Mitt. Österr. Geol. Ges. | ISSN 0251-7493 | **94** (2001) | 139-156 | Wien, August 2003

Keywords
Antimony
spring-water
mining region
hydrogeology
Austria

Aspects of the Hydrogeology of a Mining Region with a Focus on the Antimony Content of the Spring-water, Eiblschrofen Massif, Schwaz, Tyrol, Austria

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8 Figures and 8 Tables (Figure 2 as supplement)

Content

Abstract

At the Eiblschrofen Massif, Schwaz, Tyrol, Austria, spring-water used for the public supply, contains unusually high concentrations – up to 3 mg/l – of antimony (Sb). Where studied, concentrations of Sb normally range from a few ng/l to µg/l in freshwater systems (FILELLA et al., 2002a). The World Health Organisation's (WHO 1993) recommended value for Sb in drinking water is <0.005 mg/l. The large Sb content of the spring-water in Schwaz, arising from the dissolution of Sb-rich sulphidic fahlore and other assemblages hosted by the Schwaz Dolomite in the source-aquifers, was discovered during the hydrogeological monitoring programme started during the "Eiblschrofen Rock Fall Events" of July 1999. An overview of the main aspects of the Eiblschrofen Massif's hydrogeology, influenced by centuries of mining, is also presented.

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1. Introduction

On 10th July 1999, the first of a series of rock fall events, accumulating in a total volume of approx. 20000 m^3 occurred on the Eiblschrofen Massif, Tyrol, Austria. These events led to the closing of a number of businesses and the evacuation of over 270 people who were living within the lie of the proposed trajectories for a larger event, in the suburbs of Ried and Zintberg, of the city of Schwaz (Fig. 1 and 2).

Under the direction of the "Forsttechnischer Dienst für Wildbach- und Lawinenverbauung – Geologische Stelle" (Forest Engineering Service on Torrent and Avalanche Control – Geological Division, Tyrol, Austria) a large scale monitoring programme was set up. It included geological, geophysical, physical, geodetic and hydrogeological surveying methods coupled with an array of alarm systems, and technical and emergency teams.

During this time, two large rock fall retaining dams were constructed near the base of the mountain using the tailings from the large number of old silver mines which dot the Eiblschrofen Massif. In addition, a 130 m long rock fall catchment net was erected to the east of Zintberg to protect buildings which lie to the side of the trajectories (Fig. 2). These dams and the net allowed for the eventual safe resettlement of all the evacuees – see also SCHEIKL et al. (2000), SCHEIKL et al. (2001), REICHL & WAGNER (1999), POISEL et al. (2001), HEISSEL & MATTLE (2001), PÖTTLER (2001) and BAYER et al. (2000).

The main aim of the hydrogeological monitoring programme during the Eiblschrofen Rock Fall Event was to detect any sudden changes in the behaviour of the springs due to shallow and/or deep reaching underground deformation. This paper presents results from the hydrogeological monitoring programme carried out by ILF Consulting Engineers (MILLEN & BRANDNER 2000, ILF 2000a, b, ILF 2002) and focuses on the large Sb content of the spring-water occurring in the region.

2. Methods

2.1 Initial Field Survey and Spring Classification

An initial field survey of all known groundwater outflows was carried out during the first few days of the crisis. A few of the outflows are natural and housed, however most of the outflows are captured groundwater ingresses (gravitationally driven outflow) which were encountered during mining in the area. For simplicity, all outflows are classified as "springs", although not all of them emerge naturally. The old mine shafts now act as casings or, where the shafts have collapsed, spring houses have been built close to the abandoned mines. For clarity, the real names of the springs have not been used, instead they have been numbered 1-45 (Fig. 2).

2.2 Hydrological Monitoring Programme and Measurements

The initial monitoring programme included the daily measurement of flow-rate, air temperature, water temperature and electrical conductivity of 45 springs. After the construction works were completed, and the rock fall events subsided, the number of springs monitored was lowered and the interval of measurement was reduced to approx. once every 4 weeks.

The housed nature of the springs allowed for a relatively accurate measurement of the flow-rate and the taking of water samples at defined points (reproducibility). Flow-rates at Spring 30 were determined using a 110° V-notch

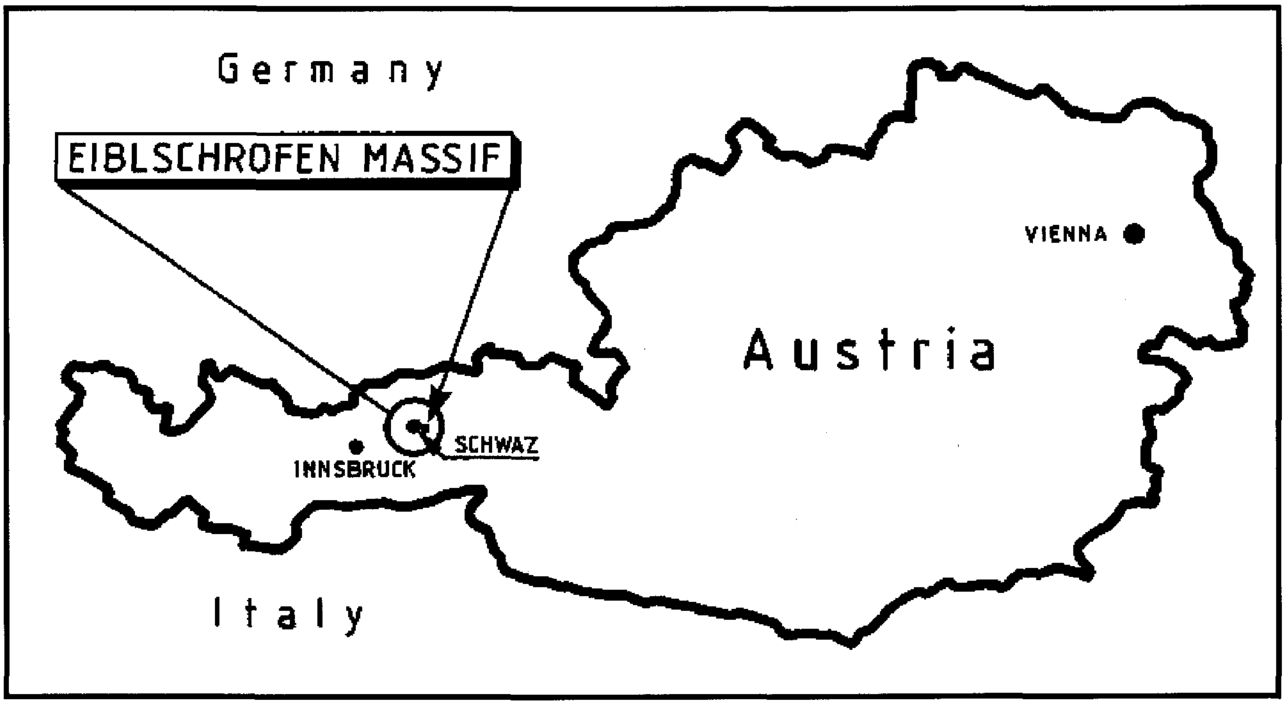


Figure 1
Location of the study area.

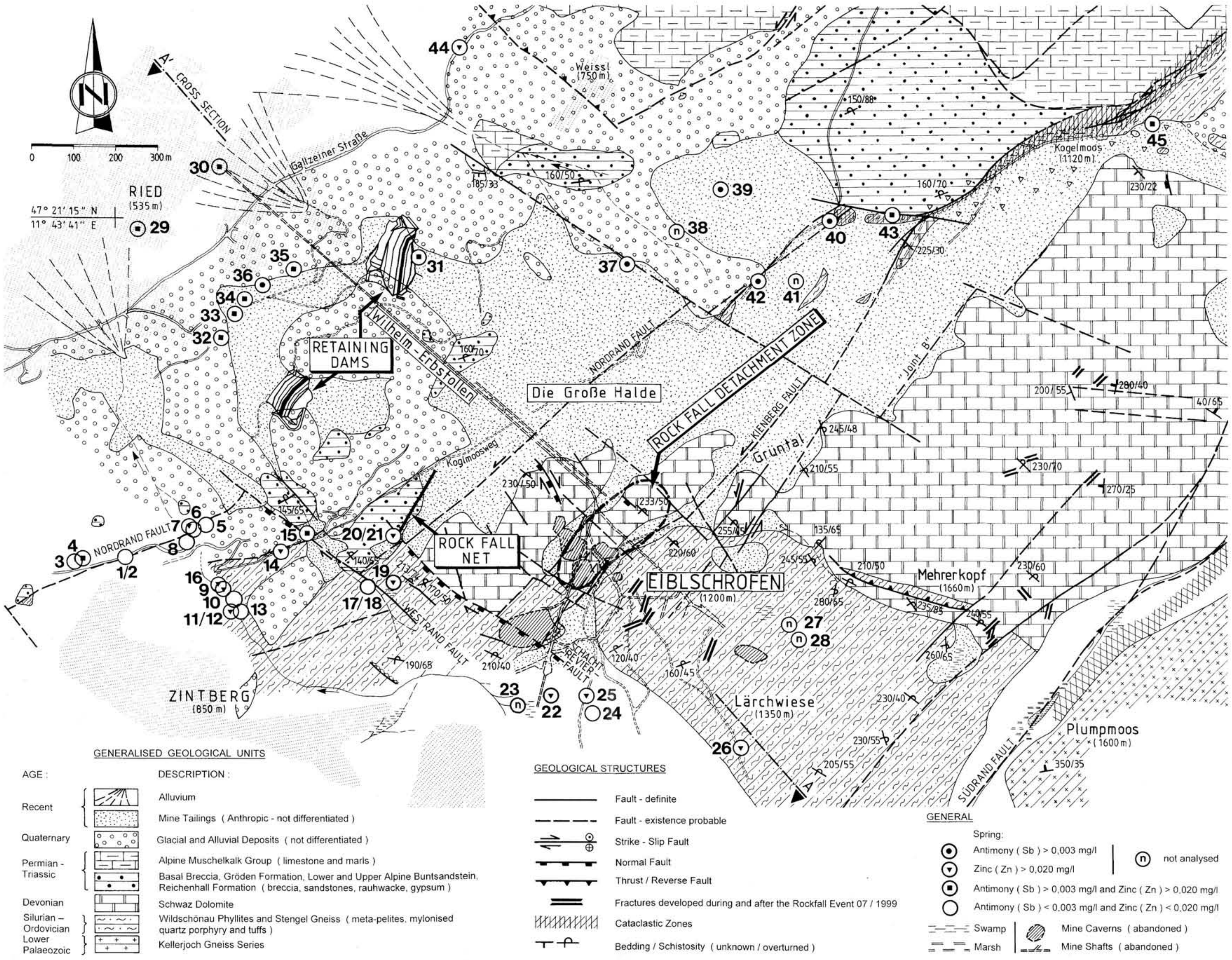


Figure 2
Schematic geology of the Eiblschrofen Massif, Schwaz. Also shown are the position of the springs and their Sb and Zn contents plus the main geographic localities.
Modified and simplified after Brandner & Reiter (2000)

