Atmospheric Deposition of V, Cr, and Ni since the Late Glacial: Effects of Climatic Cycles, Human Impacts, and Comparison with Crustal Abundances

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Vanadium, Cr, and Ni accumulating in a Swiss peat bog since 12 370 ^{14}C yr B.P. have been measured using inductively coupled plasma-mass spectrometry (ICP-MS) after acid dissolution in a microwave autoclave. Strict quality control schemes were applied to guarantee the accuracy of the applied analytical methodology. The concentration gradients in the peat column and comparison with Pb indicate that V, Cr, and Ni are effectively immobile in the ombrotrophic section of the peat profile but that Ni is added to the minerotrophic peat layers by chemical weathering of the underlying sediments. The lowest metal concentrations were found during the Holocene climate optimum (5320–8230 ^{14}C yr B.P.) when "natural background" values averaged 0.55 ± 0.13 μg g^{-1} V, 0.76 ± 0.17 μg g^{-1} Cr, and 0.46 ± 0.09 μg g^{-1} Ni ($n = 18$); given the average bulk density (0.05 g/cm^3) and accumulation rate (0.05 cm/yr) of peat in this zone, the corresponding atmospheric fluxes are approximately 14, 19, and 12 μg m^{-2} yr^{-1} for V, Cr, and Ni, respectively. The highest concentrations of V, Cr, and Ni were found during the Younger Dryas cold climate event (centered at 10 590 ^{14}C yr B.P.) when background values were exceeded by about 40 times. Elevated concentrations and accumulation rates were also found at 8230 and 5320 ^{14}C yr B.P., which are consistent with the elevated dust fluxes recorded by Greenland ice cores. By far the greatest contribution of the three elements to the peat inventory is atmospheric soil dust, and the metal fluxes vary not only with climate change but also land-use history (especially the beginning of forest clearing for agriculture ca. 6 millennia ago). The V/Sc, Cr/Sc, and Ni/Sc ratios were remarkably similar to their corresponding ratios in the earth's crust until the onset of the Industrial Revolution (240 ^{14}C yr B.P.), which largely validates the use of crustal concentrations for calculating enrichment factors (EF) for these elements. In modern samples, the EFs of V, Cr, and Ni reach maximum values between 2.4 and 4.1, relative to background; anthropogenic emissions are a more likely explanation of the elevated EFs than either plant uptake or chemical diagenesis. This study demonstrates the usefulness of peat bogs as archives of atmospheric metal deposition and underpins the potential of peat cores to help distinguish between lithogenic and anthropogenic metal sources.

Introduction

Carpet-forming terrestrial mosses are widely used to monitor airborne metal pollution (*1*). Frequently, *Sphagnum* mosses from bogs are investigated for this purpose because they receive their principal nutrients solely from precipitation and dry deposition (*2*). Except for herbarium specimens, a retrospective study of atmospheric metal deposition using mosses is generally restricted to a few years. In contrast, *Sphagnum*-dominated peat cores from ombrotrophic (rain-fed) bogs can provide historical trends over thousands of years (*3*). Recently, peat cores have proved to be meaningful archives of ancient atmospheric metal deposition, especially for Pb (*4–15*), Hg (*16–19*), and some lithogenic trace elements (*20–22*).

Vanadium, Ni, and Cr have found widespread industrial uses, primarily in metallurgical applications, with global production on the order of 50 000, 500 000, and 20 000 t/yr (*23*). The greatest single use of these metals is in the manufacturing of stainless steel. Fugitive emissions of these metals to the environment include oil burning, as V is commonly enriched in crude oils (*23, 24*); roasting and refining nickel sulfide ores; and disposal of tannery wastes and wastewaters, as most leather is tanned using Cr (*23*). Despite their commercial importance, we know of no complete, long-term time series of atmospheric deposition of these metals.

