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The impact of mining activities on the environment reflected by pollen, charcoal and geochemical analyses

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ABSTRACT

This article presents results of a multi-proxy study of a fen deposit in the former mining district of Falkenstein near Schwaz in the Tyrol, Austria. The aim of the study in the framework of the special research program HiMAT (The History of Mining Activities in the Tyrol and Adjacent Areas – Impact on Environment & Human Societies) was to disclose the ecological impact of mining in pollen and heavy metal diagrams and to create a model combining the changes in palaeoecological proxies with historical evidences for mining. The application of this palaeoecological–historical model to prehistoric times allowed us to reconstruct the impact of mining and metallurgic activities in the surroundings of the fen during the last millennia. The results of stratigraphy, radiocarbon dating, LOI, pollen and micro-charcoal analyses as well as geochemical analyses of scandium, lead and lead isotopes validated by historical and archaeological data are hereby presented.

1. Introduction

Human impact on the environment is mainly expressed by settlement activities and agriculture, but also mining – encompassing ore exploitation and processing – has significant ecological consequences. Mires as archives of vegetation history, anthropogenic activities and atmospheric metal deposition are predestinated to reconstruct the impact of mining on the environment. The palaeoenvironmental data of pollen, micro-charcoal and geochemical analyses are useful to explain human–environment interactions in the mining landscape (Mighall et al., 2002a).

Geochemical analyses of the last decades disclose peat deposits as archives for both palaeobotanical purposes and as a source of information about past atmospheric pollution (Shotyk, 1996a; and Martínez-Cortizas et al., 2002b). Beside studies about the reconstruction of atmospheric pollution in peat and lake deposits across Europe (Bränvall et al., 1997; Martínez-Cortizas et al., 1997; Shotyk, 2002; De Vleeschouwer et al., 2007) and the impact of mining on regional and local scales (Bränvall et al., 1999; Mighall et al., 2002b, 2009; Le Roux et al., 2004; Cloy et al., 2005), the multi-proxy research on the environmental impact of palaeometallurgy by pollen and geochemical analyses (Monna et al., 2004a,b; Baron et al., 2005; Jouffroy-Bapicot et al., 2007) seems to reveal the past more clearly.

In the majority of the recent palaeoecological studies in former mining areas, lead is used to detect mining phases in pollen diagrams in order to recognise mining-induced changes in the vegetation. In ombrotrophic peat bogs lead is effectively immobilized (Vile et al., 1995, 1999; Shotyk et al., 1997; MacKenzie et al., 1997; Weiss et al., 1999a,b), allowing them to be used as archives for the reconstruction of atmospheric Pb deposition (Bränvall et al., 1997; Cortizas et al., 1997; Farmer et al., 1997; Shotyk et al., 1998, 2002). Although bogs are thought to provide better geochemical data, it has recently been shown that fens, too, are suitable to record atmospheric deposition without significant distortion. The lead concentration profiles in minerogenic peat deposits suggest that atmospheric sources of lead are quantitatively more important than Pb supplied by groundwater (Shotyk et al., 2000). Additionally, West et al. (1997) showed that the variations in lead concentrations might not be the result of inputs from weathering of local soils and

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rocks as well as changes in the mineral fraction sedimentation, if the atmospheric deposition appears more important. Thus, the isotopic ratio of lead $^{206}Pb/^{207}Pb$ could be helpful in distinguishing between these two sources.

Here we present a pollen, micro-charcoal and geochemical study of a minerotrophic peat core sampled in the former prominent mining area of Schwaz in the Tyrol. The objective is to analyse the palaeoenvironmental impact since the beginning of mining activities in this area. Geochemical analyses of the peat disclose mining activities, whereas parallel pollen studies reveal the impact of mining and settlement activities on the local vegetation. Additionally, historical and archaeological data available for the last 4000 years validate the pollen data. This approach should enable the separation of the signals of mining and settlement in the pollen data and to create a palaeoecological model for mining, applicable to other mining regions.

2. Context, sampling site and study location

The Eastern Alps contain a big amount of profitable ore deposits, thus being a region with a long tradition of mining (Eibner, 1992; Höppner et al., 2005). One of the most prominent mining areas beside the Mitterberg region near Salzburg and the Kelchalpe near Kitzbühel is the region between Schwaz and Brixlegg in the Tyrolian Inn-valley. In this area man has been extracting copper ores from the bedrock since at least the Early to Middle Bronze Age (Goldenberg, 1998; Goldenberg and Rieser, 2004) and the local use of copper for creating artefacts is already documented for the beginning of the fourth millennium BC (Matuschik, 1997; Huijsmans et al., 2004). Archaeological findings and historical references confirm metallurgic activities concerning copper and silver production in the mining district of Falkenstein near Schwaz in Prehistoric and Post-Roman Times (Bartels et al., 2006). In such a situation of successive periods of mining activity, the reconstruction of the mining history of the site may be envisaged through the combination of pollen and geochemical analyses of mires (Monna et al., 2004a).

The investigation area in the lower Inn-valley (Tyrol – Austria) is located nearby Schwaz at the orographically right side to the river Inn at the north-western slope of the Mehrerkopf (Fig. 1). The northern Austroalpine Greywacke Zone around the former mining centre Schwaz consists of dolomites, schists and porphyric gneisses. The ore deposits situated in the Devonian Schwaz Dolomite are thought to be the result of hydrothermal metal transport in the lower Devonian sedimentation environment. This mineral deposit exploited at the Falkenstein mining district contains mainly fahlore of the tennantite–tetrahedrite series ($Cu_{12}As_4S_{13}$–$Cu_{12}Sb_4S_{13}$) (Gstrein, 1988). Copper, antimony, arsenic and sulphur are the main components as indicated by the formula. Minor components are silver, mercury, iron, zinc and bismuth which substitute copper in the fahlore crystals. Chalcopyrite and galena are also present in the ore, but scarce. Therefore the lead concentration in the ore is low and ranges between 2 and 180 μg/g in some of the chemically analyzed samples. In the Bronze Age, the ores were mined for copper, whereas silver was the main target in medieval and (early) modern times. Due to low lead concentrations