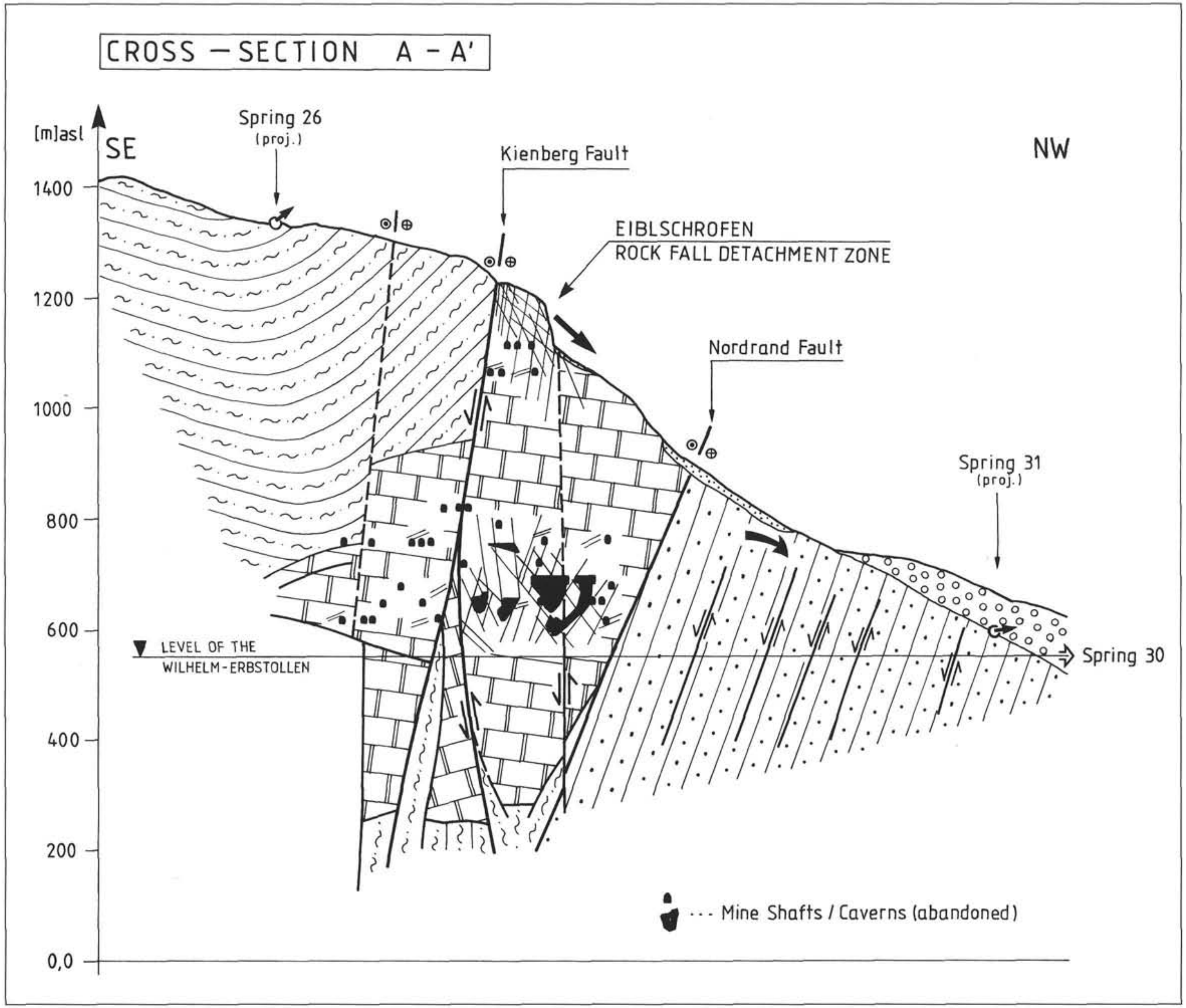


Figure 3
Section A-A' through the Eiblschrofen Massif, Schwaz, showing the main geological structures, the position and size of some of the old mining caverns and shafts, the projected position of springs 26, 31 and 30, and the rockfall detachment zone. For legend see Figure 2.
Modified and simplified after BRANDNER & REITER (2000)

Table 1
Period of observation and the maximum, minimum and average values of the flow-rate (l/s), water temp. (°C) and electrical conductivity (µS/cm) of the springs at Eiblschrofen, Schwaz. Springs displaying "base-flow" marked by "karst-like flow-rate peaks" are noted.
n. m. = not accurately measurable

	Period of Observation		Flow-Rate (l/s)			Water Temp. (°C) accuracy ± 0.2°C			elec. Conductivity (µS/cm) accuracy ± 1.5%			Base flow
Spring	**Begin**	**End**	**Max.**	**Min.**	**Av.**	**Max.**	**Min.**	**Av.**	**Max.**	**Min.**	**Av.**	-
1	21.07.99	07.08.01	3.00	0.08	0.33	10.6	5.5	9.4	285	242	264	
2	21.07.99	07.08.01	2.08	0.14	0.29	10.5	6.2	9.3	374	279	347	
3	21.07.99	07.08.01	0.75	0.18	0.30	9.7	7.4	8.7	416	344	375	
4	23.07.99	07.08.01	0.13	0.04	0.06	10.0	6.2	8.7	419	358	385	
5	21.07.99	07.08.01	0.26	0.10	0.16	10.3	5.5	8.5	316	238	269	
6	21.07.99	07.08.01	0.24	0.15	0.20	11.2	4.3	9.8	272	202	237	
7	21.07.99	07.08.01	0.18	0.09	0.13	9.5	6.1	8.7	410	327	361	
8	21.07.99	07.08.01	0.54	0.11	0.20	10.6	5.3	9.0	507	285	322	
9	21.07.99	07.08.01	0.61	0.28	0.35	8.4	7.9	8.2	280	273	276	
10	19.07.99	07.08.01	0.43	0.13	0.20	8.4	7.5	7.9	269	223	234	
11	25.07.99	07.08.01	0.05	0.00	0.02	10.5	4.2	8.8	158	103	135	
12	25.07.99	07.08.01	n. m.	n. m.	n. m.	10.1	4.9	7.8	150	104	128	
13	20.07.99	07.08.01	n. m.	n. m.	n. m.	8.7	7.2	7.9	243	218	234	
14	19.07.99	07.08.01	0.10	0.02	0.04	11.2	5.5	9.2	399	227	353	
15	21.07.99	07.08.01	0.30	0.02	0.05	9.0	4.1	7.7	284	187	262	
16	20.07.99	07.08.01	0.16	0.05	0.09	9.6	6.6	8.3	275	242	258	
17	19.07.99	07.08.01	0.16	0.05	0.07	9.2	5.4	8.3	461	407	444	yes
18	19.07.99	07.08.01	0.20	0.01	0.04	8.0	6.3	7.6	303	166	238	
19	19.07.99	07.08.01	0.18	0.02	0.06	11.4	2.6	8.8	409	346	388	yes
20	19.07.99	07.08.01	0.09	0.00	0.03	12.7	2.4	10.1	372	288	329	
21	19.07.99	07.08.01	0.14	0.00	0.02	11.6	3.0	9.6	190	115	139	
22	21.07.99	07.08.01	0.87	0.13	0.32	6.5	5.8	6.3	97	76	83	yes
23	21.07.99	07.08.01	2.24	0.34	0.74	12.1	0.7	7.5	90	55	74	yes
24	20.07.99	07.08.01	1.47	0.00	0.28	6.5	5.8	6.3	93	69	81	yes
25	21.07.99	07.08.01	0.10	0.03	0.05	7.4	4.9	6.4	89	68	77	
26	24.07.99	07.08.01	0.93	0.00	0.22	6.7	4.7	5.9	136	80	123	yes
27	19.07.99	07.08.01	0.29	0.01	0.06	6.6	2.5	5.2	144	105	129	yes
28	19.07.99	07.08.01	0.43	0.01	0.06	6.7	3.0	5.5	144	102	129	yes
29	20.07.99	21.01.02	22.03	8.55	11.91	11.0	9.7	10.5	620	563	589	
30	20.07.99	21.01.02	64.50	22.54	33.70	10.3	9.2	9.9	497	408	462	yes
31	31.07.99	07.08.01	1.50	0.10	0.61	8.8	5.8	6.7	498	344	375	
32	05.10.99	14.03.00	n. m.	n. m.	n. m.	6.0	3.6	5.7	451	346	400	
33	02.11.99	14.03.00	n. m.	n. m.	n. m.	11.1	3.8	8.0	248	210	227	
34	04.08.99	07.08.01	0.04	0.00	0.02	13.8	1.9	7.6	317	182	231	
35	04.08.99	07.08.01	0.22	0.05	0.09	9.2	5.9	8.5	552	420	481	
36	04.08.99	07.08.01	0.50	0.03	0.07	8.7	6.5	8.0	575	387	553	
37	20.07.99	07.08.01	0.74	0.10	0.33	6.1	4.8	5.7	306	253	282	yes
38	20.07.99	07.08.01	0.18	0.00	0.05	12.2	5.1	10.6	475	355	435	
39	20.07.99	07.08.01	5.57	0.46	1.57	5.9	5.1	5.5	293	257	276	yes
40	20.07.99	07.08.01	0.36	0.14	0.18	9.9	4.0	7.0	387	349	374	
41	21.07.99	07.08.01	n. m.	n. m.	n. m.	6.7	5.0	6.0	430	414	422	
42	21.07.99	07.08.01	1.19	0.06	0.30	6.1	4.6	5.5	238	221	227	yes
43	20.07.99	07.08.01	2.49	0.52	1.25	5.9	5.3	5.7	336	293	314	yes
44	06.08.99	07.08.01	0.07	0.07	0.07	15.4	4.7	10.0	609	564	574	
45	20.07.99	07.08.01	n. m.	n. m.	n. m.	5.7	4.9	5.3	281	259	273	

Table 2

Results of some of the metal and metalloid analyses of the spring-water, Eiblschrofen, Schwaz. Refer also to Fig. 2.

Analyses carried out by: 1. Institute for Environmental Hygiene, University of Innsbruck, Austria, all left-hand values – samples taken on 11. 11. 1999 and 2. Hydrologische Untersuchungsstelle, Salzburg, Austria – samples taken on 6. 10. 1999 marked *; n.a. = not analysed; samples marked ° were not filtered during analysis

Spring	Cu (mg/l)	Zn (mg/l)	As (mg/l)	Sb (mg/l)
1	<0.005	0.008	<0.001	<0.003
2	<0.005	0.012	<0.001	<0.003
3	<0.005	0.014	<0.001	<0.003
4	<0.005	0.031	<0.001	0.013
5	<0.005	0.012	<0.001	<0.003
6	<0.005	0.012	<0.001	<0.003
7	<0.005	0.027	<0.001	<0.003
8	<0.005	0.009	<0.001	<0.003
9	<0.005	0.023	0.001	<0.003
10	<0.005 & <0.005*	0.008 & <0.02*	<0.001 & <0.005*	<0.003 & <0.01*
11	0.005	0.038	<0.001	<0.003
12	n.a.	n.a.	n.a.	n.a.
13	<0.005	0.01	<0.001	<0.003
14	<0.005	0.026	<0.001	<0.003
15	0.085	0.029	0.003	0.19
16	<0.005	0.027	0.001	<0.003
17	<0.005	0.008	<0.001	<0.003
18	<0.005	0.009	<0.001	<0.003
19	<0.005	0.031	<0.001	<0.003
20	<0.005	0.03	<0.001	<0.003
21	<0.005	0.01	<0.001	<0.003
22	<0.005	0.028	<0.001	<0.003
23	n.a.	n.a.	n.a.	n.a.
24	<0.005	0.016	<0.001	<0.003
25	<0.005	0.035	<0.001	<0.003
26	<0.005	0.025	<0.001	<0.003
27	n.a.	n.a.	n.a.	n.a.
28	n.a.	n.a.	n.a.	n.a.
29	0.09 & 0.089*	0.047 & <0.02*	0.003 & <0.005*	0.26 & 0.25*
30	0.054 & 0.049*	0.024 & <0.02*	0.002 & 0.009*	0.36 & 0.32*
31	0.010 / 0.011° & 0.025*	0.006 / 0.019° & 0.03*	<0.001 & 0.034*	0.87 / 0.89° & 1.0*
32	0.292 / 0.511° & 0.31*	0.075 / 0.084° & 0.08*	<0.001 & 0.127*	3.2 / 3.0° & 2.5*
33	0.127	0.316	<0.001	2.1
34	0.267 & 0.22*	0.04 & 0.04*	0.002 & 0.113*	1.5 & 1.5*
35	0.078 & 0.085*	0.029 & 0.02*	<0.001 & <0.005*	1.1 & 1.0*
36	<0.005 & 0.008*	<0.005 & <0.02*	<0.001 & <0.005*	0.65 & 0.60*
37	<0.005	<0.005	0.001	0.72
38	n.a.	n.a.	n.a.	n.a.
39	<0.005	0.018	<0.001	0.56
40	<0.005	0.01	<0.001	0.018
41	n.a.	n.a.	n.a.	n.a.
42	0.006	0.008	<0.001	0.84
43	<0.005 & <0.005*	0.023 & <0.02*	<0.001 & <0.005*	0.011 & 0.02*
44	<0.005	0.03	<0.001	<0.003
45	0.012	0.033	<0.001	0.006

weir. For all the other springs, the scaled bucket (smallest and largest interval 0.01 and 25 litre respectively) and stop watch (smallest interval 100th of a second) method was used.