Many examples of local anthropogenic V, Cr, and Ni contamination can be found in the literature (*1, 2, 25*), but these are mainly restricted to specific point sources such as metal mines and refineries. In fact, there is very little information about temporal trends in atmospheric deposition of V, Cr, and Ni in uncontaminated continental areas (*1, 26*). About 25 yr ago, Aaby and Jacobsen (*27*) quantified the three elements in Danish ombrotrophic peat columns, but they did not distinguish between anthropogenic and lithogenic contributions of V, Cr, and Ni to the peat inventory. As a result, it is not clear if the elevated concentrations of these elements in modern peat samples as compared with deeper, older layers are simply the result of increased inputs of soil dust or whether they represent true enrichments of these metals in the aerosols deposited on the bog surface. Complete vertical concentration profiles of V, Cr, and Ni from three *Sphagnum* bogs were reported by Shotyk et al. (*26*); however, these peat samples investigated were not age-dated. Consequently, no historical information on atmospheric elemental deposition can be derived from that study. Therefore, these early studies (*26, 27*) provide very limited quantitative information about the changing rates and predominant sources of atmospheric V, Cr, and Ni deposition, and more detailed studies are required to fully elucidate the atmospheric geochemical cycle of these elements and the impact of man.

Accurate and precise analytical data are one important prerequisite for a meaningful reconstruction of ancient metal deposition rates. A major analytical problem is frequently caused by the dissolution of siliceous matter present in largely

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varying amounts in peats by hydrofluoric acid (28, 29). "Excess HF" will cause precipitation of fluorides, which, in turn, will consequently lead to poor results. As part of our research on the development of reliable analytical procedures for the determination of trace elements in peat (28–31), we recently developed a new digestion procedure based on the use of nitric acid and tetrafluoroboric acid (HBF_4) combining the positive effects of both HF and H_3BO_3 by simultaneously attacking the silicates while preventing the precipitation of fluorides (28, 29).

The main goals of this study are (i) to determine the concentration profiles of V, Cr, and Ni in age-dated peat samples from a bog extending back 12 370 ^{14}C yr B.P.; (ii) to determine which section of the peat column has received these metals exclusively from the atmosphere; (iii) to establish "natural background values" for V, Cr, and Ni concentrations in pre-anthropogenic, ombrotrophic peat and to estimate the atmospheric fluxes; and (iv) using Sc as a surrogate for soil dust inputs, to compare the "background" M/Sc ratios with the corresponding values for crustal rocks. Before addressing these issues, we consider the possible importance of metal contamination from the stainless steel coring equipment used to collect the samples and the possible importance of post-depositional metal migration.

Experimental Section

Apparatus. Aliquots (~200 mg) of powdered peat and plant samples were dissolved in a microwave autoclave (ultra-CLAVE II, MLS, Leutkirch, Germany) at elevated pressure.

ICP-MS measurements were carried out with an ELAN 5000 (Perkin-Elmer-Sciex) equipped with an autosampler (AS 90, Perkin-Elmer) and a cross-flow nebulizer. For the reliable determination of Ni, an ultrasonic nebulizer (USN) with membrane desolvation (U-6000 AT$^+$, Cetac Technologies, Omaha, NE) was employed. Gas flows and the position of the torch were adjusted to obtain lowest possible oxide formation rates for Ce and Ba and maximum count rates for ^{103}Rh.

Scandium was determined previously (6) using instrumental neutron activation analysis (INAA) at a commercial laboratory (ACTLABS, Activation Laboratories Ltd., Ancaster, ON, Canada).

Reagents. For the preparation of all solutions, high-purity water (18.2 MΩ·cm) from a MilliQ-system (Millipore, Milford, MA) was used. Nitric acid (65%, analytical-reagent grade, Merck, Darmstadt, Germany) was further purified by sub-boiling distillation (MLS). Additionally, tetrafluoroboric acid solution (HBF_4, ~50%, purum, Fluka, Buchs, Switzerland) and hydrogen peroxide (30%, Baker analyzed, J. T. Baker, Deventer, Holland) were employed for sample digestion.