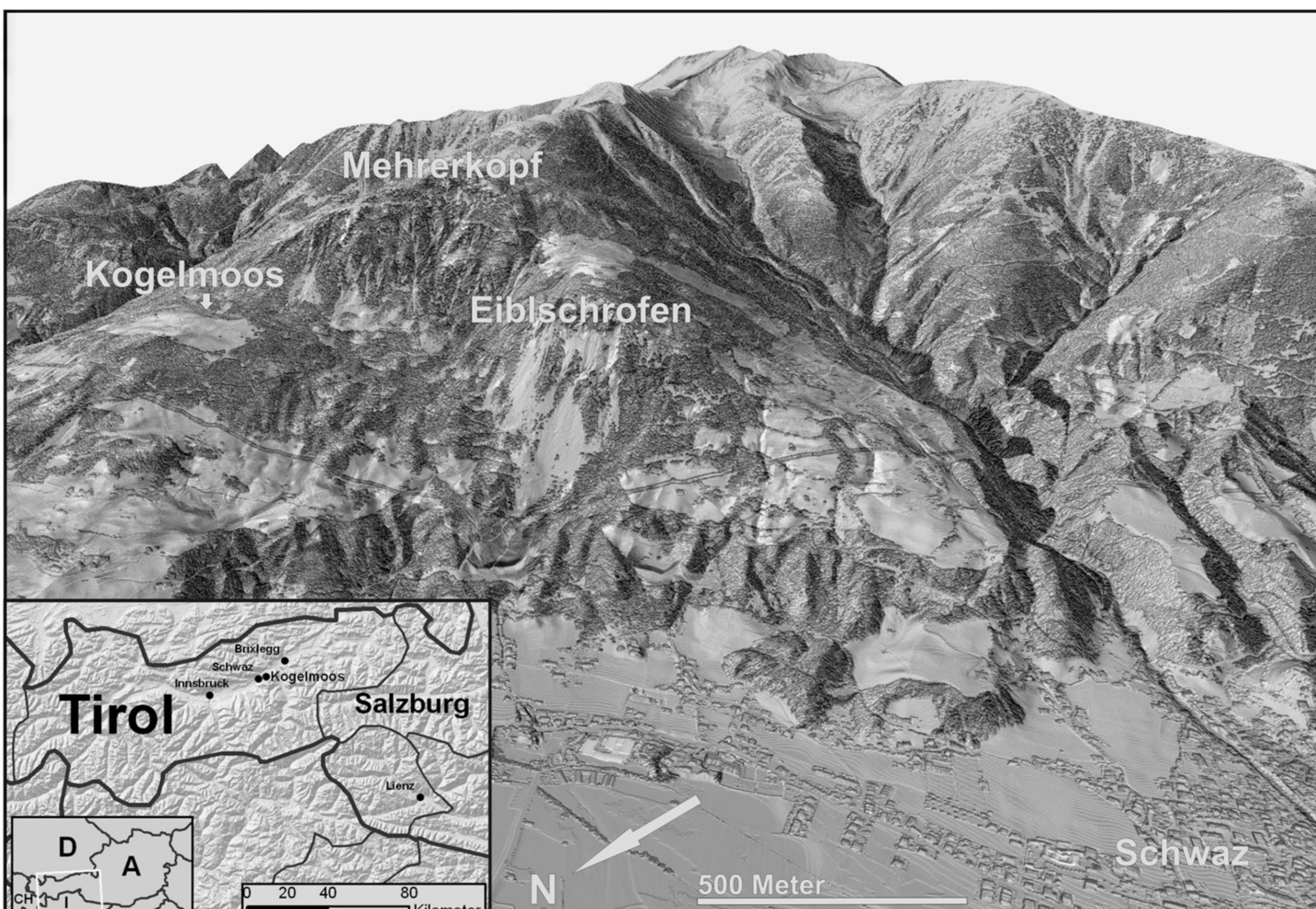

Fig. 1. General map of the former mining district Falkenstein on the north-western slope of the Mehrerkopf (©Land Tirol).

in the ores, only minor lead pollution in the Inn-valley was caused by ore smelting and copper production. However, large quantities of lead were used for extracting silver from the silver-bearing copper during the Saigerhütten process and the process of cupellation. These industrial procedures have to be seen as the main cause of lead pollution in medieval and (early) modern times.

The mire in the copper and silver-ore mining area Falkenstein was selected after detailed prospections at the north-western slope of the Mehrerkopf. The fen Kogelmoos lies in close proximity to the farmsteads bearing the same name, situated between coniferous woodlands and intensively farmed meadows at an altitude of 1120 m above sea level. This 0.2 ha sized mire is occasionally used as pasture. The surrounding vegetation consists of a spruce forest (*Picea*). The area to the west of the mire is characterised by various mining waste heaps, which even nowadays partly lack vegetation cover. In the higher altitude the spruce forest (*Picea*) is mixed with larch (*Larix*) and in the lower areas with fir (*Abies*) and beech (*Fagus*).

3. Archaeological and historical background

The region around Schwaz in the Tyrolian Inn-valley was the setting for mining activities since the first half of the Middle Bronze Age (Goldenberg, 1998). Archaeological findings (Rieser and Schrattenthaler, 1998/99) and radiocarbon analyses (Goldenberg and Rieser, 2004) in the Falkenstein area, which was one of the biggest mining districts of Schwaz, suggest that some galleries date back to prehistoric times. The remains of prehistoric mining activities in that area can be dated between Late Bronze Age (Urnfield culture) and the first half of Iron Age (Hallstatt culture) (Rieser and Schrattenthaler, 1998/99).

The first written mention of a farm settlement at the “Hohenchogel” (today: hamlet of Kogelmoos) can be found in the oldest rent-roll of the monastery of St. Georgenberg-Fiecht and dates back to the years between 1361 and 1370 (Bachmann, 1981).

In 1409, according to legend, a bull revealed a vein of ore by pawing the ground with its hoofs in the hamlet of Kogelmoos. The 1556 “Schwazer Bergbuch” (Schwaz Mining Book) states that the first ores were extracted some 110 years before (Bartels et al., 2006). On the basis of an onomastic analysis of mining-relevant by-, family- and occupational names taken from early tax lists and subject registers, the existence of intensive mining activities in the mountains of Schwaz as early as 1400 has been shown (Kathrein, 2009). Mining activities in and around Schwaz are also documented in clerical, sovereign and communal sources from the 1440s onward (Tschan and Hofmann, 2008). The first “Bergordnung” (mining order) especially enacted for the mining district of Schwaz dates back to the year 1449 (Tschan, 2008). By the beginning of the 16th century Schwaz had risen from a small market place on the shores of the river Inn to the centre of European copper and silver mining, leaving other European silver-producing centres such as the districts in Mansfeld (today: Thuringia), Oberungarn (today: Slovakia), as well as the towns in the Saxon and Bohemian Erzgebirge (ore mountains) far behind. Between 1470 and 1525 more than half of the silver produced in the before mentioned European districts was mined in the various sub-districts of Schwaz (Sokoll, 1994). The Schwaz mining district eventually reached its peak (regarding the quantity of ore mined) in the 1520s, as Westermann was able to prove by reference to a list of the refined-silver production in the sub-district of Falkenstein (Westermann, 1988). The decline of mining activities in Schwaz eventually started from the second half of the 16th century onward. In 1657 the Fugger, the last private “Gewerken” (mining operators), sold their mine-holdings to the sovereign and in 1827 the state-operated silver and copper production was finally abandoned (Mutschlechner, 1951).