Temperature and electrical conductivity measurements in the field were taken using a Wissenschaftlich-Technische Werkstätten (WTW) LF 318 conductivity meter and TetraCon 325 standard-conductivity cell. The reference temperature was set at 25 °C, at a compensation of natural water (nLF) according to EN 27888, the cell constant was fixed at 0.475 cm^{-1}. Accuracies are given in Table 1.

In addition, the daily precipitation (mm) and air temperature (°C) records from the Schwaz Weather Station were gathered.

2.3 Water Chemistry Analysis

A chemical and bacteriological analysis of nearly every spring was carried out in accordance with the Austrian Drinking Water Codex (BGBL 1998), at government registered institutes. The results of the bacteriological analysis are not relevant for the paper and are therefore not given.

2.4 Metal and Metalloid Analysis

When Spring 32, which emerges from beneath the southern most dam (Fig. 2), became cloudy with sediment particles during the construction works, further analyses of the spring-waters were carried out to determine the content of the metals and metalloids Al, Sb, As, Cd, Cr, Cu, Fe, Pb, Mn, Hg and Zn, in accordance with the Austrian Drinking Water Codex (BGBL, 1998) at government registered institutes. Concentration values correspond to contents in filtered (0.45 μm pore size filters) samples except where stated (Table 2).

2.5 $\delta^{18}O$ Analysis

Oxygen-18 ($\delta^{18}O$) analysis was carried out by a government registered institute on the stored water samples of a few selected springs in the months preceding the main rock fall events (Table 3). The samples were measured fully automatically using a Finnigan MAT 250 gas isotope ratio mass spectrometer coupled to an equilibration device, following the principle of isotope exchange by means of CO_2 (response time 4 hours). The evaluation of the raw data obtained was done using the test readings of processed samples of the laboratory standard ST3 which has been calibrated against VSMOW (Vienna Standard Mean Ocean Water).

2.6 Calculation of the Average Altitude of a Spring Catchment Area – AASCA

In general, in order to correctly interpret $\delta^{18}O$ values for calculating and determining the Average Altitude of a Spring Catchment Area (AASCA), at least the values from one hydrological cycle (annual variation) should be known. In the following calculations this is not the case. However, the sample selection process for analysis involved looking at the flow-rate curves and selecting a range of average and extreme value samples from various hydrogeologically important springs (Table 3).

Making use of the fact that condensation temperature is dependent on altitude (Dansgaard 1964, Craig & Gordon 1965), $\delta^{18}O$ values obtained from precipitation can be used *to calculate the altitude of rain water infiltration in a given area*. The temperature reduction with increasing altitude, called the "temperature – altitude effect" is generally regarded to follow a linear function resulting in a $\delta^{18}O$ regression line (Fig. 4). This temperature – altitude effect is very variable in the Alpine Areas of Central Europe (Kralik 1999, Schotterer et al. 2000).

An alternative method to calculate the altitude of infiltration is by using spring-water $\delta^{18}O$ values under the following conditions:

1. It is known that the reduction of the amount of $\delta^{18}O$ in precipitation normally lies between 0.25-0.50 ‰ per one hundred metres of increasing altitude (Moser & Rauert 1980). For the Alpine Regions of Central Europe the values typically lie between 0.15-0.35 ‰ per one hundred metres of altitude (Schotterer et al. 2000, Kaiser et al. 2001)
2. Using the average $\delta^{18}O$ values of reference springs, it is possible to calculate a "$\delta^{18}O$ regression line" for the

Table 3

$\delta^{18}O$-values (VSMOW) from some of the springs at Eiblschrofen, Schwaz and the interpreted average altitude of their catchment areas – see also Fig. 4.

AASCA = Average Altitude of the Spring Catchment Area; asl = above sea level; n.a. = not analysed; $\delta^{18}O$ analyses carried out by Bundesforschungs- und Prüfzentrum Arsenal, Vienna, Austria

	Sampling Date and $\delta^{18}O$ Values (‰ VSMOW)					Average $\delta^{18}O$	Standard Deviation	Outflow Altitude	AASCA
Spring	**04.08.99**	**01.09.99**	**13.10.99**	**19.01.00**	**11.04.00**	**‰**		**m asl**	**m asl**
10	-12.10	-12.00	-11.90	-11.98	-12.19	-12.03	0.11	775	1280
28	-12.66	-12.57	-12.54	n.a.	-12.83	-12.65	0.13	1390	1480
29	-11.95	-12.04	-12.00	-12.01	-11.96	-11.99	0.04	530	1260
30	-12.61	-12.54	-12.40	-12.46	-12.46	-12.49	0.08	540	1430
34	n.a.	-10.33	-10.04	-10.32	-12.23	-10.73	1.01	600	840
39	-12.69	-12.73	-12.64	-12.53	-12.78	-12.67	0.10	865	1490
43	-12.97	-12.90	-12.84	-12.72	-12.78	-12.84	0.10	1070	1550

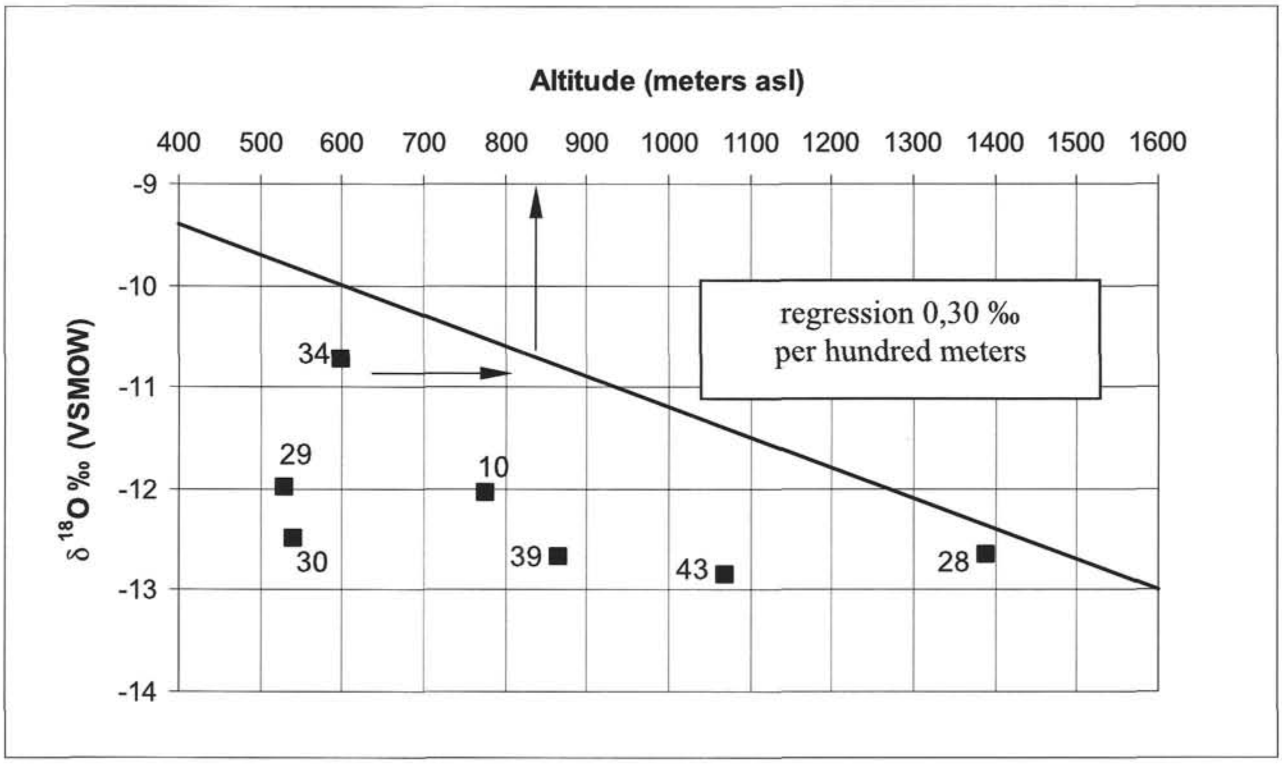


Figure 4
$\delta^{18}O$ – regression line for the area of the Eiblschrofen Massif, Schwaz. Regression is 0.30 ‰ per one hundred metres (temperature-altitude effect – see text for explanation). Squares indicate average $\delta^{18}O$ plotted against outflow altitude of the springs 10, 28, 29, 30, 34, 39 and 43. By projecting the outflow altitude $\delta^{18}O$ value onto the regression line and then onto the altitude axis (x), one can calculate the AASCA.
AASCA = Average Altitude of the Spring Catchment Area (m asl); $\delta^{18}O$ analyses carried out by Bundesforschungs- und Prüfzentrum Arsenal, Vienna, Austria

survey area, as long as the geological, hydrological, and topographic systems of the spring catchment areas are well understood. Normally, this means that the springs should have a small catchment area (i. e. low flow-rate), and only a small variation in their $\delta^{18}O$ content (annual cycle). In this study springs 28 and 34 were selected. Whereas Spring 28 fully complies with the above criteria, Spring 34 does not do so during extreme hydrological events, when (infiltration) water from higher altitudes reaches its source-aquifer e. g. during the snow melting period (Table 4). However, due to its very small flow rate (0.004-0.035 l/s), and large temperature fluctuations (1.9-13.8 °C), Spring 34's base-flow catchment area is presumed to be in its immediate surroundings (outflow altitude is at 600 m asl – above sea level) at an average altitude of approximately 680 m asl. Taking this as one fixed point (Spring 34: –10.23 ‰, 680 m asl) and Spring 28 (–12.65 ‰, 1480 m asl) as another, a $\delta^{18}O$ regression line for the study area was constructed (Fig. 4). The $\delta^{18}O$ regression is 0.30 ‰ per one hundred metres (temperature-altitude effect) for the area which correlates well with other values published from the Alpine Regions of Central Europe.

Table 4
$\delta^{18}O$ behaviour of Spring 34 vs. flow-rate.
AASCA = Average Altitude of the Spring Catchment Area; asl = above sea level; $\delta^{18}O$ analyses carried out by Bundesforschungs- und Prüfzentrum Arsenal, Vienna, Austria

Datum	$\delta^{18}O$ Value	Flow-rate	AASCA
	(‰ VSMOW)	(l/s)	(m asl)
01.09.1999	-10.33	0.016	710
13.10.1999	-10.04	0.014	610
19.01.2000	-10.32	0.004	710
11.04.2000	-12.23	0.025	1340

Table 5
Some of the elution properties and mass substance of tailings (Pochwerkssande) from the area of the retaining dams, Eiblschrofen, Schwaz.
Analyses carried out by the Institute for Environmental Hygiene, University of Innsbruck, Austria – samples taken on the 21. 09. 1999

Element	Elution Value (mg/kg)	Mass Substance (mg/kg)
Sb	3.2 – 13.0	not analysed
As	2.3 – 5.3	280 - 480
Cu	1.8 – 3.3	1600 -2700
Hg	0.01 – 0.03	45 - 110
Ag	0.02 – 0.06	15 - 25

2.7 Elution and Mass Substance Analysis

Some of the tailings, consisting of sand sized crushed dolomite (Pochwerkssande), used in the construction of the retaining dams were analysed for their elution property and mass substance, at a government registered institute in accordance with Austrian law concerning landfills (BGBL 1996). The results revealed that the elements Sb, As, Cu, *Hg and Ag exceeded the recommended values (Table 5).* However, due to the fact that the concentrations were of geogenic origin and the tailings were not removed from the immediate area, no particular treatment or precautions were undertaken for their use in the construction of the dams.

3. Geological Overview of the Eiblschrofen Massif Area

The geology of the Eiblschrofen Massif was first described in detail by Pirkl (1961).

The following geological overview is taken from Ortner & Reiter 1999 and Brandner & Reiter 2000. For simplicity and clarity, the geology shown in Fig. 2 and 3 has been modified and simplified.

The oldest rocks of the Eiblschrofen Massif are Palaeozoic in age and include:

1. The Ordovician-Silurian Wildschönau Phyllites and Stengel Gneiss composed of meta-pelites and mylonised quartz porphyry and tuffs respectively.
2. The Basal Quartzite.
3. The Devonian Schwaz Dolomite which is a thin to massively bedded carbonate succession.