Calibration solutions were prepared daily by adequate dilution of a multi-element stock standard solution (Merck VI, 5% nitric acid) containing 10 mg L^{-1} of each element under investigation with 0.42 mol L^{-1} high-purity nitric acid. To correct for instrumental drifts and plasma fluctuations, all analyte solutions were spiked with a rhodium standard solution (SPEX, Metuchen, NJ) to a final concentration of 50 μg L^{-1}. Final dilution factors amounted to approximately 220.

Collection and Preparation of Peat Samples. Two complete vertical peat cores were collected from Etang de la Gruère (EGR), a raised bog in the Jura Mountains of Switzerland. The samples were taken in the central part of the bog where it is strongly domed and peat accumulation is more than 6 m. The top 100 cm of peat was sampled using a Wardenaar peat profile sampler (32) to remove a monolith 10 × 10 × 100 cm (core 2F) that was subsequently cut into 3-cm slices for further analysis. The peats below 100 cm were cored with a Belorussian peat sampler (33, 34) that removes semicylindrical cores 50 cm long and 10 cm in diameter (core

TABLE 1. Quality Control Data Underpinning Reliable Determination of V, Cr, Ni, Mn, Rb, and Ba by the Microwave Digestion/ICP-MS Approach

	GBW 07602 bush branches and leaves, $n = 28$		CTA-VTL-2 Virginia tobacco leaves, $n = 4$	
element	found	certified	found	certified
V	2.31 ± 0.13	2.4 ± 0.2	4.25 ± 0.04	4.00 ± 0.42
Cr	2.26 ± 0.24	2.3 ± 0.2	1.94 ± 0.09	1.87 ± 0.16
Ni	1.72 ± 0.16	1.7 ± 0.3	1.95 ± 0.18	1.98 ± 0.21
Mn	56.9 ± 2.9	58 ± 3	77.0 ± 1.0	79.7 ± 2.6
Rb	4.11 ± 0.11	4.2 ± 0.2	50.2 ± 0.7	48.6 ± 2.3
Ba	18.7 ± 0.5	19 ± 2	42.8 ± 1.2	42.7 ± 6.6

2P). This 2P core was cut into 10-cm slices. Details of the sample collection procedure, the preparation of the peat samples, and previous geochemical studies have been published elsewhere (35, 36). Both sets of corers were constructed of stainless steel, but we failed to find any evidence of V, Cr, or Ni contamination in any of the peat samples (see below). All peat samples were milled in an ultracentrifugal mill (Retsch, Haan, Germany) equipped with a titanium sieve and rotor.

Selected samples from deeper peat layers of both cores were dated using ^{14}C by decay counting, and the uppermost peat layers of the 2F core were dated using ^{210}Pb (6, 37). The average long-term rate of peat accumulation is 0.45 mm yr^{-1}, averaged over 14 500 calendar years (8). Age dates and the ash content of the peat samples investigated in this study have been published earlier (20).

Acid Digestion in the Microwave Autoclave. Sample aliquots (approximately 200 mg) were weighed to 0.1 mg into 20-mL PTFE vessels. The acid mixtures contained 3 mL of HNO_3 and 0.1 mL of HBF_4. Up to 40 samples can simultaneously be digested under identical experimental conditions in the microwave autoclave. A starting pressure of 50 bar (with Ar) was applied to the reaction chamber. Vessels were then heated in the microwave autoclave for 76 min, increasing the temperature up to 240 °C; during this phase the pressure in the reaction chamber reached about 120 bar, as described in detail earlier (28, 29). After cooling for about 35 min, well below the boiling point of the acid mixture at atmospheric pressure, the reaction chamber was opened. Colorless, homogeneous digestion solutions were obtained, which indicates efficient destruction of the organic matter. The contents of the digestion vessels were quantitatively transferred into graduated 15-mL polypropylene tubes (Falcon, Becton Dickinson, Meylan Cedex, France) and filled to the mark with high-purity water.

