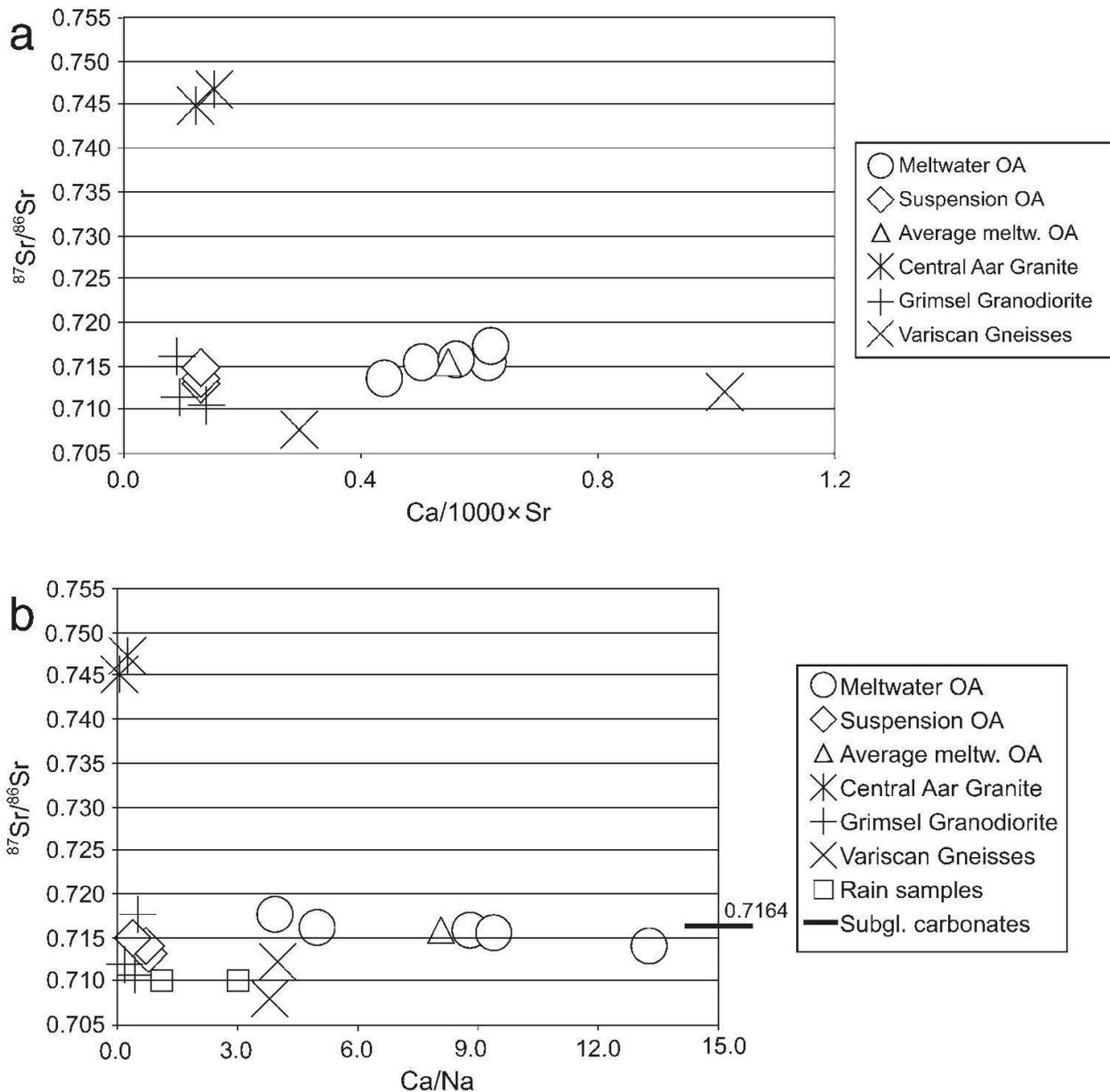


Fig. 3 (a) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $\text{Ca}/(1000 \times \text{Sr})$ and (b) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. Ca/Na for water, bedrock and suspended sediment samples from Oberaar catchment.