4. Methods

4.1. Field sampling

After exploring the fen Kogelmoos with an avalanche probe, a core was taken from the deepest part in the middle of the bog. The core, extracted with a Geonor-piston-corer, is 2 m long and has a diameter of 52 mm. Additionally the uppermost layers were excavated and, in order to minimize the compression of the more recent deposits, a 1 m thick peat column was collected by 50×10×10 cm sized cassettes.

4.2. Laboratory methods

4.2.1. Pollen, micro-charcoal

In the laboratory the cores were ejected, the peat was removed from the cassettes and stored in a cooling chamber until sample preparation. The stratigraphy of the deposits was determined according to Troels-Smith (1955). For the chemical treatment of the pollen samples a constant volume of 1 cm^3 was taken in an interval of 5 cm from 180 to 130 cm. From 131 cm on, the sample interval was 2 cm, whereas in the critical section between 123 und 75 cm pollen was sampled every centimetre. The preparation of the samples for pollen analysis followed the standard procedure of the Institute of Botany at the University of Innsbruck according to Erdtman (1960) and Seiwald (1980) using HCl, chlorination, acetolysis and, if necessary, HF. At the beginning of the chemical treatment a defined amount of exotic pollen (*Lycopodium*-tablets) was added to the samples for the calculation of pollen concentrations (Stockmarr, 1971). The slides were mounted in glycerine and coloured by fuchsine. Pollen counting was conducted at the 400× magnification, and at the 1000× magnification for critical determinations. Pollen types were identified by using the standard identification keys of the central-European pollen flora (Beug, 1961; Punt, 1976; Punt and Clarke, 1980, 1981, 1984; Punt et al., 1988; Moore et al., 1991; Reille, 1992, 1995; Faegri and Iversen, 1993) as well as the reference collection of the Botanical Institute of Innsbruck University. At least 1000 tree pollen grains were counted for each pollen spectrum. Furthermore non-pollen palynomorphs (NPPs) like fungal hyphae, spores of coprophile fungi, zoological residues and micro-charcoal were specified and quantified.

The pollen diagrams were calculated by the program FAGUS (Gelmini, 1997), developed at the Botanical Institute of Innsbruck University. The pollen sum is constituted of arboreal and non-arboreal pollen counted, whereby Cyperaceae, Cichoriaceae, waterplants, spores and NPPs were excluded from the pollen sum. The comparative diagrams of pollen and heavy metals data were drawn by the program C2 (Juggins, 2007).

The pollen diagrams are subdivided into “local pollen assemblage zones (lpaz)” according to Cushing (1967), however, chronozones according to Mangerud et al. (1974) are additionally displayed in the pollen diagrams.

Table 1
Stratigraphy of the Kogelmoos fen deposits, stratigraphy follows Troels-Smith (1955).

Depth [cm]	Sediment description	Troels-Smith classification
0–32	Brown moss – sedge peat	Dg2 Tb1 Th1
32–83	Densely rooted sedge peat, clayey	Tb1 Th2 As1
83–95	Brown moss – sedge peat	Dg2 Tb1 Th1
95–165	Dark brown coarse detritus gyttja	Dg2 Dh2 As+
165–180	Brown coarse detritus gyttja	Dg2 Dh2 As+
180–200	Blue/grey clay	As4

Table 2
Radiocarbon dates from Kogelmoos, * = residue after ABA-treatment.

Laboratory no.	Sample name	Depth [cm]	Material	Uncalibrated date BP	Calibrated age range (2 sigma)	Calibrated calendar year BC/AD
VERA-4290HS	Kogelmoos KMK 1a	30	Sedge peat	230 ± 30	cal AD 1640–1946	1659 AD
VERA-4291HS	Kogelmoos KMK 1a	50	Sedge peat	465 ± 35	cal AD 1409–1477	1438 AD
VERA-4461	Kogelmoos KMK 2 *	65	Sedge peat	1655 ± 35	cal AD 261-527	410 AD
VERA-4464	Kogelmoos KMK 2 *	75	Sedge peat	1750 ± 30	cal AD 245–340	287 AD
VERA-4292HS	Kogelmoos KMK 2	100	Coarse detritus gyttja	3045 ± 35	cal BC 1407–1133	1362 BC
VERA-4462	Kogelmoos KMB 2 *	119	Coarse detritus gyttja	4030 ± 35	cal BC 2826–2467	2518 BC
VERA-4293HS	Kogelmoos KMB 2	130	Coarse detritus gyttja	4535 ± 35	cal BC 3366–3097	3146 BC
VERA-4294	Kogelmoos KMB 3	180	Coarse detritus gyttja	7655 ± 40	cal BC 6588–6432	6463 BC

4.2.2. Loss-on-ignition

The determination of weight percent organic matter and carbonate content in the sediment of Kogelmoos is based on the standard LOI method specified in Heiri et al. (2001).

4.2.3. Geochemistry

After the peat samples were oven dried at 105 °C, about 1 g of each sample was ground and homogenized in an agate mortar. An aliquot of 50 mg was weighted into a Teflon beaker and digested. First, the organic matter was removed using 1 ml of distilled nitric acid (14 N HNO_3; Pb blank <0.5 pg/g) carefully mixed with 3 ml of hydrogen peroxide (30% H_2O_2; Merck Suprapur). Then, the sample solutions were evaporated at 95 °C. The inorganic residue was dissolved in a second step with 3 ml of a 3:1 mix of distilled hydrofluoric with nitric acid (30% HF, 14 N HNO_3; Pb blank <0.5 pg/g), at a temperature of 95 °C and afterwards evaporated. In a third step, the residue of each sample was gathered up with 1 ml hydrochloric acid (6 N HCl; Pb blank <0.5 pg/g). Aliquots of these solutions were used for trace element analyses and for lead isotope analysis.