Quality Control. A peat reference material with certified elemental concentrations is currently not available. Therefore, two plant reference materials with certified concentrations (GBW 07602 bush branches and leaves, Institute of Geophysical and Geochemical Exploration, Langfang, China; CTA-VTL-2 Virginia tobacco leaves, Institute of Nuclear Chemistry and Technology, Warszawa, Poland) were analyzed with every batch of samples to ensure the accuracy of the applied analytical procedures. The data summarized in Table 1 highlight the excellent agreement between experimentally established and certified elemental concentrations in both reference materials. A detailed description of the development and evaluation of the newly developed analytical methodology for the determination of V, Cr, Ni, Mn, Rb, and Ba in peat is given elsewhere along with further quality control data (29).

Each peat sample of both cores was digested twice. Each diluted digestion solution was analyzed for trace elements by ICP-MS twice on different days, yielding a total of four analytical values per sample that normally agreed within an uncertainty of <5%.
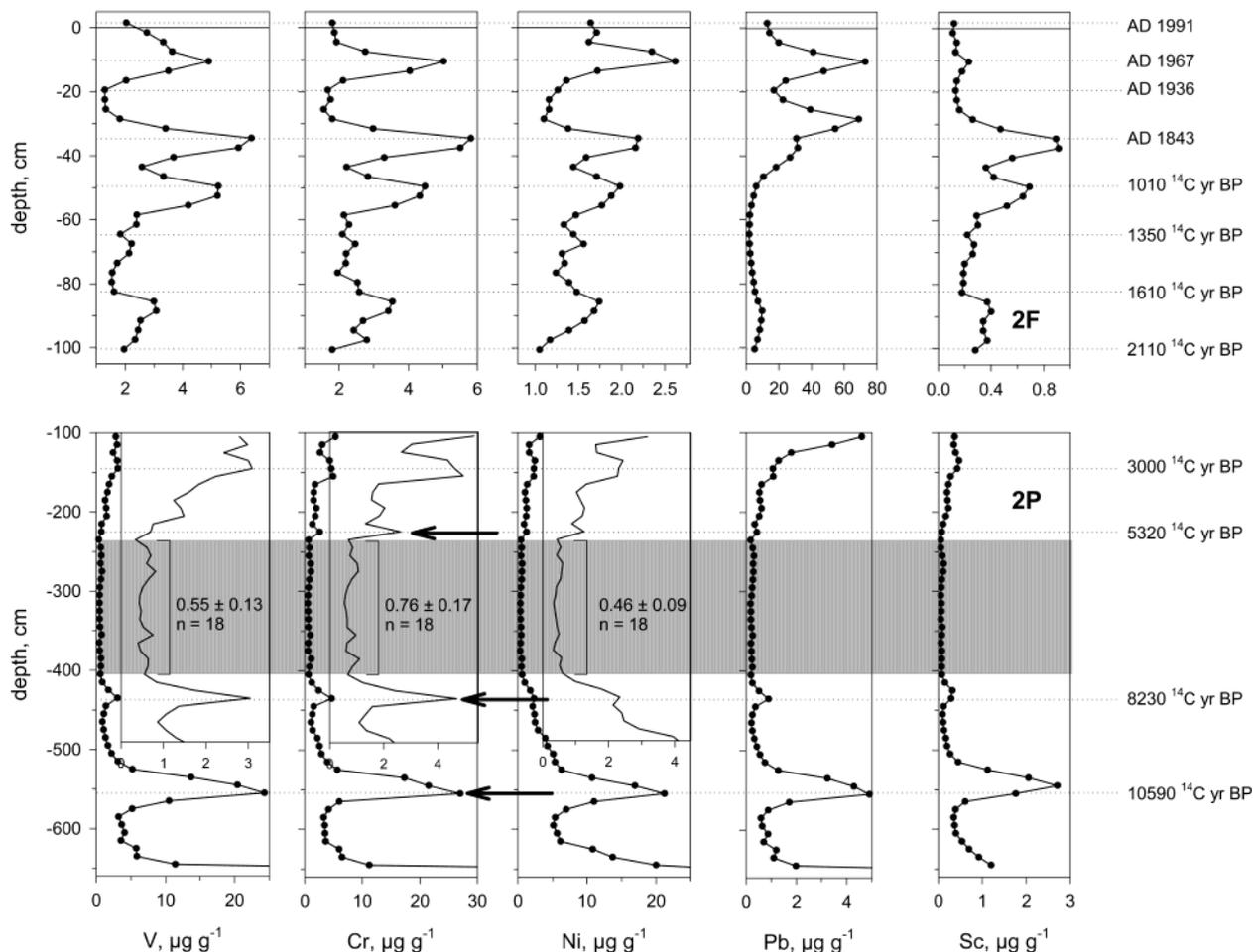
FIGURE 1. Vanadium, Cr, and Ni concentrations in the 2F and 2P cores from EGR, respectively. The shaded area (ca. 5320 to 8230 14C yr B.P.) corresponds to the Holocene Climate Optimum when rates of atmospheric soil dust deposition were at their lowest (*20, 21*). Arrows in the 2F plots indicate periods of enhanced soil dust deposition. The smaller, inserted plots show the concentration profiles of V, Cr, and Ni from 100 to 490 cm in more detail.