These three units were deformed (folded) and reached greenschist facies with the formation of the dolomite during the Variscian Orogeny. Possibly during the Upper Carboniferous and Permian, extension and hydrothermal alteration led to the formation of a silver and antimony bearing sulphidic fahlore and other assemblages within a system of conjugate faults. The complex was then (or at the same time?) exhumed, underwent weathering, developed a relief and was karstified.

Permian – Triassic sedimentary rocks transgressionally overlie the Wildschönau Phyllites, Stengel Gneiss and Schwaz Dolomite. They include from oldest to youngest:

1. The Basal Breccia, Gröden Formation and Lower and Upper Alpine Buntsandstein which are made up of red coloured conglomerates, sand and silt stones and include gypsum and green claystone deposits towards the stratigraphic top.
2. The Reichenhall Formation which is very variable and includes thin bedded dolomites, carbonate sandstones, gypsum and rauhwacke, marls and clays.
3. Some members of the calcareous Alpine Muschelkalk Group, namely the Steinalm, Annaberg, Virgloria and Reifling Formations, consisting mainly of dolomites, limestones and marls.
4. The younger Partnach Formation consisting mainly of marls and limestones.

These Palaeozoic and Permian – Triassic rocks, now forming part of the Tirolic (Inntal) Nappe, have undergone polyphase deformation including extension (Jurassic), stacking with metamorphism (Cretaceous), long period compression (thrusting – Eocene) and strike-slip faulting (Oligocene and Miocene). They now form steeply SE dipping fault bound units within the Inn Valley Fault System.

Finally, appearing locally are:

1. Quaternary glacial and alluvial deposits, which in the greater Schwaz area of Vomp show recent deformation due to normal faulting.
2. Tens of metres thick (pre)historic anthropic rocks, namely mine tailings.
3. Thin to a few metres thick weathering and talus deposits.

4. Antimony Bearing Sulphidic Assemblages

The hydrothermal silver and antimony bearing fahlore deposits at Schwaz are hosted mostly by the Devonian Schwaz Dolomite. The majority of the fahlores lie within the middle of the tetrahedrite-tennantite solid solution series, total range is 35-100 wt. tetrahedrite end-member, and can be well described by the simplified formula $(Cu,Ag)_{10}(Fe,Zn,Hg)_2(Sb,As)_4S_{13}$. Other sulphidic assemblages occurring at Schwaz are stibnite (Sb_2S_3) and pyrite (FeS_2) (Artl & Diamond 1998). Table 6 shows some of the metal and metalloid concentrations of the fahlore occuring at Schwaz (Weber 1997).

5. Antimony

Antimony (Sb) is the 51st element of the periodic table, belonging to group Va, the same group as arsenic. It most commonly occurs as Sb(III) and Sb(V). The most common ore of Sb is stibnite (Sb_2S_3). Uses of Sb vary from being a constitute of alloys, batteries, safety matches and paint pigment. It is also used in medicinal and cosmetic substances (Daintith 1999 and Filella et al. 2002a).

5.1 Antimony in Natural Water

According to Filella et al. (2002a), Sb has received the scantiest of attention when considering research on geo-

Table 6
The metal and metalloid concentrations of the fahlore occurring at Schwaz, Tyrol.
From Weber 1997 pg. 411, Table 6 (various sources)

As %	Sb %	Bi %	Cu %	Ag %	Hg %	Zn %	Fe %	Cd ppm	Ge ppm	Sn ppm
3-10	10-20	0.04 -1.0	37.5	0.04 -2.8	0.2-5.4	1.5-10	0.8-6.2	10-370	µ200	µ20

chemical and biogeochemical processes of metalloids in natural waters. The distribution and speciation of Sb in freshwater systems has not been extensively studied and concentrations range from a few ng/l to a few µg/l depending on location. These concentrations are minute in comparison to those occurring in the spring-water at the Eiblschrofen Massif (Table 2 and Fig. 2).

Antimony and the common compounds of Sb are generally considered to be practically insoluble in water (AYLWARD & FINDLAY 1994). When present, Sb(V) is the predominant species present in oxygenated systems, although Sb(III) also occurs. The true speciation of Sb under anoxic conditions remains unclear (FILELLA et al. 2002a, b).

5.2 Toxicity of Antimony

Compounds of Sb are considered highly toxic, with trivalent compounds being considered more toxic than pentavalent compounds. The toxicity of Sb is usually compared with that of arsenic because of its elemental similarities. Antimony poisoning, through ingestion, however is seldom in comparison to arsenic poisoning. This is probably due to the fact that it is not as easily absorbed through the walls of the stomach and intestines as arsenic. However, it is known that acute exposure causes nausea, vomiting and diarrhoea. The effects on humans from long-term exposure are poorly understood mainly due to a lack of solid research on the subject, but are given as decreased longevity, and altered levels of glucose and cholesterol within the blood. There is insufficient evidence to state whether or not Sb has the potential to cause cancer, however co-exposition with arsenic could increase its carcinogenic potential (USEPA 1999, GEBEL 1999a, b).

6. Results

6.1 Electrical Conductivity, Water Temperature, Flow-rate

Field measurements of the springs revealed that (Table 1):

1. The electrical conductivity is highly variable, with average values ranging between 70 and 600 µS/cm. At individual springs, large fluctuations (>100 µS/cm) in the electrical conductivity are observed.
2. The average water temperatures range between 5.2 and 10.6°C, and do not systematically decrease with increasing geographical height. Also, some springs have small 1-2°C annual temperature fluctuations. Average monthly air temperatures for the year 2000, taken at the Schwaz Weather Station (535 m asl), ranged from -3.2°C in Ja-

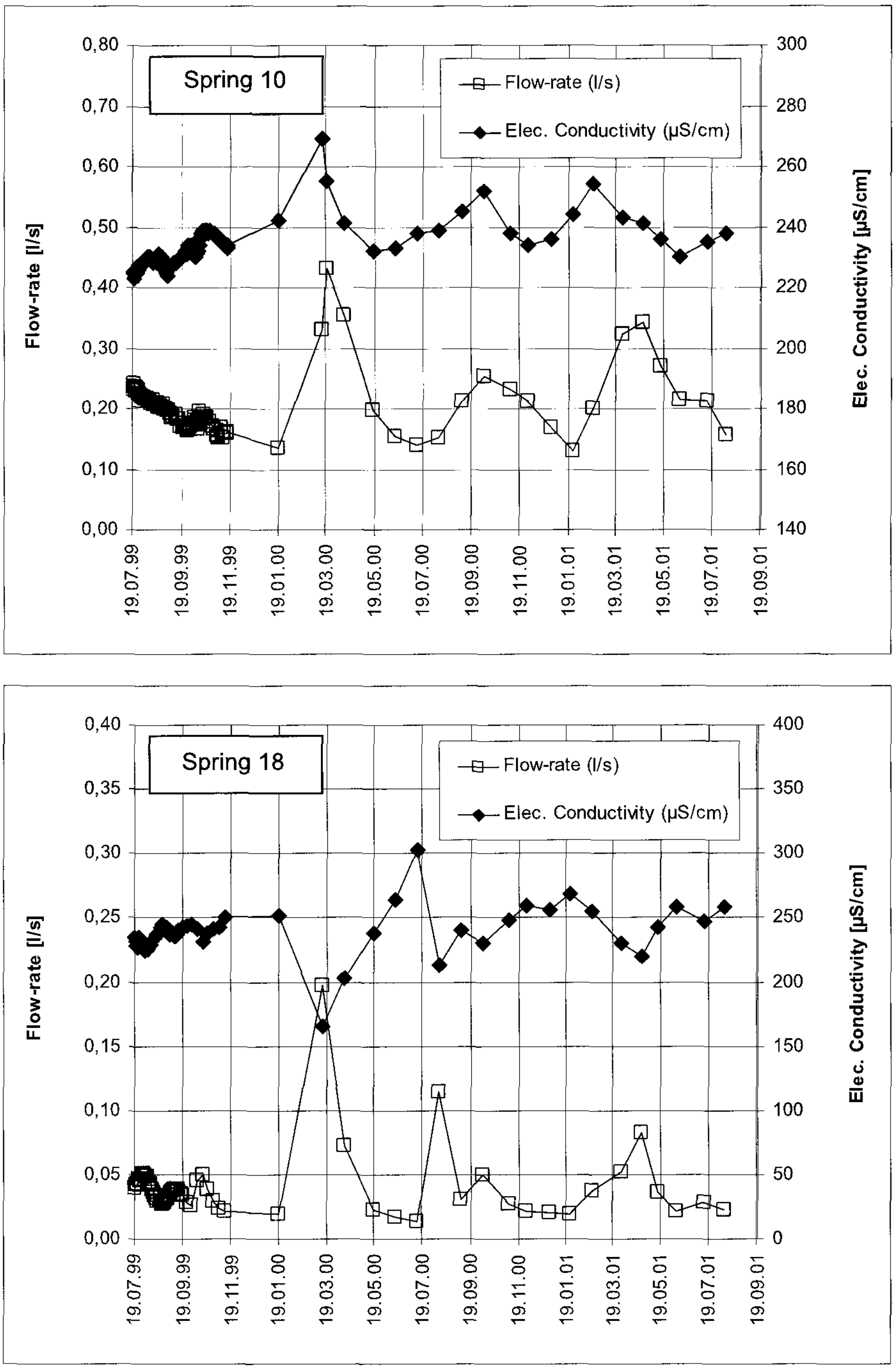
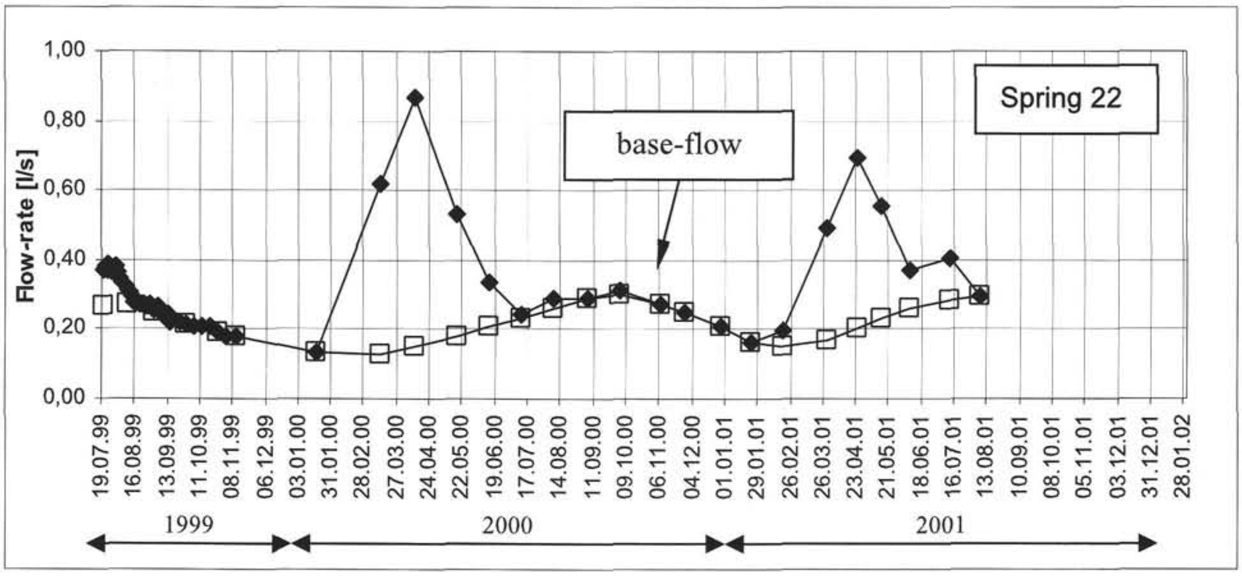
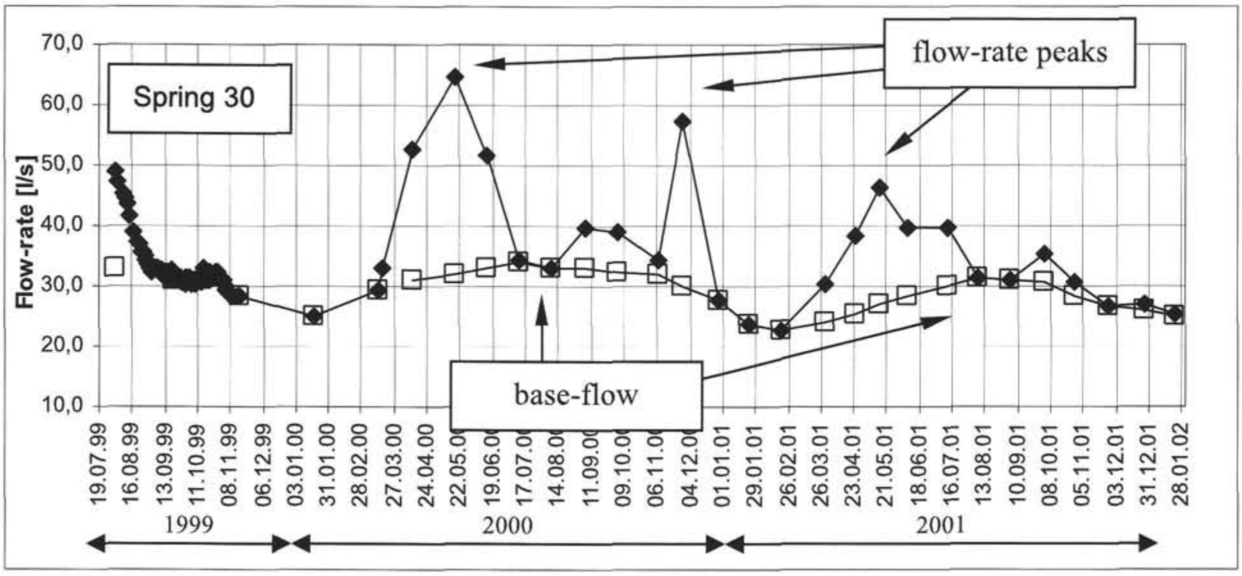