Pb and Sc total concentrations were determined using a Quadrupole Inductively Coupled Plasma-Mass Spectrometer (Thermo Scientific XS 2). The hydrochloric acid sample solutions were diluted with high-purity water by a factor 1:5. Merck's single element ICP standards for Pb and Sc (certiPUR) were used for calibration. The relative standard deviation for the measurements was <2% for Pb and 1–8% for Sc. Original concentrations in the peat samples were calculated using the net weights (dried samples).

Lead isotope ratios ($^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$, $^{206}Pb/^{204}Pb$) of the peat samples were measured with a double-focusing magnetic sector based Multi Collector-Inductively Coupled Plasma-Mass Spectrometer (AXIOM, VG Elemental). The hydrochloric acid sample solutions were evaporated to dryness. Lead was chemically separated with 3 N HNO_3, using EICHROM Sr resin on Teflon columns, following the methods of Horwitz et al. (1991a,b). The MC-ICP-MS analytical method is described in detail in Niederschlag et al. (2003). SRM-981 standard material was used for calibration and accuracy check measurements.

4.3. Dating methods

The AMS radiocarbon dating measurements were carried out at the Environmental Research Accelerator of the Faculty of Physics-Isotope Research at the University of Vienna. The radiocarbon dates are calibrated by using the Calib 4.1. radiocarbon calibration program (Stuiver and Reimer, 1993) and are shown in calibrated calendar years in BC/AD (BC = before Christ; AD = anno domini).

5. Results and interpretations

5.1. Stratigraphy

The Kogelmoos deposits are 2 m thick and consist mainly of gyttja and brown moss – sedge peat. A full description of the stratigraphy is provided in Table 1. According to Troels-Smith (1955) the degree of humicity changes from 4 (180–95 cm) to 3 (95–0 cm) in a depth of 95 cm.

5.2. Radiocarbon dating

Eight peat samples for AMS radiocarbon dating were collected from the Kogelmoos core due to palynostratigraphic aspects after a first exploratory pollen analysis. The results are shown in Table 2. These dates are used to establish a chronology for the pollen and geochemical data. The oldest radiocarbon date at 180 cm locates the onset of the organic material accumulation at 6588–6432 BC (95.4% confidence level). The age–depth model (Fig. 2) shows a steady growth of the Kogelmoos deposit, except between 245 and 527 AD and from 1409 AD onwards. These periods reflect an enhanced peat accumulation.

5.3. Vegetation history

According to radiocarbon dates the Kogelmoos deposits (Fig. 2; Table 2) encompass the vegetation development since the Mesolithic. During the Atlantic chronozone the surrounding of the fen Kogelmoos was dominated by a dense spruce forest (*Picea*) with no indications for human impact. The first period (lpaz KM-1) (Table 3) is initially dominated by high spruce (*Picea*) values (80–95%) and the low amount of grass (*Poaceae*) pollen (Fig. 3). Single alder (*Alnus*) individuals thrive close to the fen and some pine (*Pinus*) trees intermingle in the spruce forest. Pollen from hazel (*Corylus*) and birch (*Betula*) arrive in the mire by long distance transport from opened, light zones in the further proximity. On fresh soils in the lower areas individuals of a mixed deciduous forest, such as oak (*Quercus*), lime (*Tilia*) and elm (*Ulmus*), appear. At the end of KM-1

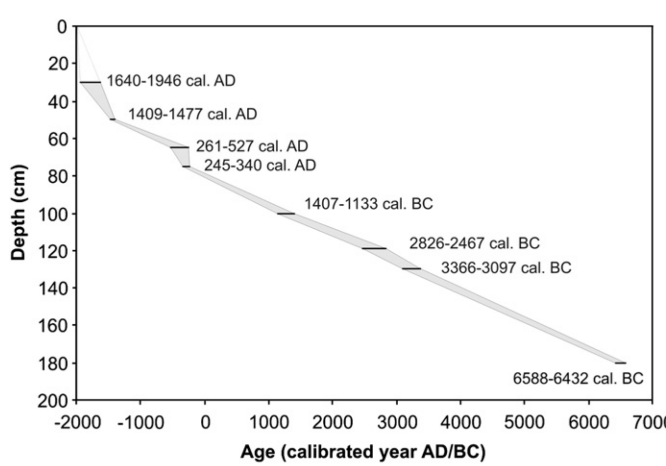

Fig. 2. Age–depth curve for Kogelmoos based on calibrated radiocarbon dates (the black bars are given at 95.4% confidence level).

Table 3
Definition of the local pollen assemblage zones of the pollen diagram Kogelmoos.

Lpaz	Name	Depth [cm]	Upper limit	Chronozones
KM-3	*Pinus–Picea–Poaceae* zone	49–1	Recent surface of the fen	Subatlantic pp.
KM-2	*Abies–Picea* zone	131–49	Decrease of *Abies*; increase of *Poaceae*, *Cyperaceae*	Subboreal pp., Subatlantic pp.
KM-1	*Pinus–Picea* zone	180–131	Decrease of *Picea*; increase of *Abies*	Atlantic pp., Subboreal pp.

fir (*Abies*) immigrates into the spruce forests in the vicinity of the Kogelmoos fen and starts to compete with spruce (*Picea*) in the montane spruce forest.