Results

Our bedrock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios generally correspond well with published data for the same rocks (Table 2). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Central Aar Granite (0.7449) concurs with the data from Challandes (2001). Our $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the Grimsel Granodiorite (0.7106 and 0.7115) are also comparable with Challandes (2001; 0.7088–0.7114). For the Variscan Gneisses two $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7121 and 0.7078) were measured. There are no published values for this lithology. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Rhone suspended sediments are between 0.7279 and 0.7306, whereas the Oberaar suspended sediments have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.7130 and 0.7148.

The meltwaters from both glaciers contain similar concentrations of Sr: 0.006–0.027 and 0.079–0.479 $\mu\text{mol l}^{-1}$ for Rhone and Oberaar, respectively (Table 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the meltwaters sampled throughout the ablation season show little variation (0.7251–0.7258 for Rhone and 0.7137–0.7174 for Oberaar samples), and those of the rain samples measured are quite similar (Table 3).

Calcite was detected in all bedrock samples of all lithologies (Table 2). The calcite content of the Grimsel Granodiorite (0.11 wt%) is lower than that of the Central Aar Granite (0.27 wt%). The Variscan Gneisses contain 9 and 0.15 wt% of calcite, respectively; this large difference reflects the heterogeneity of these rocks (Arn, 2002).

The strong acid attack (14 M HNO₃) of Oberaar suspended sediment yielded smaller ⁸⁷Sr/⁸⁶Sr ratios (SA samples: 0.7130 and 0.7138) than the bulk sample (TD, 0.7148). We attribute this to differences in sample size. The SA samples contain the sediment of several subsequent sampling sessions, whereas the TD sample was taken on one single day. All Oberaar meltwater samples lie above the two ⁸⁷Sr/⁸⁶Sr ratios of the Variscan Gneisses (bulk samples, TD, 0.7078 and 0.7121). The strong acid attack of Rhone suspended sediment yielded values comparable to those of the bulk sample (Table 2).

Discussion

General trends of meltwater

Suspended sediment consists of bedrock that was recently mechanically abraded at the glacier base (Benn and Evans, 1998; Drewry, 1986), and its mineral content represents an average of the different bedrock compositions of today's glacier catchments (Arn, 2002). The composition of suspended sediment is affected by subglacial geology, by abrasion and transport, and by the relative susceptibility (i.e. hardness) of lithologies and their constituent minerals to mechanical erosion. Minerals leaving a glacier may be leached subglacially, and further proglacial leaching may not correspond to the initial leach.

The Sr isotopic signal of the meltwaters is usually dominated by disseminated calcite, due to its high dissolution rate and its preferential weathering in subglacial environments, as reported from other glaciated areas (e.g., Tranter et al., 1993; Fairchild et al., 1994; Anderson et al., 1997; Fairchild et al., 1999a; White et al., 1999; Tranter et al., 2002; Hosein et al. 2004; this study). The Rhone and Oberaar meltwaters show elevated Ca/Na ratios supporting the hypothesis that Ca-rich minerals are weathered preferentially (Figs. 2b, 3b). The granitic rocks in the studied areas contain measurable amounts of disseminated calcite, but the Variscan Gneisses (found solely in Oberaar catchment) contain up to 9 wt% calcite (Table 2). This is the most likely source of Ca enrichment in the Oberaar catchment.

A daily trend in subglacial meltwater regime was not identified from our samples unlike in the studies of Sharp et al. (2002) or Anderson et al. (2000). The variable Ca enrichment, however, allows us to discuss the different sources of the Sr present in our meltwaters.

We suggest the main sources of Sr to be the preferential weathering of disseminated calcite,

contained within the different bedrock lithologies, together with easily hydrated ions derived from freshly cleaved silicate surfaces, whose early release is nonstoichiometric and may not correspond to the bulk mineral signature (Brantley et al., 1998). The relative importance of these sources is not the same in the two studied catchments (see below).