Figure 5
Spring 10 showing an increase in electrical conductivity with an increasing flow-rate leading to the conclusion that older, more highly mineralised water, is extruded during rapid infiltration of precipitation. Spring 18 showing a rapid decrease in electrical conductivity with an increase in flow-rate reflecting the highly permeable and porous nature of the source-aquifers. Closed diamonds and open squares are the measured values.


Spring 22
base-flow
Flow-rate [l/s]
1,00
0,80
0,60
0,40
0,20
0,00
19.07.99
16.08.99
13.09.99
11.10.99
08.11.99
06.12.99
03.01.00
31.01.00
28.02.00
27.03.00
24.04.00
22.05.00
19.06.00
17.07.00
14.08.00
11.09.00
09.10.00
06.11.00
04.12.00
01.01.01
29.01.01
26.02.01
26.03.01
23.04.01
21.05.01
18.06.01
16.07.01
13.08.01
10.09.01
08.10.01
05.11.01
03.12.01
31.12.01
28.01.02
1999
2000
2001


Spring 30
flow-rate peaks
base-flow
Flow-rate [l/s]
70,0
60,0
50,0
40,0
30,0
20,0
10,0
19.07.99
16.08.99
13.09.99
11.10.99
08.11.99
06.12.99
03.01.00
31.01.00
28.02.00
27.03.00
24.04.00
22.05.00
19.06.00
17.07.00
14.08.00
11.09.00
09.10.00
06.11.00
04.12.00
01.01.01
29.01.01
26.02.01
26.03.01
23.04.01
21.05.01
18.06.01
16.07.01
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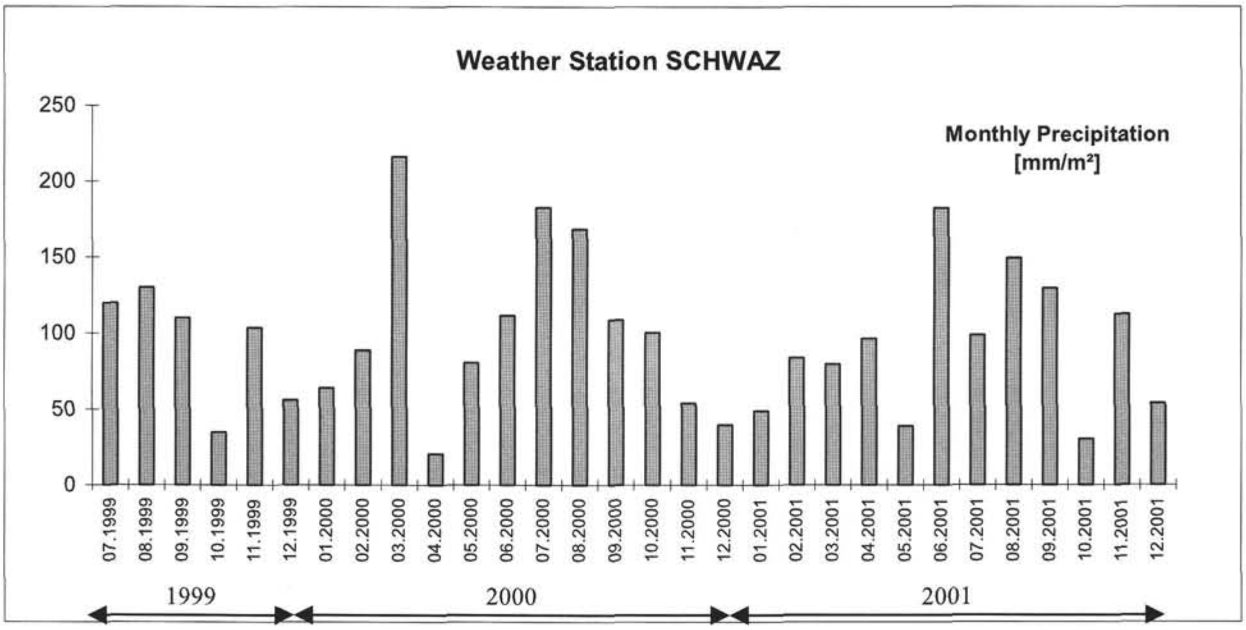
03.12.01
31.12.01
28.01.02
1999
2000
2001


Weather Station SCHWAZ
Monthly Precipitation [mm/m²]
250
200
150
100
50
0
07.1999
08.1999
09.1999
10.1999
11.1999
12.1999
01.2000
02.2000
03.2000
04.2000
05.2000
06.2000
07.2000
08.2000
09.2000
10.2000
11.2000
12.2000
01.2001
02.2001
03.2001
04.2001
05.2001
06.2001
07.2001
08.2001
09.2001
10.2001
11.2001
12.2001
1999
2000
2001

nuary to 18.9 °C in August. The average mean temperature, from data recorded from 1961 to 2000, is 8.2 °C.

3. The average flow-rates range between 0.02 and 33 l/s. Most springs show an immediate increase in flow-rate during or shortly after a precipitation event. The largest flow rates were measured at springs 29 and 30, which are the gravitational groundwater drainage systems of the now abandoned major mining areas within the Schwaz Dolomite (Fig. 3).

In general, flow-rates and temperatures reach a minimum in winter and a maximum in spring (snow melting period). The electrical conductivity in most springs decreases with increasing flow-rate. However, in some springs the opposite behaviour is observed, that is, increasing electrical conductivity with increasing in flow-rate (Fig. 5).

6.2 Groundwater Behaviour During Extreme Hydrological Events

During a heavy precipitation event from 16th to 17th of March 2000, when 125.9 mm of rain were recorded falling on a melting dm-thick cover of snow, tens of litres per second of groundwater (approx. temperature 4-5 °C, electrical conductivity 200-400 μS/cm) were extruded along fine grained sequences within the Buntsandstein behind the retaining dams, and Quaternary deposits in Zintberg and Ried. Other outflows were observed along the projection of the Nordrand Fault near springs 20 and 21. These groundwater outflows caused a series of small water saturated landslides (ILF 2000a). At the same time, or shortly after, the highest observed flow-rates of the springs were recorded (Fig. 5 and 6).

6.3 Base-flow marked by Karst-like Flow-rate Peaks

Of particular interest, is the flow-rate behaviour of springs 17, 19, 22, 23, 24, 26, 27, 28, 30, 37, 39, 42, 43 (Table 1 and Fig. 6). By close examination of the annual flow-rate curve, a sinus-like "base-flow", controlled by slow seepage of groundwater from the source-aquifers, is recognisable and marked in most cases by precipitation induced "karst-like flow-rate peaks". After a flow-rate peak the discharge decreases in these springs to that controlled by the base-flow. Dependent on the spring, the base-flow maximums occur sometime between July and September. At springs 17, 19, 30, 37, 39, 42 and 43 the flow-rate peaks occur frequently and are induced by precipitation events. In other cases, springs 22 and 23, the flow-rate peaks only occur during extreme hydrological events, such as the spring rains and snow melting period. Lastly, springs 24, 26, 27, and 28 exhibit behaviour that lies between the two extremes.

← Figure 6
Springs displaying "base-flow" marked by "karst-like flow-rate peaks". The behaviour of Springs 22 and 30 is shown. Closed diamonds are the measured flow-rates, open squares are the in-part interpreted base-flow values. Note the sinus-like base-flow controlled by slow seepage of groundwater from the source-aquifers. After a flow-rate peak the discharge decreases to that controlled by the base-flow. The monthly precipitation (mm/m^2) from the Weather Station Schwaz* is given (raw data).
*Data source: Hydrographischer Dienst, Innsbruck, Tyrol, Austria

6.4 Average Altitude of the Spring Catchment Areas Based on $\delta^{18}O$ Analysis

Based on $\delta^{18}O$ analysis, springs 28, 30, 39 and 43 have their AASCA between 1430 and 1550 m asl in the areas of the Lärchwiese and Mehrerkopf, ESE and E respectively, of the Eiblschrofen (Table 3 and Fig. 2 and 4). It is also possible that the catchment area of Spring 43 reaches into the region of Plumpmoos (Kellerjoch Gneiss Series), south of the Südrand Fault.

Springs 10 and 29 have an AASCA at approximately 1260-1280 m asl which is the area directly around the Eiblschrofen.

As discussed in Chapter 4, Spring 34 has highly variable $\delta^{18}O$ values (Table 4). During low flow-rates the spring has an AASCA of approximately 650 m asl, which is not much higher than its out-flow altitude of approx. 600 m asl. However, during high discharge e. g., on 11. 4. 2000, the $\delta^{18}O$ value approximates an infiltration altitude of around 1340 m asl.

6.5 Hydrochemistry

Table 7 gives the major chemical constituents of the springs. Six water types are observed, based on the occurrence of the major ions and the amount of dissolved substances (Table 8, Figs. 7 and 8):

Type 1: Ca-Mg-HCO_3 with a Ca/Mg ratio >1.8 and dissolved substances between 4 and 8 mmol/l. In some springs substantial amounts of K is present (up to 10 molar-%).

Type 2: Ca-Mg-HCO_3 with a Ca/Mg ratio >1.8, dissolved substances <4 mmol/l and in most cases a substantial amounts of SO_4 and Na (molar-%). Potassium is also present.

Type 3: Ca-Mg-HCO_3 and/or Mg-Ca- HCO_3 (variable behaviour from the same spring) with a Ca/Mg ratio <1.8 and dissolved substances between 4 and 8 mmol/l. Sulphate is also present.

Type 4: Ca-Mg-HCO_3 with a Ca/Mg ratio <1.8 and dissolved substances >8 mmol/l. Substantial amounts of SO_4 can also be present (up to 14 molar-%).

Type 5: Mg-Ca-HCO_3 and/or Ca-Mg-HCO_3 (variable behaviour from the same spring), substantial amounts of SO_4 can also be present (up to 16 molar-%)

Type 6: Mg-Ca-HCO_3-SO_4 and Ca-Mg-HCO_3-SO_4 (variable behaviour). Total dissolved substances >8 mmol/l.

6.6 Metal and Metalloid Content of the Spring-water

The content of the metals and metalloids Al, Cd, Cr, Fe, Pb, Mn and Hg, occurring in the spring-water, are either below the detectable limits or are found in small amounts which are well below recommended limits for drinking water and are therefore not given in Table 2.