At the beginning of the second local pollen assemblage zone (Table 3) the first findings of beech (*Fagus*) pollen appear (Fig. 3). In the period with continuous alder (*Alnus*) values at the end of the Neolithic, a cutback of fir (*Abies*) values is shown synchronously to the rise of the spruce values. This development in the dominating tree species may be due to the reaction of the vegetation on a worsening of climatic conditions at the north-western slope of the Mehrerkopf. This climatic signal is consistent with the results of different proxy studies which indicate a brief but well marked cooler and wetter period between 2950 and 2750 BC (Bortenschlager, 1970; Stuiver et al., 1998; Magny, 2004; Magny et al., 2006). After 500 years, fir (*Abies*) increases up to about 20% while the values of spruce (*Picea*) reduced to about 70%. The dead wood debris of the previous climate deterioration in the fir–spruce woods caused a higher forest fire hazard around Kogelmoos, which is shown in elevated micro-charcoal values at the Neolithic to Bronze Age transition. At the end of the Neolithic, at about 2600 BC, first charcoal peaks (>100 μm) indicate the occurrence of local fires in the vicinity. In these opened patches in the landscape the photophilic larch (*Larix*) was able to gain ground for a short time. At the transition to the Bronze Age elevated alder (*Alnus*) and beech (*Fagus*) values can be found. In addition, slightly higher grass values with some pasture indicators (Table 4) occur. In the middle of this phase, with the first findings of settlement indicators (Table 4), a gain in local charcoal is visible. The isochronal occurrence of settlement indicators and high charcoal values during the second half of the Bronze Age reflects the human impact, which is also represented in a small increase of grasses (*Poaceae*) and herbs. These plants are the first to grow on small-scaled forest clearings, followed by light demanding species like hazel (*Corylus*), pine (*Pinus*) and larch (*Larix*). The changes in tree species in the surroundings of the Kogelmoos appear in an increase of pine (*Pinus*) and larch (*Larix*) and a decrease in the values for mixed deciduous tree species. A similar succession, with high larch (*Larix*) values up to nearly 6%, occurs at the end of Bronze Age, and lasts for about 1500 years. In this time span rare findings of juniper (*Juniperus*) and bracken pollen (*Pteridium aquilinium*) appear. The Iron Age is characterized by a fir–spruce forest dominated by high charcoal and larch (*Larix*) values, as well as rising fir (*Abies*) values. Beside indications of a fir-dominated forest with a high proportion of larch (*Larix*), the first findings of cultural indicators (Table 4), like cereals (*Cerealia*), occur at the beginning of Roman Times. Another change in the composition of tree species around Kogelmoos takes place at the end of Roman Times. The ongoing increase of fir (*Abies*) up to about 35% is accompanied by a reduction of beech (*Fagus*), pine (*Pinus*) and larch (*Larix*) values. This configuration remains stable during the Middle Ages, except *Fagus* values are able to rise again. Some individual findings of rye (*Secale*) and cereals (*Cerealia*) in the Medieval Times with low charcoal, pine (*Pinus*) and larch

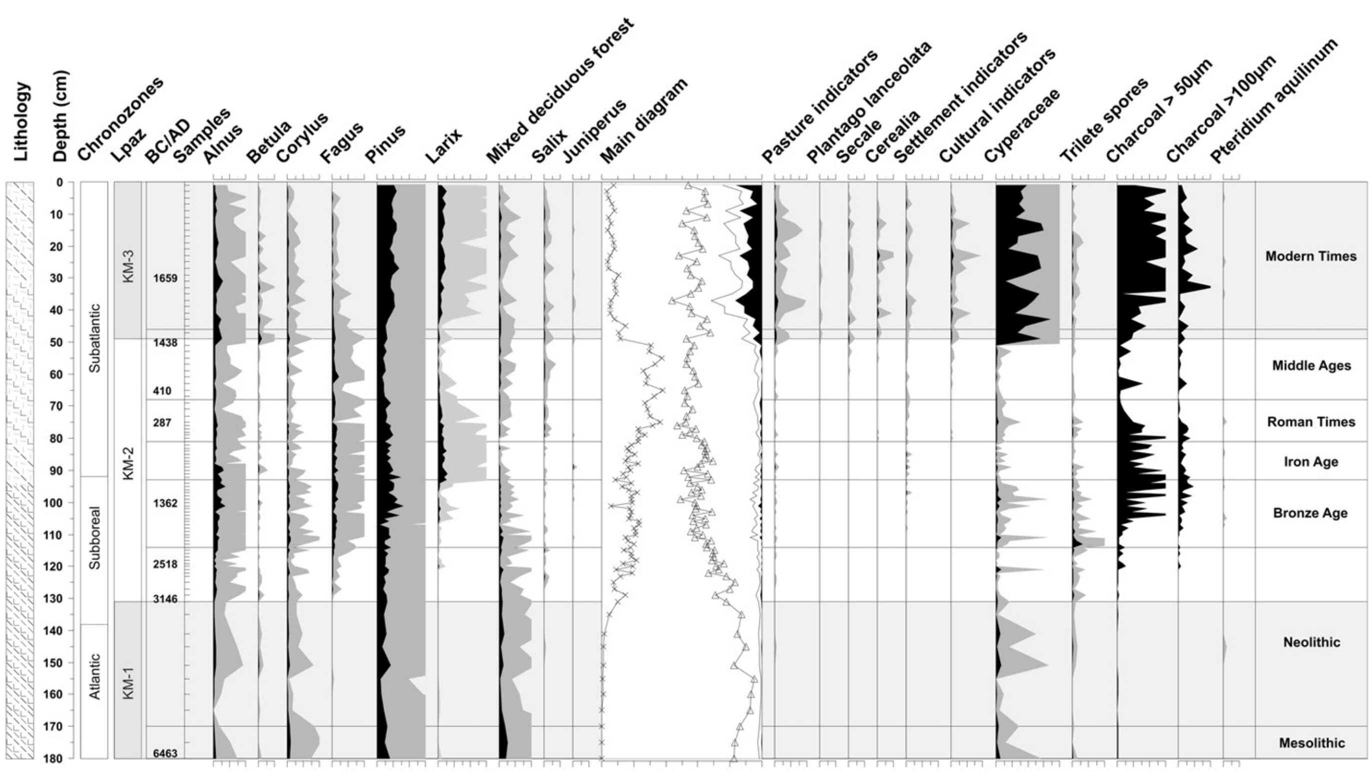

Fig. 3. Simplified percentage pollen diagram of the Kogelmoos (only selected species shown). Pollen data are presented in percentages. Black area = fraction of different species in %; grey area = fraction of different species multiplied by 10; main diagram: x = values of fir (*Abies*), △ = values of spruce (*Picea*), solid line = border of fraction of tree and non-tree species, black area = values of grasses (*Poaceae*).

Table 4
Definition of pasture, settlement and cultural indicators in this article.

Pasture indicators	*Achillea* sp., *Centaurea* sp., *Juniperus* sp., *Pteridium aquilinum*, *Ranunculus acris*, *Rosaceae*, *Scabiosa* sp.
Settlement indicators	*Artemisia* sp., *Chenopodiaceae*, *Plantago lanceolata*, *Polygonum aviculare*, *Rumex acetosa*
Cultural indicators	*Castanea sativa*, *Cerealia*, *Humulus lupulus*, *Juglans regia*, *Secale*

(*Larix*) values are shown in the pollen diagram and indicate a moderate human impact during the Middle Ages.