The concentrations of PO₄ measured in meltwaters from both glaciers are comparable even though the suspended sediment from the Oberaar catchment contains significantly more apatite than that from the Rhone catchment (average concentrations of total PO₄ are 0.07 (± 0.03) and 0.10 (± 0.04) μmol l⁻¹ for Rhone and Oberaar ablation period runoff, respectively. Mean detrital PO₄ concentrations in suspended sediment are 0.32 and 0.58 (± 0.05) mg g⁻¹ for Rhone and Oberaar, respectively (Hosein, 2002). Thus, we propose that apatite may only act as a minor source of Sr in the meltwaters studied here, and therefore, that its influence on the Sr signal is negligible. The lower ⁸⁷Sr/⁸⁶Sr ratio of the Rhone meltwaters (Fig. 2b), compared to bulk suspended sediment, may imply that the atmospheric input (with its generally low ⁸⁷Sr/⁸⁶Sr ratios) also has an impact on the meltwater signal. However, looking at the Ca/Na ratios of two of the rain samples, it appears that this influence is most probably negligible for Rhone meltwaters. Oberaar meltwater ⁸⁷Sr/⁸⁶Sr and Ca/Na ratios are higher than the suspended sediment and rain values, therefore atmospheric inputs are clearly negligible in the Oberaar catchment (Fig. 3b).

Rhone systematics

a) Suspended sediment vs. catchment lithologies. Using a mass balance approach, we calculated the portions of the two bedrock lithologies within the catchment (Central Aar Granite and Grimsel Granodiorite). The ⁸⁷Sr/⁸⁶Sr ratios and Sr concentrations of the two main lithologies in the Rhone catchment are listed in Table 2. Considering the suspended sediment to be a mixture of the two recently mechanically eroded bedrock lithologies (bulk suspended sediment (TD) ⁸⁷Sr/⁸⁶Sr ratio and Sr concentration) we calculated the portions of these lithologies within the suspended sediment. This calculation yields approximately 76 ± 1% of Central Aar Granite and 24 ± 1% of Grimsel Granodiorite. Assuming comparable overall hardness and erosion rates for both areas, this result further indicates that the subglacial exposure of the two lithologies are approximately 76 and 24% (Table 1). The values are quite different from an estimated distribution using different

maps, which give approximately 90 and 10% for Central Aar Granite and Grimsel Granodiorite, respectively (Table 1). However, the available maps are not precise for the glacier-covered parts of the catchment, hence our calculated distribution of the two lithologies is probably more reliable.

b) Rhone meltwater signal. At the Rhone glacier, the meltwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is smaller than that of the suspended sediment. We propose two reasons for this fact: (1) The Ca enrichment of the Rhone meltwaters is significant relative to Na compared to the Rhone suspended sediment, therefore we assume that the dissolution of disseminated calcite exerts a dominant impact on the meltwater chemistry (Hosein et al., 2004). The presence of subglacially precipitated carbonate crusts in front of the Rhone glacier suggests that they may also occur beneath the ice. Their subglacial dissolution exerts another lowering influence on the meltwater Sr signal ($^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7192, Fig. 2b). (2) The nonstoichiometric Sr release from silicates during initial subglacial weathering seems to further lower the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in our meltwaters. The feldspars from Grimsel Granodiorite have a higher Sr concentration (1.498–3.311 $\mu\text{mol g}^{-1}$) than those from the Central Aar Granite (0.711–0.822 $\mu\text{mol g}^{-1}$). They may therefore dominate the nonstoichiometric Sr release and according to their lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7101–0.7105 compared to 0.7338–0.7434 for Central Aar Granite feldspars), they may decrease the meltwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The importance of nonstoichiometric Sr release from biotites is difficult to estimate, as the available Sr concentrations are similar but show a high degree of scattering. The Sr concentrations in biotite are all lower than in the feldspars from the Grimsel Granodiorite.

Summarizing, the Sr signal of Rhone meltwaters shows the influence of dissolution of disseminated calcite as well as the influence of nonstoichiometric Sr release from silicates.