Copper and Zn are widely detectable (Table 2 and Fig. 2). At some springs low levels of As were recorded. However, the Sb content in springs 4, 10, 15, 29, 30, 31, 32, 33, 34, 35, 36, 37, 39, 40, 42, 43 and 45 was up to 600 times above the World Health Organisation's (WHO 1993) recommended limits for drinking water (<0.005 mg/l).

Table 7
Major chemical constituents in the spring-water at Eiblschrofen, Schwaz. pH-values were measured in the laboratory.
Analyses carried out by Hydrologische Untersuchungsstelle, Salzburg (HUS)

Spring	Date of Sampling	pH Value	HCO_3	Ca	Mg	Na	K	Fe Total	Fe II	Mn	NH_4	NO_2	NO_3	Cl	SO_4	PO_4
			mg/l	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
1	28.07.99	7.24	146	38.9	7.2	2.7	2.2	<0.02	<0.02	<0.05	<0.02	<0.003	7.3	1.6	5.7	<0.01
2	28.07.99	7.64	185	46.9	10.4	4.5	3.8	0.13	0.13	<0.05	<0.02	<0.003	13.3	3.4	8.8	<0.01
3	28.07.99	7.49	173	44.0	9.6	4.9	15.4	0.18	0.18	<0.05	<0.02	<0.003	21.1	6.4	11.2	<0.01
4	28.07.99	7.55	188	49.7	10.3	4.6	11.0	0.12	0.12	<0.05	<0.02	<0.003	18.8	5.3	14.0	<0.01
5	28.07.99	7.21	156	36.2	10.2	2.9	3.0	0.07	0.07	<0.05	<0.02	<0.003	4.3	2.2	7.5	0.01
6	28.07.99	7.16	126	30.3	7.5	3.4	3.6	<0.02	<0.02	<0.05	<0.02	<0.003	4.9	2.3	6.4	0.03
7	28.07.99	7.75	204	44.7	14.9	3.8	3.1	<0.02	<0.02	0.12	<0.02	<0.003	5.0	3.2	9.8	<0.01
8	28.07.99	7.71	186	49.3	8.9	3.2	1.9	0.19	0.17	<0.05	<0.02	<0.003	4.3	2.6	7.3	<0.01
9	28.07.99	7.76	151	35.8	9.9	3.6	2.9	<0.02	<0.02	<0.05	<0.02	<0.003	6.7	2.5	9.9	<0.01
10	28.07.99	7.92	126	32.5	6.1	2.8	3.2	<0.02	<0.02	<0.05	<0.02	<0.003	5.3	1.8	6.2	<0.01
10	06.10.99	7.77	131	32.1	7.6	2.8	3.1	<0.02	<0.02	<0.05	<0.02	<0.003	5.1	1.9	7.0	<0.01
11	28.07.99	6.96	84.1	21.9	4.1	2.8	3.2	<0.02	<0.02	<0.05	<0.02	<0.003	3.6	1.6	6.4	<0.01
12	28.07.99	7.01	61	14.3	3.6	2.8	3.2	<0.02	<0.02	<0.05	<0.02	<0.003	3.1	1.7	5.9	<0.01
13	28.07.99	7.92	126	33.9	5.7	2.8	2.1	0.23	0.22	<0.05	<0.02	<0.003	4.5	1.8	6.0	<0.01
14	28.07.99	8.07	226	51.9	14.2	2.1	1.3	0.14	0.14	<0.05	<0.02	<0.003	4.9	1.2	4.8	<0.01
15	28.07.99	8.04	158	35.1	11.9	1.8	1.2	<0.02	<0.02	<0.05	<0.02	<0.003	3.1	0.5	7.6	0.08
16	28.07.99	7.83	136	34.3	7.7	3.0	3.1	0.21	0.20	<0.05	<0.02	<0.003	5.9	2.1	7.5	<0.01
17	28.07.99	7.99	259	38.1	32.4	3.2	2.3	<0.02	<0.02	<0.05	<0.02	<0.003	4.6	0.9	21.0	<0.01
18	28.07.99	7.72	138	31.0	9.0	1.9	1.0	<0.02	<0.02	<0.05	<0.02	<0.003	1.2	0.3	4.6	<0.01
19	28.07.99	7.52	216	46.1	20.6	3.2	1.8	0.14	0.12	<0.05	<0.02	<0.003	7.2	1.0	22.5	<0.01
20	28.07.99	7.49	192	40.0	15.7	2.0	1.0	0.72	0.71	<0.05	<0.02	<0.003	3.4	0.4	10.2	<0.01
21	28.07.99	7.23	70.8	14.4	4.4	1.4	2.5	<0.02	<0.02	<0.05	<0.02	<0.003	0.9	0.1	0.8	<0.01
22	28.07.99	6.61	37.5	9.0	2.9	2.4	1.0	0.15	0.14	<0.05	<0.02	<0.003	1.6	1.1	6.5	<0.01
23	28.07.99	7.30	39	8.9	2.7	2.2	0.8	0.31	0.30	<0.05	<0.02	<0.003	0.5	0.9	5.0	<0.01
24	28.07.99	6.49	36.9	8.7	2.5	2.2	1.0	0.16	0.15	<0.05	<0.02	<0.003	1.8	1.0	5.0	<0.01
25	28.07.99	6.48	36.2	9.0	2.2	2.2	1.0	0.07	0.04	<0.05	<0.02	<0.003	1.5	1.2	4.8	0.02
26	28.07.99	7.15	66.5	15.4	4.6	1.7	1.2	0.16	0.16	<0.05	<0.02	<0.003	2.1	0.3	5.5	<0.01
27	28.07.99	7.11	73.1	19.4	3.5	1.4	0.9	<0.02	<0.02	<0.05	<0.02	<0.003	1.0	0.3	5.2	<0.01
28	28.07.99	7.00	68.9	17.6	3.7	1.4	1.0	0.22	0.21	<0.05	<0.02	<0.003	1.5	0.4	5.3	<0.01
29	28.07.99	7.87	228	69.0	32.8	3.8	2.4	0.09	0.09	<0.05	<0.02	<0.003	5.4	2.6	116.0	0.05
29	06.10.99	8.02	229	61.7	39.2	3.7	2.2	0.10	0.08	<0.05	<0.02	<0.003	5.5	2.5	125.0	0.04
30	28.07.99	8.00	206	44.9	28.9	2.4	1.6	0.18	0.17	<0.05	<0.02	<0.003	5.0	0.9	60.7	0.03
30	06.10.99	8.05	210	43.0	35.7	3.1	1.9	<0.02	<0.02	<0.05	<0.02	<0.003	5.3	1.0	79.2	0.04
31	24.08.99	7.93	216	38.2	26.6	0.8	1.2	0.05	0.03	<0.05	<0.02	<0.003	5.4	1.1	23.5	0.10
31	06.10.99	8.01	209	38.7	22.6	0.3	0.5	<0.02	<0.02	<0.05	<0.02	<0.003	5.8	0.2	10.6	0.12
32	06.10.99	8.12	214	32.8	31.7	0.8	1.9	0.74	0.74	<0.05	<0.02	<0.003	7.1	0.6	33.9	0.35
34	24.08.99	7.91	121	26.4	11.5	0.3	0.5	0.05	0.04	<0.05	<0.02	<0.003	4.7	0.2	9.7	0.22
34	06.10.99	7.67	113	21.4	13.2	0.4	0.6	<0.02	<0.02	<0.05	<0.02	<0.003	5.8	0.3	10.7	0.24
35	24.08.99	8.08	303	65.2	26.4	1.3	1.1	<0.02	<0.02	<0.05	<0.02	<0.003	5.3	0.9	18.9	0.05
35	06.10.99	8.23	282	50.4	31.2	1.2	1.1	<0.02	<0.02	<0.05	<0.02	<0.003	7.4	0.7	19.0	0.07
36	24.08.99	7.77	312	75.0	26.6	1.7	1.2	<0.02	<0.02	<0.05	<0.02	<0.003	6.6	1.7	40.6	<0.01
36	06.10.99	7.87	320	66.3	35.9	1.8	1.1	<0.02	<0.02	<0.05	<0.02	<0.003	7.1	1.7	41.9	<0.01
37	28.07.99	8.04	166	30.4	16.8	0.5	0.8	0.26	0.25	<0.05	<0.02	<0.003	3.8	0.4	7.7	0.10
38	28.07.99	7.88	292	51.8	28.5	0.6	0.3	0.16	0.16	<0.05	<0.02	<0.003	6.1	0.1	4.9	<0.01
39	28.07.99	8.03	162	29.7	16.9	0.4	0.7	<0.02	<0.02	<0.05	<0.02	<0.003	4.1	0.4	6.9	<0.01
40	28.07.99	7.70	234	36.7	25.5	3.4	1.4	0.16	0.16	<0.05	<0.02	<0.003	2.0	0.6	12.5	<0.01
41	28.07.99	7.87	267	29.8	33.4	6.6	4.5	0.59	0.51	0.53	0.23	0.003	<0.1	0.4	15.0	<0.01
42	28.07.99	8.05	135	26.4	12.3	0.3	0.5	0.17	0.15	<0.05	<0.02	<0.003	4.0	0.3	4.9	0.04
43	28.07.99	8.04	195	36.3	18.5	0.8	0.8	0.22	0.21	<0.05	<0.02	<0.003	3.3	0.6	3.8	<0.01
43	06.10.99	8.05	207	33.6	22.5	0.9	0.9	<0.02	<0.02	<0.05	<0.02	<0.003	3.3	0.5	5.4	<0.01
44	24.08.99	7.50	309	73.5	31.0	2.1	0.4	<0.02	<0.02	<0.05	<0.02	<0.003	30.9	2.3	32.5	<0.01
45	28.07.99	8.07	168	30.1	17.3	0.4	0.4	0.26	0.26	<0.05	<0.02	<0.003	4.2	0.3	5.6	<0.01

Table 8
Major ions, total dissolved substances, Ca/Mg molar ratio, Na molar-%, SO_4 molar-% and water types occurring in the springs at the Eiblschrofen, Schwaz. For clarity, when two water analyses exist from the same spring, these are shown.

* Major cations and anions are in descending order where the mmol-equivalent concentrations are >20%