At the transition to the third local pollen assemblage zone (KM-3) (Table 3) pasture and cultural indicators increase significantly (Fig. 3). In the pollen diagram short peaks of alder (*Alnus*), birch (*Betula*) and hazel (*Corylus*) occur, but they decrease alongside the values of beech (*Fagus*) at the beginning of Modern times, when the landscape around Kogelmoos opened. The close fir-dominated coniferous forest shifted to a more opened spruce forest with widespread occurrence of larch (*Larix*). Higher values of grasses (*Poaceae*; up to 15%) and herbs reflect this trend in the pollen diagram. With the dramatic decrease of fir (*Abies*) values a steep gain in charcoal, pine (*Pinus*) and larch (*Larix*) values takes place at that time. The elevated values of pasture, settlement and cultural indicators with several findings of juniper (*Juniperus*), ribwort plantain (*Plantago lanceolata*) and bracken (*P. aquilinium*) are signs for an intensive human impact in Modern Times.

5.4. Loss-on-ignition

The mineral fraction shown in Fig. 4 is the sum of the non-organic fraction of the LOI-investigation of the Kogelmoos core. The lowest parts consist of over 80% of mineral material, which appears to indicate the staggered deposition of organic material. At about 5500 BC the mineral fraction drops and fluctuates between 20% and 60% in the Neolithic. The rise in the Early Bronze Age (up to about 50%), which indicates elevated erosion in the catchment area of the fen, is followed by a continuous decrease of the mineral fraction values in the second half of the Bronze Age. The deposit of the fen Kogelmoos from the Iron Age is made up of about 20% of inorganic material. In the second half of the Roman Times the mineral fraction value breaks down from nearly 30% to below 20% and remains at that level during the Middle Ages. This period of less erosion during Medieval Times ends at the transition to Modern Times. The mineral matter peak (values between 50% and 75%) at the beginning of the youngest epoch lasts approximately 100 years. In the last 400 years the mineral fraction fluctuates between 30% and 50%.

5.5. Geochemistry

5.5.1. Lead and scandium

The total scandium concentrations (Fig. 4) of the layers from the Kogelmoos are quite high in the Neolithic and the Bronze Age (10–20 ppm). At the transition to the Iron Age, with the change from a coarse detritus gyttja to sedge peat, a decrease to about 15 ppm takes place. Another reduction of the scandium values occurs in the second half of the Roman Times. These low Sc concentrations (below 5 ppm) persist during the Middle Ages and are consistent with the minor erosion indicated in a low fraction of mineral matter in the peat. In the Modern Times the total scandium values range about 6–8 ppm. The total lead concentration (Fig. 4) fluctuates between 30 and 60 ppm, except elevated values in Bronze Age (70–117 ppm) and Modern Times (86–136 ppm).

Previous studies about metal deposition in mires have shown that natural variations in the abundance of mineral matter generally have an important effect on elements in the deposit (Shotyk, 1996a,b; Weiss et al., 1997, 1999a; Shotyk et al., 2001, 2002). Normalising the total lead concentration to the conservative element

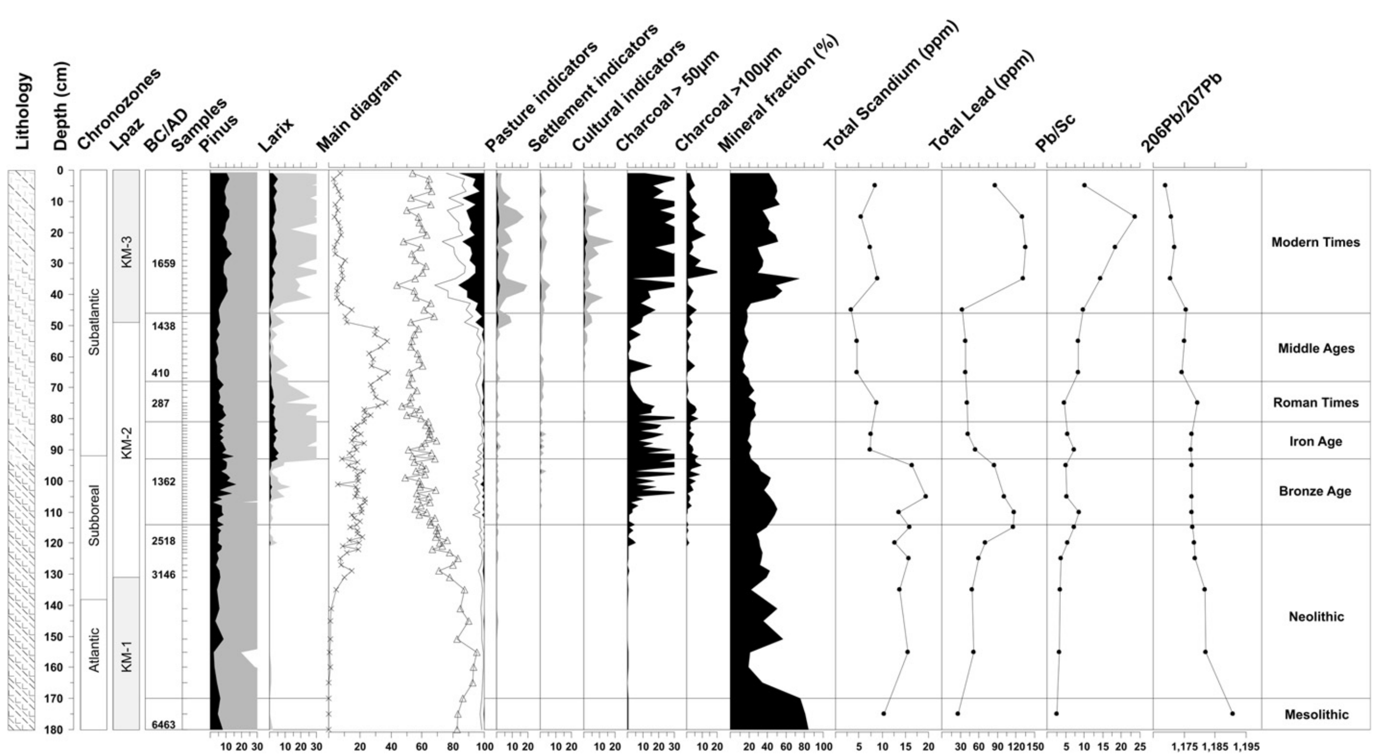

Fig. 4. Pollen (only selected species shown) and geochemistry diagrams of the Kogelmoos. Pollen data are presented in percentages. Black area = fraction of different species in %; grey area = fraction of different species multiplied by 10; main diagram: x = values of fir (*Abies*), △ = values of spruce (*Picea*), solid line = border of fraction of tree and non-tree species, black area = values of grasses (*Poaceae*).

scandium, which has no anthropogenic origin, makes it possible to estimate the extent of anthropogenic contribution to the natural deposition. Beside Sc, also Zr, Ti and Al (Martínez-Cortizas et al., 1997, 2002a; Shotyk et al., 1997, 2001, 2002; Schettler and Romer, 1998; Kempter and Frenzel, 2000; Shotyk, 2002; Weiss et al., 2002;) as well as the ash content (West et al., 1997; Alfonso et al., 2001) are used for normalisation.