Correction for the Moisture Content. All reference materials and peat samples were used as bottled. Results were corrected for the moisture content in the reference materials as determined on 200-mg aliquots of each material by an electronic moisture analyzer (MA 100 H, Sartorius, Göttingen, Germany) (*38*). As only a limited amount of each peat sample from the two peat cores was available, no correction of the moisture content of the dry powders (previously dried at 105 °C and then stored in airtight low-density polyethylene bags) was performed.

Assessment of Possible Contamination of the Samples by the Stainless Steel Corer. To estimate the possible importance of V, Cr, and Ni contamination of the peats by the stainless steel corer, one 48-cm peat core (EGR 2i) was collected using a purpose-built stainless steel (SS) tube, and a second core (EGR 2j) was collected using a PVC pipe. Both cores were cut by hand into 3-cm slices using a stainless steel bread knife, then dried, and milled as described above. Samples of 8−10 g were measured for Cr and other trace metals using INAA (ACTLABS, Ancaster, ON, Canada). The results showed no systematic differences in Cr concentrations between the samples collected using SS versus PVC, and only two of the 16 SS samples contained more Cr than the PVC samples. However, five of the PVC samples contained higher Sc, La, and Sm concentrations, suggesting that the differences in metal concentrations between the cores were due primarily to natural variations in the abundance of the metals within the bog surface. Thus, the stainless steel coring

equipment used to collect the samples is unlikely to have contaminated the peat samples described in this paper.

Results and Discussion

Abundance and Distribution of V, Cr, and Ni. The concentration profiles of V, Cr, and Ni in both peat cores (2F and 2P) are plotted next to Sc in Figure 1. The concentration profile of lead is also shown in Figure 1, denoting much greater changes in abundance relative to Sc as compared to V, Cr, and Ni. Lead was selected for this comparison because analyses of the isotopic composition of Pb at EGR (*6, 20, 39*) as well as other Swiss bogs (*5*) and herbarium samples of *Sphagnum* moss (*15*) showed that Pb is immobile in ombrotrophic peat. Like Pb, the concentration profiles of V, Cr, and Ni also include sharp peaks that represent pronounced changes in concentration over short vertical distances: the presence of these peaks suggest that V, Cr, and Ni probably are also well preserved in the peat profile.