Spring	Date of Sampling	Major Cations and Anions*	Total Dissolved Substances	Ca/Mg Molar Ratio	Na Molar %	SO_4 Molar %	Water Type
			mmol/l				
1	28.07.99	Ca-Mg-HCO3	5.382	3.28	4.3	4.4	1
2	28.07.99	Ca-Mg-HCO3	7.019	2.73	5.6	5.2	1
3	28.07.99	Ca-Mg-HCO3	7.188	2.78	5.9	6.5	1
4	28.07.99	Ca-Mg-HCO3	7.639	2.93	5.2	7.6	1
5	28.07.99	Ca-Mg-HCO3	5.693	2.15	4.4	5.5	1
6	28.07.99	Ca-Mg-HCO3	4.712	2.45	6.2	5.7	1
7	28.07.99	Ca-Mg-HCO3	7.420	1.82	4.5	5.5	1
8	28.07.99	Ca-Mg-HCO3	6.730	3.36	4.1	4.5	1
9	28.07.99	Ca-Mg-HCO3	5.691	2.19	5.5	7.2	1
10	28.07.99	Ca-Mg-HCO3	4.658	3.23	5.2	5.5	1
10	06.10.99	Ca-Mg-HCO3	4.857	2.56	5.0	6.0	1
11	28.07.99	Ca-Mg-HCO3	3.249	3.24	7.5	8.3	2
12	28.07.99	Ca-Mg-HCO3	2.434	2.41	10.0	10.1	2
13	28.07.99	Ca-Mg-HCO3	4.658	3.61	5.2	5.4	1
14	28.07.99	Ca-Mg-HCO3	7.805	2.22	2.3	2.6	1
15	28.07.99	Ca-Mg-HCO3	5.652	1.79	2.8	5.6	3
16	28.07.99	Ca-Mg-HCO3	5.102	2.70	5.1	6.1	1
17	28.07.99	Mg-Ca-HCO3	9.547	0.71	2.9	9.1	5
18	28.07.99	Ca-Mg-HCO3	4.781	2.09	3.4	4.0	1
19	28.07.99	Ca-Mg-HCO3	8.338	1.36	3.3	11.3	4
20	28.07.99	Ca-Mg-HCO3	6.851	1.55	2.5	6.2	3
21	28.07.99	Ca-Mg-HCO3	2.400	1.98	5.1	1.4	2
22	28.07.99	Ca-Mg-HCO3	1.630	1.88	12.7	16.8	2
23	28.07.99	Ca-Mg-HCO3	1.570	2.00	12.1	13.4	2
24	28.07.99	Ca-Mg-HCO3	1.533	2.11	12.5	13.6	2
25	28.07.99	Ca-Mg-HCO3	1.505	2.48	12.7	13.3	2
26	28.07.99	Ca-Mg-HCO3	2.504	2.03	5.9	9.2	2
27	28.07.99	Ca-Mg-HCO3	2.671	3.36	4.5	8.1	2
28	28.07.99	Ca-Mg-HCO3	2.552	2.88	4.8	8.7	2
29	28.07.99	Ca-Mg-HCO3-SO4	12.685	1.28	2.6	38.3	6
29	06.10.99	Mg-Ca-HCO3-SO4	13.041	0.96	2.5	39.9	6
30	28.07.99	Mg-Ca-HCO3-SO4	9.517	0.94	2.2	26.6	6
30	06.10.99	Mg-Ca-HCO3-SO4	10.472	0.73	2.6	31.7	6
31	24.08.99	Mg-Ca-HCO3	8.311	0.87	0.8	11.8	5
31	06.10.99	Ca-Mg-HCO3	7.563	1.03	0.3	5.9	5
32	06.10.99	Mg-Ca-HCO3	8.703	0.63	0.8	16.2	5
34	24.08.99	Ca-Mg-HCO3	4.560	1.39	0.6	8.9	3
34	06.10.99	Mg-Ca-HCO3	4.366	0.98	0.8	10.2	3
35	24.08.99	Ca-Mg-HCO3	10.981	1.50	1.0	7.2	5
35	06.10.99	Mg-Ca-HCO3	10.320	0.98	1.0	7.7	5
36	24.08.99	Ca-Mg-HCO3	12.149	1.710	1.2	13.8	4
36	06.10.99	Ca-Mg-HCO3	12.648	1.12	1.2	13.9	4
37	28.07.99	Ca-Mg-HCO3	5.905	1.10	0.7	5.4	3
38	28.07.99	Ca-Mg-HCO3	9.958	1.10	0.5	2.0	4
39	28.07.99	Ca-Mg-HCO3	5.784	1.07	0.6	5.0	3
40	28.07.99	Mg-Ca-HCO3	8.624	0.87	3.6	6.3	5
41	28.07.99	Mg-Ca-HCO3	9.370	0.54	6.1	6.6	5
42	28.07.99	Ca-Mg-HCO3	4.749	1.30	0.6	4.3	3
43	28.07.99	Ca-Mg-HCO3	6.742	1.19	1.0	2.4	5
43	06.10.99	Mg-Ca-HCO3	7.163	0.91	1.1	3.1	5
44	24.08.99	Ca-Mg-HCO3	12.624	1.44	1.4	10.7	4
45	28.07.99	Ca-Mg-HCO3	5.909	1.06	0.6	4.0	3

6.7 Elution and Mass Substance Analysis

The mass substance analysis of the tailings, consisting of sand sized crushed dolomite (Pochwerkssande), revealed that the elements Cu, Hg and Ag were present in large amounts (Table 5). The elution experiments, using distilled water, revealed that Sb, As and Cu could be readily removed from the absorbent (Pochwerkssande).

7. Geological Controls of Groundwater Movement

Geological units which are hydrogeologically important in the study area are the Wildschönau Phyllites, Stengel Gneiss and Schwaz Dolomite containing the antimony rich sulphidic deposits, the Basal Breccia, Gröden Formation, Lower and Upper Alpine Buntsandstein and Reichenhall Formation, and the Quaternary and anthropic rocks along with the weathering and talus deposits.

Rock units with good porosity and permeability are the Schwaz Dolomite, some parts of the Reichenhall Formation e. g. dissolved parts of the rauhwackes and tectonically deformed limestones, the mine tailings and the weathering and talus deposits. The Wildschönau Phyllites and Stengel Gneiss generally have a poorer porosity and lower permeability except when deformed (tectonics, mass movement and mining practices) in a brittle manner. Finally, parts of the Quaternary glacial deposits and the fine grained and weathered sequences within the Buntsandstein form observable hydrological barriers (aquitards).

The open bedding and schistosity planes, joints, faults and natural and man-made fractures, which are found in the basement units, play a very important role in the hydrogeological behaviour of the area and the location of the springs. At the surface, the bedding and schistosity planes in the Palaeozoic rocks are overturned and generally dipping moderately SW, east and south-east of the Eiblschrofen and moderately S-SSW, west of the Eiblschrofen. The bedding planes of the Permian – Triassic rocks are also overturned, generally dipping moderately to steeply to the SSE. The younger NW-SE striking faults (e. g. Westrand Fault) and the open NE-SW trending fractures (related to recent mass movement), act as hydrological conductors. The older E to NE striking, sub vertical to steeply SE-dipping faults (e. g. Nordrand Fault) act as hydrological barriers. The hundreds of abandoned mine shafts and caverns also enhance the karst-like behaviour of the groundwater, particularly within the Schwaz Dolomite (Figs. 2 and 3).

8. Aspects of the Source-Aquifers and Spring Behaviour

The source-aquifers of the Eiblschrofen Massif are complex, consisting of anthropic and natural rocks and influenced by both natural and man-made deformation. The "springs" are either naturally occurring gravity springs or groundwater ingresses (gravitationally driven outflow) which were encountered and captured during mining in the area. The springs, regardless of whether they are natural or not, are located/emerge: 1) along faults 2) at the contact between two litho-units e. g. tailings and basement rock 3) directly along open bedding and schistosity planes, joints and fractures.

Most springs show an increase in flow-rate followed by a rapid decrease in the electrical conductivity, during or shortly after a precipitation event and/or during the snow melting period (Figs. 5 and 6). Such behaviour reflects the highly permeable and porous nature of the source-aquifers within the Eiblschrofen Massif. Faulting and fracturing due to tectonics, mass movement culminating in the development of cavities and fractures – the result of both natural (geological and geomorphological framework) and man-made causes (large-scale underground mining), fracturing caused by explosives, the many mining shafts and caverns and the pervious nature of the talus and tailings are the major reasons why the source-aquifers have a highly porous and permeable nature.

In other springs, an increase in the electrical conductivity occurs slightly before an increase in the flow-rate, leading to the conclusion that older, more highly mineralised water, which is extruded during rapid infiltration of precipitation, is present in the source-aquifers. In addition, springs 9, 10, 13,18, 22, 24, 26, 29, 30, 37, 39, 41, 42, 43 and 45 display small annual 1-2°C water temperature fluctuations (Table 1), and where data exists, small fluctuations in the their $\delta^{18}O$ values (Table 3). Such properties indicate the presence of deep-reaching circulation, good mixing and longer residence times of the groundwater within the source-aquifers. Paradoxically, springs 24, 26, 37 and 42 have low or no discharge in winter, something not normally observed in springs with stable water temperatures. This lacking or low discharge is probably not caused by the "drying-up" of their source aquifers, but more likely caused by the "low level" of the groundwater prevailing in the source-aquifers during winter. With the onset of spring, aquifer recharge occurs and with it a rapidly rising groundwater table resulting in an "overflow" situation, which causes these springs to discharge again.

With the exception of springs 9, 10, 18 and 29 – for springs 13, 41 and 45 an accurate flow-rate could not be measured – all springs, with small annual 1-2°C water temperature fluctuations, also possess the sinus-like "base-flow" curve, marked by precipitation induced "karst-like flow-rate peaks", as described in Chapter 8. This phenomenon is recognisable in springs occurring north of Grüntal, which have their source-aquifers mainly within the Schwaz Dolomite, and in springs around Lärchwiese and Eiblschrofen, which have their source-aquifers mainly within the Stengel Gneiss and Wildschönau Phyllites. All these areas contain fractures developed during the recent mass movements. The phenomenon can be interpreted as follows. Small pore spaces, such as open bedding and schistosity planes, provide the necessary porosity to store groundwater and create the "base-flow". The larger fractures, faults and old mine shafts, act as "karst-like elements", which during extreme hydrological conditions and heavy precipitation provide the necessary porosity to create high flow-rates.

9. Hydrochemistry – Antimony Occurrence

As presented in Chapter 8, six water types are observed in the springs of the Eiblschrofen Massif (Table 7 and 8,

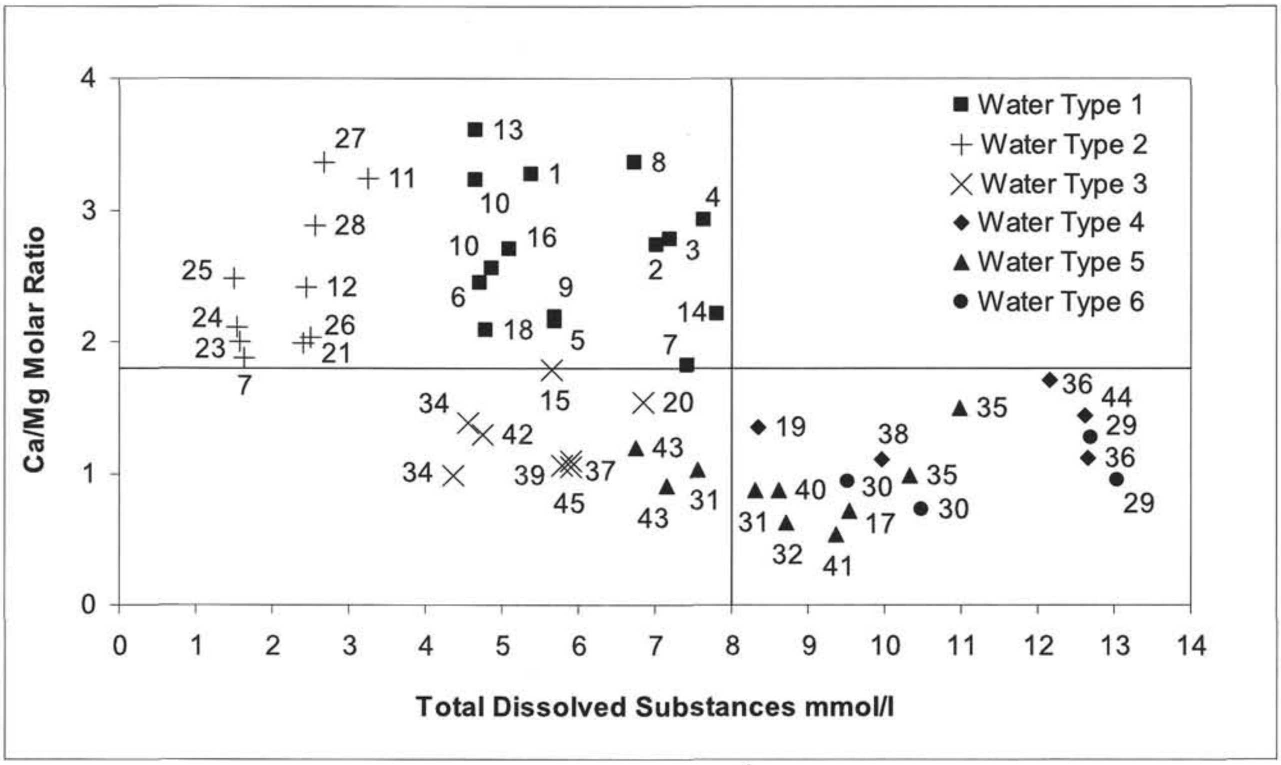


Figure 7
Ca/Mg molar ratio vs. total dissolved substances of the spring-water from the Eiblschrofen Massif. Horizontal line marks Ca/Mg ratio of 1.8. Vertical line indicates total dissolved substances of 8 mmol/l. All analyses and spring numbers are shown – note the variation in the Ca/Mg molar ratio where two analyses from the same Spring exist e. g. Spring 34. Closed squares are Water Type 1, vertical crosses are Water Type 2, diagonal crosses are Water Type 3, closed diamonds are Water Type 4, closed triangles are Water Type 5 and closed circles are Water Type 6 – see text for explanation.