Oberaar systematics

a) Comparing Oberaar lithologies and suspension. At Oberaar the lithological architecture is visible from the broad geomorphological framework: the main valley incision occurs in the zone of the highly deformed Variscan Gneisses, representing approximately 60% of the total glacier-covered area (Table 1). The remaining 40% at the glaciers' sides are composed of granitic rocks, which are harder and less erodable. The lithologies are elongated parallel to the main valley geometry from the glacier front to the top of the catchment (the Oberaar Joch). The average sus-

pending sediment flux ($\text{kg km}^{-2} \text{yr}^{-1}$) of the Oberaar glacier is 2 times higher than that of the Rhone glacier (Hosein et al., 2004). Assuming that the Variscan Gneisses represent 60% of the total glacier-covered area and that the erodability of granitic rocks is equal to 1, we calculate the erodability of the Variscan Gneisses to be 2.7 to obtain an overall flux that is 2 times higher. This corresponds to an influence of the gneiss on the bulk suspended sediment of 73%.

b) Oberaar meltwater signal. In accordance with the values of the two samples of Variscan Gneisses, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Oberaar suspended sediment (TD) and meltwaters are lower than those of Rhone (Fig. 3a and 3b, Table 2 and 3). The Oberaar meltwater shows a greater Ca/Na-enrichment compared to the suspended sediment than that of the Rhone glacier (Fig. 3b), pointing to the clear dominance of the dissolution of disseminated calcite and its impact on the meltwater chemistry and Sr signal in the Oberaar catchment. The Oberaar subglacial weathering regime is highly influenced by the presence of Variscan Gneisses with their higher erodability and calcite content compared to the granitic lithologies. However, a comparison of the varying $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as well as of the different calcite contents of the two samples of Variscan Gneisses (R8 = 0.15 wt%, R15 = 9 wt%) clearly shows the *highly* heterogeneous nature of these gneisses: they are not adequately represented by the two samples measured here. According to the Sr ratio of the meltwaters, an average gneiss calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would be expected to be close to 0.716 ± 0.001 .

The general Ca enrichment of Oberaar meltwaters may partly be explained by the dissolution of subglacial carbonate precipitates, which are quite widespread in this catchment, as observed in front of the retreating glacier front. We assume that they also exist beneath the ice, where they would participate in the subglacial weathering processes. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of one sample (0.7164) and its Ca/Na ratio, which is higher than all the meltwater samples measured, seems to have a visible impact on the meltwater isotopic signal.

Even though single-mineral data are lacking for the gneisses, the strong Ca enrichment observed points to a minor impact of nonstoichiometric Sr release from silicates on Oberaar meltwaters compared to the calcite sources.

Conclusions

This is the first report on Sr isotope systematics in purely crystalline glaciated catchments in the

Alps. In general, meltwaters draining crystalline glaciated watersheds reflect the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the underlying bedrock. Meltwater composition is influenced by different short-term subglacial processes: The dominant impact of calcite dissolution not only on major ion composition of the meltwater, but also on its Sr isotope systematics was confirmed in the Oberaar catchment (where the Variscan Gneisses contain more calcite and are more easily eroded than the other granitic rocks) by comparing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the meltwaters to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of disseminated and subglacially precipitated calcite.

The Ca-enrichment of the Rhone meltwaters that drain a purely granitic catchment also suggests that the dissolution of disseminated calcite strongly influences the major ion composition of the runoff as well as its Sr isotope systematics. It was shown that the nonstoichiometric Sr release from silicates may exert another dominant impact.

Acknowledgements

We thank Virginie Matera (Neuchâtel) and Ingeborg Hebeisen (Berne) for laboratory assistance. We also gratefully acknowledge the support of the Swiss National Science Foundation (Grants 21-53997.98 and 20-61485.00). This paper benefited from the constructive reviews of A. Galy and F. Chabaux.

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Received 21 December 2003

Accepted in revised form 27 July 2004

Editorial handling: R. Gieré