To further evaluate the possible importance of post-depositional migration of these metals, the Sc concentration profile has also been included (Figure 1). Scandium behaves conservatively during chemical weathering (*22*), and there are no significant anthropogenic sources of this metal to the atmosphere (*22*). Thus, the Sc concentration profile may be viewed as a surrogate for the abundance of atmospheric soil dust (ASD) in the peat core as described in detail elsewhere (*20*). Except for the peak in V, Cr, and Ni concentrations in the peat samples dating from A.D. 1967 (discussed below),
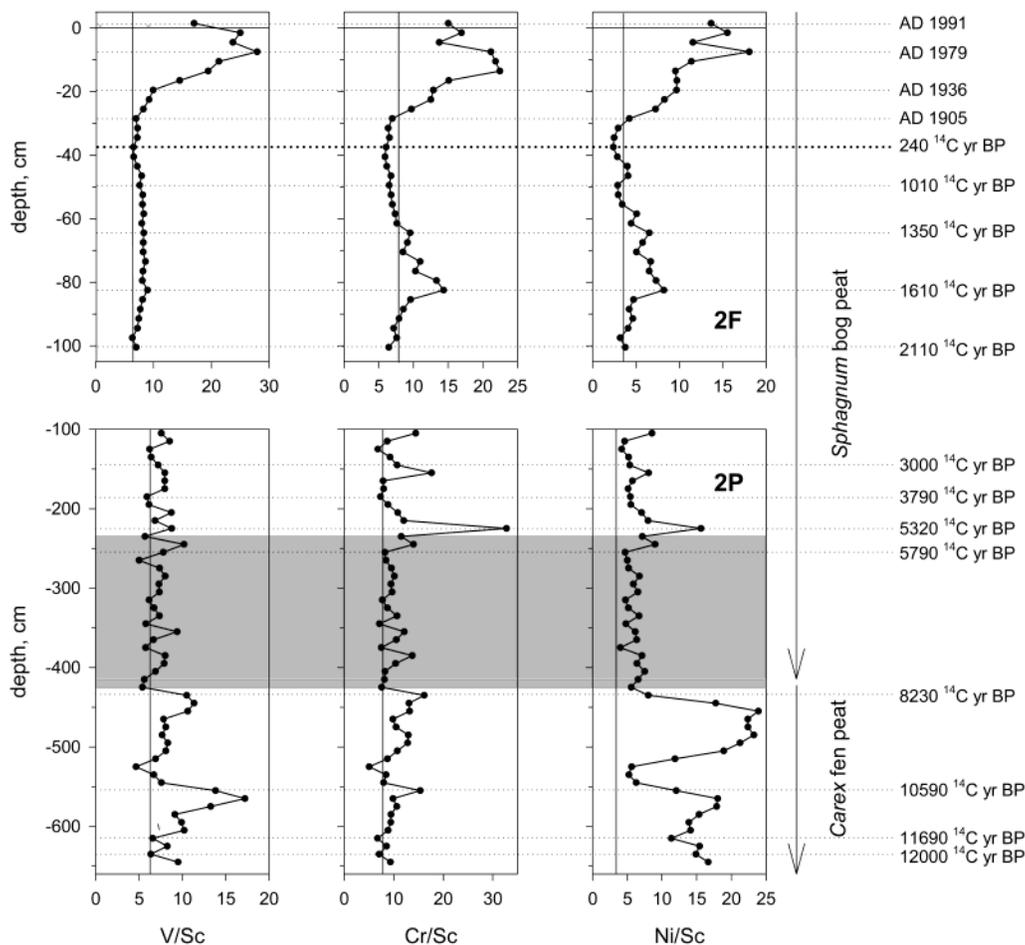
FIGURE 2. Vertical distribution of V/Sc, Cr/Sc, and Ni/Sc. The shaded bar in the 2P plots highlight the period of Holocene climate optimum (see text for details). The solid vertical line indicates the M/Sc ratio of crystal rocks (*41*).

the three pronounced peaks in V, Cr, and Ni concentrations in the 2F core below ca. 20 cm (dating from the Roman Period, centered on 1010 ^{14}C yr B.P., and A.D. 1843) all have a corresponding peak in Sc. As a result, much of the variation in the abundance of V, Cr, and Ni in the 2F core can be explained in terms of the abundance of mineral dust particles. The similarity between the distribution of V, Cr, and Ni on one hand with that of Sc on the other may help to explain the apparent immobility of the metals in this part of the peat profile: these metals appear to be associated with mineral particles that are probably well preserved in the peat, thus the metals are not available to the pore fluids for migration. Quantitative studies of the chemical composition of pore waters from this site are needed to evaluate this hypothesis. On the basis of the available data, each of the metals V, Cr, and Ni are well retained in this section of the peat profile.