Figs. 7 and 8). The chemical make-up and concentrations of the spring-waters is heavily dependent on the lithological compositions of the source-aquifers and the residence times. Water Types 1 and 2 have Ca/Mg ratios >1.8 implying dissolution of, in this study, mainly Ca-rich phyllite and/or Mg-depleted gneiss. Types 3, 4, 5 and 6 have Ca/Mg ratios <1.8, implying dissolution of mainly Mg-rich dolomite. This variation in the Ca/Mg ratio versus total dissolved substances of the springs is graphically illustrated in Figure 7. By taking into consideration the SO_4 and Na content (molar-%) of the water, further differentiation of mineralisation sources is possible (Fig. 8).

Water Type 1 occurs in springs 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 13, 14, 16 and 18 within the Zintberg area and differentiates itself from Type 2, which occurs in springs 11, 12, 21, 22, 23, 24, 25, 26, 27 and 28 in the Lärchwiese area, due to a higher amount of total dissolved substances and, in general, lower molar percentages of Na and SO_4 (Figs. 7 and 8). This difference is thought to be due to the presence of mainly Wildschönau Phyllite in the Zintberg area and Stengel Gneiss in the Lärchwiese area. The phyllite, on the one hand, is probably more soluble and/or retains the groundwater longer than the gneiss, leading to a generally greater mineralisation of the water. The gneiss, on the other hand, contains higher percentages of Na-rich feldspar (tuffs), which on dissolution taints the water with Na. Both rock types host pyrite, which is the most likely source of the SO_4 content of the water (Fig. 2 and Tables 2, 7 and 8). The Buntsandstein sequences, which contain K-feldspar, probably have an influence on the K input into Water Type 1 springs in the Zintberg area. Water Types 1 and 2 contain notable amounts of Zn (Fig. 2).

With the exception of Spring 4, no springs with Water Types 1 and 2 contain Sb. The high Sb content of Spring 4, which also has a relatively high mineralisation (Table 1 and Fig. 7), leads to the conclusion that either tailings containing Sb have been dumped in the spring catchment area or that Sb-bearing dolomite slices occur in the source-aquifer at depth.

Water Types 3, 4 and 5 occur randomly throughout the geographical area but can still be related to the varying lithological units of the Eiblschrofen Massif. Type 5 is generally more Mg-rich than Type 3 and 4, suggesting the dominance of dolomite and/or tailings in the catchment areas of springs 17, 31, 32, 35, 40, 41 and 43. Types 3 and 4 have similar Ca/Mg-ratios, however, Type 4 has a higher mineralisation. Springs 19, 36, 38 and 44, which have Water Type 4, generally emerge from within the Permian-Triassic and/or glacial deposits and with the exception of Spring 36, which probably contains groundwater which has percolated through the fahlore-rich tailings, is why they do not contain Sb. Further, it can then be presumed that the SO_4 content of Water Type 4 of springs 19, 38 and 44 most likely comes from gypsum within the Reichenhall Formation.

Springs 37, 39, 42 and 45, which have Water Type 3, probably draw their water from source-aquifers consisting of Schwaz Dolomite and Wildschönau Phyllite and/or Stengel Gneiss. This assumption is based on the results of the $\delta^{18}O$ analysis (Table 3) and the fact that they are generally richer in Ca and not as highly mineralised as springs with

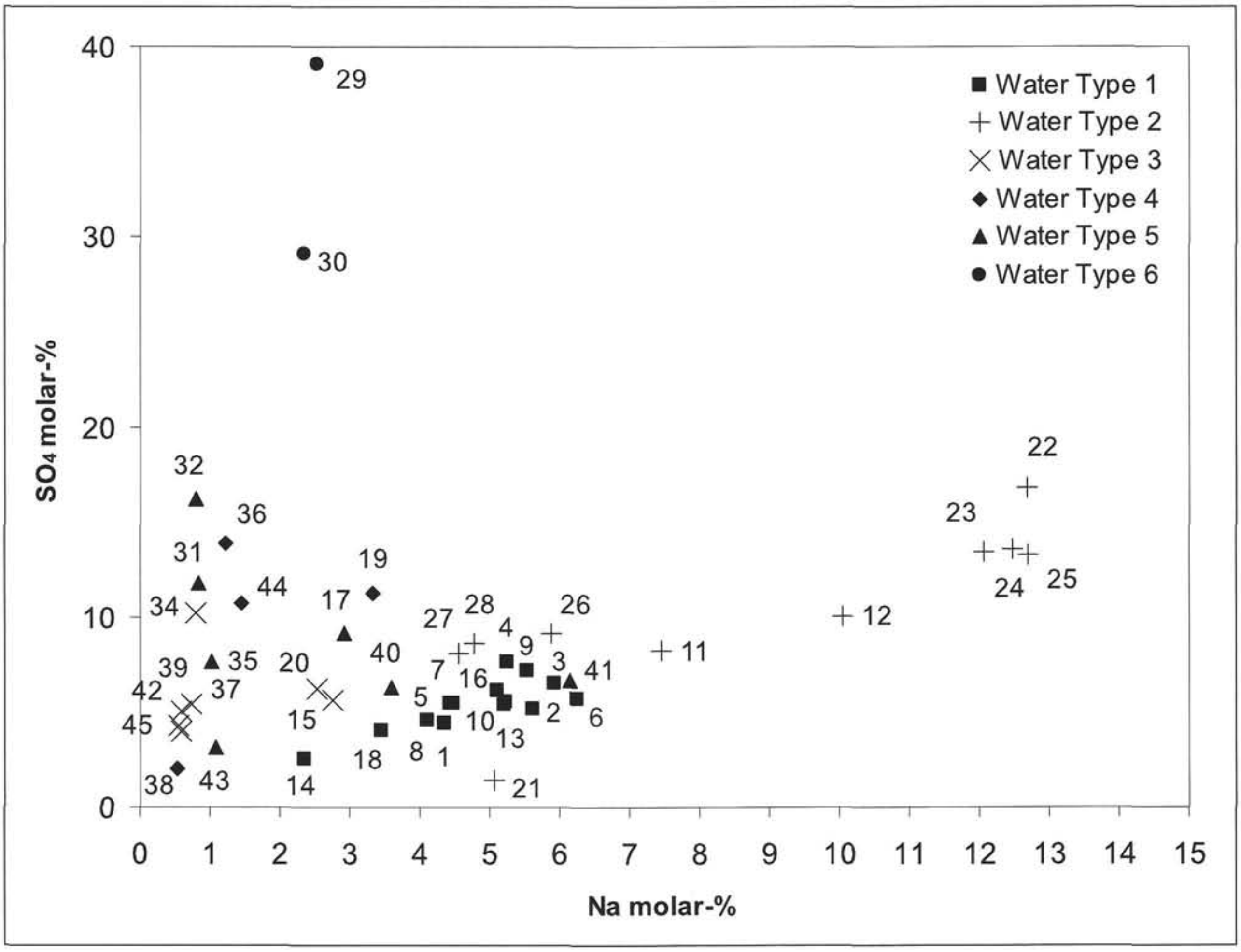


Figure 8

SO_4 molar-% vs. Na molar-% of the spring-water from the Eiblschrofen Massif. An average value is plotted where more than one analysis exists from the same spring. Note the large content of Na in Water Type 2 and SO_4 in Type 6. Spring numbers are shown. Closed squares are Water Type 1, vertical crosses are Water Type 2, diagonal crosses are Water Type 3, closed diamonds are Water Type 4, closed triangles are Water Type 5 and closed circles are Water Type 6 – see text for explanation.

Water Types 4 and 5. Spring 34, which also has Water Type 3, emerges from within tailings. The SO_4 content of Water Types 3 and 5 is probably due to the dissolution of the sulphidic assemblages hosted by the Schwaz Dolomite and/or the tailings. All springs with Water Types 3 and 5 contain Sb.

Springs 29 and 30 have Water Type 6 – variable Mg-Ca-HCO_3-SO_4 and Ca-Mg-HCO_3-SO_4 behaviour – and by far the largest average flow-rates which are 11.9 l/s and 33.7 l/s respectively. Both springs drain large abandoned mining areas deep within the Eiblschrofen. The SO_4 content of Springs 29 (116.0-125.0 mg/l) and 30 (60.7-79.2 mg/l) is large in comparison to the other springs (Fig. 8). It is known that most of the water discharging at Spring 30 emerges in the large caverns and many shafts within the Schwaz Dolomite (Fig. 3) – the results of the $\delta^{18}O$ analyses also support these findings (Table 3) – and is then channelled through the Permian-Triassic deposits in a concrete gully leading to the conclusion that the sulphidic assemblages (fahlore, pyrite and stibnite) hosted by the Schwaz Dolomite is the main source of the SO_4 content and not the gypsum within the Reichenhall Formation. The location of the water ingresses within the shafts and caverns of the mining area constituting Spring 29 are not well known. Therefore, it is possible that water emerging from within the Schwaz Dolomite is not the only source, but water emerging from within the Permian-Triassic deposits also makes-up Spring 29. This in turn could be the cause of the higher mineralisation and larger SO_4 content (gypsum – Reichenhall Formation) of Spring 29. Both Spring 29 and 30 contain Sb.

10. Nature of the Antimony Occurring in the Spring-water

The high concentrations of Sb (up to 3 mg/l) occurring in the spring-waters at the Eiblschrofen Massif are of a geogenic nature and can be attributed to the dissolution of the Sb-rich sulphidic assemblages hosted predominantly within the Schwaz Dolomite. Elution experiments on sand samples (Pochwerksande – crushed sand sized dolomite) from the tailings revealed that the Sb compounds occurring in the Eiblschrofen Massif are soluble in water (3.2-13.0 mg/kg-substance; Table 5). The reasons for their high solubility can only be speculated about. Data with regards to the oxidised forms of the sulphidic assemblages and their properties appear not to exist. The highest Sb concentrations were found in springs whose catchment areas contain large amounts of tailings e. g. in the springs emerging below the retaining dams. However, dissolution processes deep within the Schwaz Dolomite can not be ruled out due to the presence of Sb in springs which are generally regarded to be emerging primarily from hard rock (e. g. Spring 30).

The hydrous forms of the Sb occurring at the Eiblschrofen Massif are considered to be pentavalent (JENEWEIN pers. com. 1999 – Institute for Environmental Hygiene, University of Innsbruck). The spring-water in which the Sb occurs is oxygen rich and has pH values from 7.5 to 8.2 (Table 7).

No acute health problems or significant amounts of Sb in the food-chain were immediately recognisable after a testing campaign in the Eiblschrofen area (JENEWEIN pers. com. 1999 – Institute for Environmental Hygiene, University of Innsbruck). It should also be remembered that the inhabitants of Schwaz have been drinking this water for centuries with no immediately recognisable adverse health effects. This would appear to corroborate the findings of GEBEL (1999a), that a transfer of Sb to humans through geogenic exposition only takes place, if at all, in negligible amounts.

11. Conclusions

The monitoring programme carried out during and after the "Eiblschrofen Rock Fall Event" of 1999 revealed the following hydrogeological aspects; 1. The springs exhibit a wide range of temperature, electrical conductivity and discharge rates, which reflect the nature and size of the source-aquifers and the geology of the area; 2. Six distinct types of spring-water occur which can be linked to the variable lithological units of the source-aquifers; 3. The geological and anthropic deformation of the Eiblschrofen Massif plays an important role in producing the karst-like character of the source-aquifers within the Eiblschrofen Massif; 4. The Sb content of the spring-water is geogenic in nature and although extremely large (up to 3 mg/l) appears to cause no acute health problems.

12. Acknowledgements

Thanks to: the "Forsttechnischer Dienst für Wildbach- und Lawinenverbauung – Geologische Stelle (WLV)" (Forest Engineering Service on Torrent and Avalanche Control – Geological Division, Innsbruck, Austria) for allowing me to reproduce the data presented in this paper; Fini PATSCHEIDER for line drawing the geological map and cross-section; Gary POSCHER, Franz REITER, Hugo ORTNER and an anonymous person for the many helpful comments and critically reviewing the paper.

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Manuscript received: 28. 02. 2002 ●
Revised version received: 08. 11. 2002 ●
Manuscript accepted: 30. 01. 2003 ●