The lead scandium ratio of the Kogelmoos core (Fig. 4) starts to rise beyond 3 at the end of the Neolithic. These low ratios in the Mesolithic and the first part of the Neolithic seem to be pre-anthropogenic values of the Kogelmoos deposits. The increase up to nearly 9 at the beginning of Bronze Age is consistent with the high amount of mineral fraction in the deposit. This elevated ratio decreases after the first third of the Bronze Age and the ratio stabilizes at about 5 aside from one higher value (7) at the beginning of Iron Age. At the end of the Roman Times the ratio rises up to 8, but at the beginning of Modern Times an extreme rise up to 24 takes place. This gain is congruent with the historical references of enhanced mining activities in the Falkenstein district at the north-western slope of the Mehrerkopf (Mutschlechner, 1990; Egg et al., 1986).

5.5.2. Lead isotopes

The lead isotope ratio of the deepest sample (175 cm, $^{206}Pb/^{207}Pb = 1.19084$) (Fig. 4) is similar to the ratio of a rock sample which was taken from the slope above the Kogelmoos ($^{206}Pb/^{207}Pb = 1.19092$). The lead isotope ratio of two other rock samples was not able to detect because of the too low lead concentrations. In contrast to the samples dominated by bedrock material, the detritus gyttja samples of the Neolithic have a significantly different $^{206}Pb/^{207}Pb$ isotope ratio (*t*-test, $p < 0.05$), indicating that lead in all higher layers of the bog are essentially unaffected by the basal mineral sediment. These data support geochemical arguments according to Shotyk (1996b, 2002) and Weiss et al. (1997) demonstrating the relative immobility of lead and the possibility of using this record to reconstruct human impact in the surrounding of Kogelmoos, because of the predominance of anthropogenic inputs over mineral dissolution. The $^{206}Pb/^{207}Pb$ ratios (Fig. 4) come under 1.180 at the end of the Neolithic. The values for Bronze and Iron Age are similar (1.17778–1.17723), followed by 1.17937 and 1.17439 in the Roman Times. The similar $^{206}Pb/^{207}Pb$ ratios in the Middle Ages (1.17521 and 1.17565) are followed by a decrease to values between 1.17192 and 1.16909 in the Modern Times, which may indicate an input of external lead from different deposits by smelting activities in the Inn-valley.

6. Discussion

The pollen and geochemical diagrams (Figs. 3 and 4) from Kogelmoos show the changes in pollen, micro-charcoal, mineral fraction and several heavy metals data during the last 8000 years. These changes can best be explained by a combination of internal factors like stratigraphy and mineral fraction of the peat, and external impacts such as agriculture, mining and metallurgical activities.

6.1. Middle Ages and Modern Times

The coniferous forest at the Kogelmoos during the Middle Ages is dominated by fir (*Abies*) and spruce (*Picea*). During that time the fire activity is much lower than ever before and afterwards. The occurrence of pasture, settlement and cultural indicators in low but constant amount together with the low charcoal values shows a moderate human impact by agriculture during the Middle Ages. These stable conditions can be recognised in the pollen diagram from the end of Roman until the end of Medieval Times. The low mineral content and total scandium concentration values in that section suggest reduced erosion in the catchment area of the Kogelmoos fen. This change is also shown in a slight increase of the lead scandium ratio and a reduction of the lead isotope ratio at the beginning of Medieval Times, which may be caused by a natural change in the catchment area of the fen. Beside the possibility of a modification of the hydrological circumstances, another explanation for the change in geochemistry could be locally delimited metallurgic activities in the Falkenstein district. The impact of mining in the Middle Ages, which is supposed, but not verified, by archival references (Bartels et al., 2006), might be too small to be recognised in the pollen data. It has to be assumed that the regional arboreal signal was sufficient to buffer the pollen record against a local reduction in arboreal pollen (Mighall et al., 2002b).

At about 1350 AD the pattern in the pollen diagram reflects a forest clearance contemporaneous with the first historical reference of the farmyard Kogelmoos in the "Urbar" of the monastery of "St. Georgenberg-Fiecht" in 1361/1370 AD (Bachmann, 1981). The landscape was opened by settlement activity and light demanding tree species like birch (*Betula*) and hazel (*Corylus*) extended. Clearings of the fir (*Abies*) dominated coniferous forest establish space for arable and livestock farming, which is shown in continuing cultural and pastoral indicators.

From 1447 AD on documents, like the directives by Duke Siegmund to an autonomous judge of the mining community of Schwaz, support the existence of mining-related organisational structures (Tschan, 2008) and therefore confirm the rising importance of the mining districts around Schwaz. At the beginning of the Modern Times pine (*Pinus*) and larch (*Larix*) spread at the fringe of the numerous mining dumps in the surrounding of the Kogelmoos. Even nowadays this succession is observable on the loose waste rock material of the mining galleries in the Falkenstein district, which are partly overgrown by these pioneer tree species. The rise of pine (*Pinus*) and larch (*Larix*) values around 1500 AD is a sign for the increasing number of mining waste heaps on the north-western slope of the Mehrerkopf. In addition to this secondary succession on the mining waste dumps, the increasing values of micro-charcoal in the pollen diagram may be an evidence for intensive fires in the local forests concomitant with the boom of the silver mining around the Kogelmoos at that time.