Comparing the distribution of V, Cr, and Ni with Sc in the 2P core, it is clear that soil dust was the predominant source of atmospheric V, Cr, and Ni deposition since 12 370 ^{14}C yr B.P. The lowest rates of ASD deposition, indicated by accumulation rates of Sc, Ti, Zr, and REE (*20, 21*), are found in the peat samples dating from 5320 to 8030 ^{14}C yr B.P. (235−405 cm in Figure 1) and corresponding to the Holocene climate optimum; this period was characterized by a warm climate, extensive vegetation cover, low wind strength, and a minimum in the abundance of erodible soil material. The lowest concentrations of V, Cr, and Ni also are found during this period when concentrations averaged ($n = 18$) 0.55 ± 0.13 μg g^{-1} V, 0.76 ± 0.17 μg g^{-1} Cr, and 0.46 ± 0.09 μg g^{-1} Ni; given the average bulk density (0.05 g/cm³) and accumulation rate (0.05 cm/yr) of peat in this zone, these

concentrations correspond to atmospheric deposition rates of approximately 14, 19, and 12 μg m^{-2} yr^{-1} for V, Cr, and Ni, respectively. These values can be taken to represent the natural background values for the concentrations and atmospheric deposition rates of these trace elements in Central Europe and may serve as a reference point for future studies of atmospheric V, Cr, and Ni deposition, especially those employing mosses and other biomonitors. For example, the determination of the three elements in more than 600 moss samples covering an area of about 188 000 km² north of the Arctic Circle revealed the following values (median, minimum−maximum): V, 1.6 μg g^{-1}, 0.3−93.8 μg g^{-1}; Cr, 0.6 μg g^{-1}, <0.2−8.6 μg g^{-1}; Ni, 5.4 μg g^{-1}, 0.97−396 μg g^{-1} (*1*). The corresponding minimum concentrations from this remote area compares well with our natural background values, and the two data sets complement one another.

Since the Late Glacial, there have been five distinct, major periods of enhanced atmospheric soil dust deposition recorded by Greenland ice cores, each of which corresponds to a cold climate event revealed by a glacial advance (*40*). The peat profile from Etang de la Gruère appears to have recorded at least two of these major episodes: (i) 10 590 ^{14}C yr B.P., which corresponds to the Younger Dryas (YD), and (ii) 8230 ^{14}C yr B.P.; both are indicated by the arrows in Figure 1. The greatest metal concentrations (V, Cr, and Ni) by far are found in the peat samples corresponding to the YD, which clearly demonstrates the importance of climatic cycles on atmospheric deposition of trace metals.