Since the beginning of Modern Times mining activities leave strong geochemical marks in the mire. The elevated mineral content of the peat caused by increased erosion on bare rock fans display an increased exploitation of fahlore in the Falkenstein district. As aforementioned, lead concentrations in the ores are low and caused only minor lead pollution during the smelting process. After smelting, large quantities of lead were needed for the extraction of silver from silver-bearing copper (Saiger process, cupellation). The lead used for these processes did not derive from the Inn-valley and has isotopic patterns differing from the local ores and rocks. The rising Pb/Sc ratios and the reduced $^{206}Pb/^{207}Pb$ isotope ratios therewith prefigure enhanced metallurgic activities to extract high amounts of copper and silver in the 16th century. At that time the mining districts around Schwaz were one of the most important centres of European copper and silver production (Sokoll, 1994, Fischer, 2001). Additionally, the Saiger-technique was finally implemented in the Tyrolean mining sites around 1492 (Ingenhaeff and Bair, 2002). This special smelting technique enabled the extraction of silver from melted copper by using high amounts of lead, which was imported from neighbouring regions, because there are no lead ore deposits around Schwaz. This lead from ores of mining districts near Villach in Carinthia, Gossensass in South Tyrol and other deposits (Bartels et al., 2006) have different isotope ratios than the one from Kogelmoos. The use of external lead in the smelting process altered the isotope ratio in the fen, visible in the reduction of the $^{206}Pb/^{207}Pb$ ratio at the beginning of Modern Times. The secondary succession with pine (*Pinus*) and larch (*Larix*) on the mining dumps is isochronal with the changes in the geochemistry in the sediment and corroborates the palynological pattern of the impact of mining in the pollen diagram. This historical model could be applied to prehistoric times, which makes it possible to reconstruct the impact of mining and metallurgic activities in the surroundings of the fen in times without written records.

6.2. Prehistory

If this signal of mining in pollen and geochemical data is transferred to prehistory, it might be possible to recognise mining phases during these times. The first elevation of the lead scandium ratio at the Neolithic to Bronze Age transition might be due to an enhanced lateral input to the gyttja sediment from the catchment area of the fen, which is shown in elevated heavy metals and mineral matter values at that time. This characteristic pattern of high pine (*Pinus*) values with larch (*Larix*) values over 1% and elevated charcoal values occurs both in the Middle Bronze Age and at the beginning of Modern Times. This section seems to indicate an early phase of prehistoric mining during Bronze Age, although this is not shown in the geochemical data due to the low lead values of the predominant ore in the Falkenstein area or the rough sample interval in that layer. Rieser and Schrattenthaler (1998/99) found mining tools like stone mallets, miner's hammers, bed plates and bone tools as well as fireplaces with ceramic shards, an awl handle and food remains in prehistoric galleries about 1.5 km to the west of the Kogelmoos. These galleries called "Heidenzechen" (heathen pits) were dated to the Urnfield culture in the Late Bronze Age. Some charcoal of the firesetting debris in these prehistoric excavations was radiocarbon dated by Goldenberg and Rieser (2004) as the same age (2655 ± 55 BP, ETH 10128, cal. BC 932–762, 95% confidence interval, AMS). To the east of the Kogelmoos some galleries created by firesetting and several glory-holes dated by prehistoric ceramic shards and stone tools were found (Rieser and Schrattenthaler, 1998/99).

The beginning of Iron Age is characterised by another distinct increase of larch (*Larix*) values, in addition to the highest charcoal values in prehistory as well as a slight elevation of the lead scandium ratio. All the findings in the Falkenstein district are dated between Late Bronze Age (Urnfield culture) and the first half of Iron Age (Hallstatt culture), which might display the end of the intensive mining phase in prehistory (Rieser and Schrattenthaler, 1998/99). As mentioned above, pollen records during Urnfield culture (Late Bronze Age) and Hallstatt culture (first half of Iron Age) are in good agreement with the sparse archaeological knowledge available for prehistoric mining activities in the vicinity of the Kogelmoos.

In the second half of the Iron Age and the beginning of Roman Times pine (*Pinus*) and larch (*Larix*) values slowly but steadily decrease whilst fir (*Abies*) is able to increase. The charcoal values are smaller and tend to be correlated with enhanced settlement activities around Kogelmoos indicated by the first findings of cereal pollen in the peat at the beginning of Iron Age. As there was no additional lead needed for the copper smelting technique in prehistoric times, no significant change in the isotope composition from the late Neolithic to the middle of Roman Times could be detected. Additionally, the impact of early mining activities seems to be spatially limited to certain small-sized areas in the Falkenstein district. Further palaeoecological data from peat bogs close to prehistoric mines and metalworking sites suggest that the impact of mining on local woodland in prehistory was negligible and any local deforestation was short-lived (Dörfler, 1995; Marshall et al., 1999; Mighall and Chambers, 1993, 1997; Mighall et al., 2000). Due to the limited number of sites investigated and the variation in age, duration and intensity of mining, a pattern of small, local woodland clearance appears to be emerging in the palynological record (Mighall et al., 2002b). The pollen data from the Kogelmoos core displays a change in the composition of the tree species, with elevated pine (*Pinus*) and larch (*Larix*) values, but no significant hints for large-scaled forest clearings in prehistory.

It is quite rare not to detect a Roman lead peak in European peat deposits. The fact that lead pollution from the Romans is not detected in this study could be attributed to the rough sampling interval. Another explanation could be the small size of the fen Kogelmoos (only 0.2 ha) which causes a predominantly local catchment area for pollen and heavy metals. Therefore it is possible that the local signal from the lower Inn-valley is more determinant than the Roman lead pollution signal from the Mediterranean region.

7. Conclusion

The results of this multi-proxy study reveal that the combination of palynology and geochemistry enables a detailed reconstruction of the palaeoecology of mining in the surroundings of the Kogelmoos. The model developed for historic times, makes it possible to separate the signal of mining and agriculture in the pollen diagram, thus enabling the detection of mining phases in prehistoric times.

The analyses of the sediment show several phases of mining activities recorded from the Kogelmoos fen. Beside changes in the pollen data, peaks in lead scandium ratios occur which date periods of intensive mining to the beginning of Modern Times and the first half of the Iron Age. Another mining phase in prehistoric times, detected in the pollen data, is not supported by geochemical data. This might be due to the low lead values of the predominant ore of the region, making lead a weak indicator of prehistoric mining in the area around Schwaz. Another problem could be the rough sample interval at that time, because mining activities in the surroundings of the fen Kogelmoos in Late Bronze Age are confirmed by archaeological findings at different sites. The oldest peak of the lead scandium ratio in the gyttja section of the sediment core is dated to the Neolithic to Bronze Age transition. This is suggested to be a problem of an enhanced lateral input from the hydrological catchment area of the fen, which is shown in elevated heavy metals and mineral matter values at that time. Clearly, further research in deposition of heavy metals in non-peat deposits of minerotrophic mires is needed.

Notwithstanding the complications outlined above, this promising approach of using different proxies to explain human–environment interactions in the mining landscape is going to be applied in further palynological studies in western Austrian mining districts.

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