Metal/Sc Ratios. To emphasize the differences between these elements, the ratios of V, Cr, and Ni to Sc are plotted in Figure 2. In general, the M/Sc ratios show remarkably
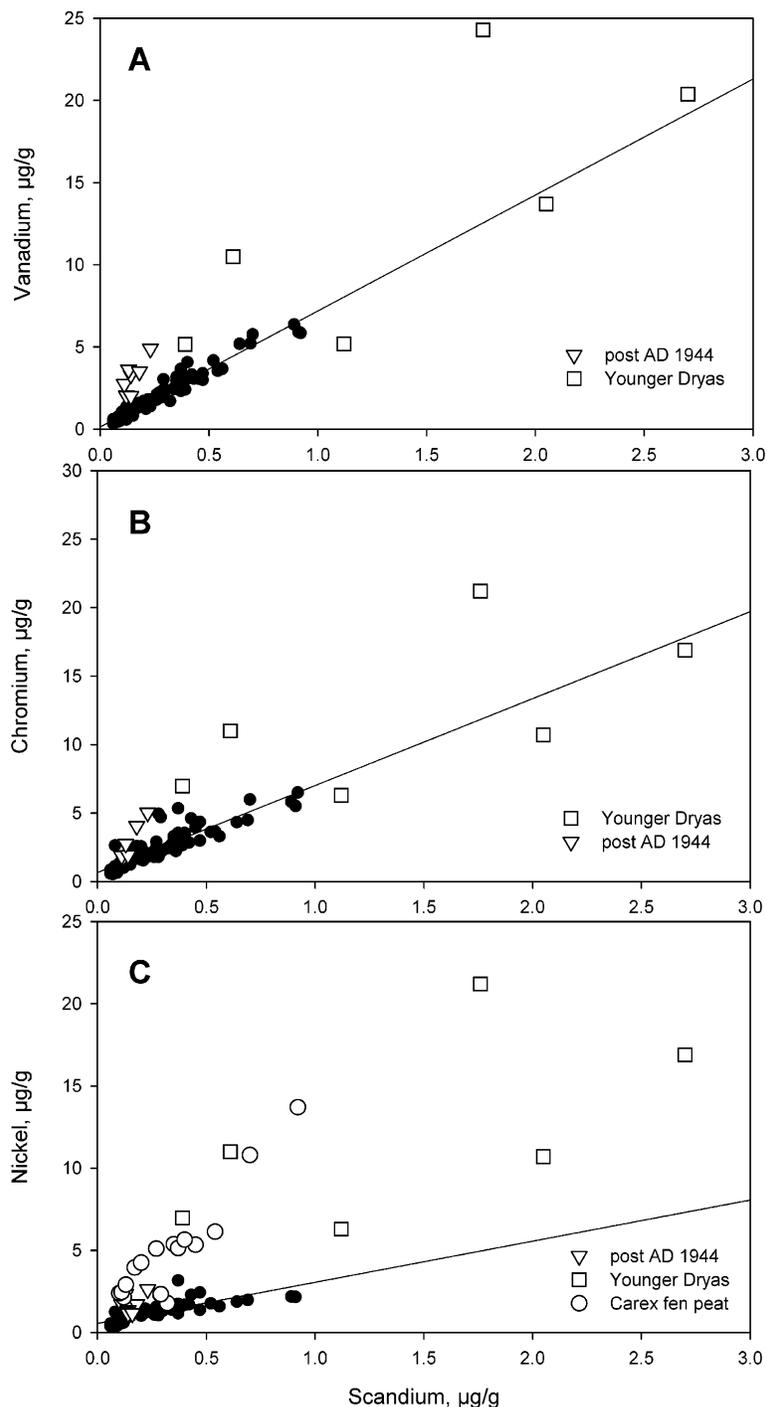
FIGURE 3. Concentrations of V, Cr, and Ni vs Sc in the peat samples from EGR (see text for details).

constancy with time, with the following exceptions. First, Ni is clearly enriched in the *Carex* fen peat layers at the bottom of the bog, out of proportion with Sc. Second, the uppermost layers are enriched in all three metals relative to Sc. Finally, there are several peaks in Cr/Sc and Ni/Sc in deep, pre-anthropogenic peat layers, such as the one at 5320 ^{14}C yr B.P. We note that the Greenland ice core record shows a minor period of enhanced soil dust deposition at this time (*40*) and interpret this change (in Cr/Sc and Ni/Sc) as the result of a natural change in predominant source area, wind strength, or both. Support for this interpretation is found in a previous study which found that Ti, Zr, Hf, and the REE are clearly enriched in this sample, relative to Sc, as compared to samples above and below this depth (*20, 21*).

To further examine the correlation with Sc, the concentrations of V, Cr, and Ni have been plotted against Sc in Figure 3. To quantify the predominant M/Sc ratio in soil dust, the outlying M/Sc values have been plotted using separate symbols. Specifically, with respect to V, this meant plotting the samples corresponding to the YD and the modern samples separately (Figure 3a); the remaining values show a strong linear correlation, with $V = 7.05 \, [Sc] + 0.144$ ($r^2 = 0.949$, $n = 76$). With the exception of the "anomalous" samples that were removed from the linear regression, most of the variation in V concentrations can be explained by the abundance of soil dust, as revealed by Sc concentrations. When the Cr data are treated similarly (Figure 3b), the following linear regression is obtained: $Cr = 6.47 \, [Sc] + 0.56$
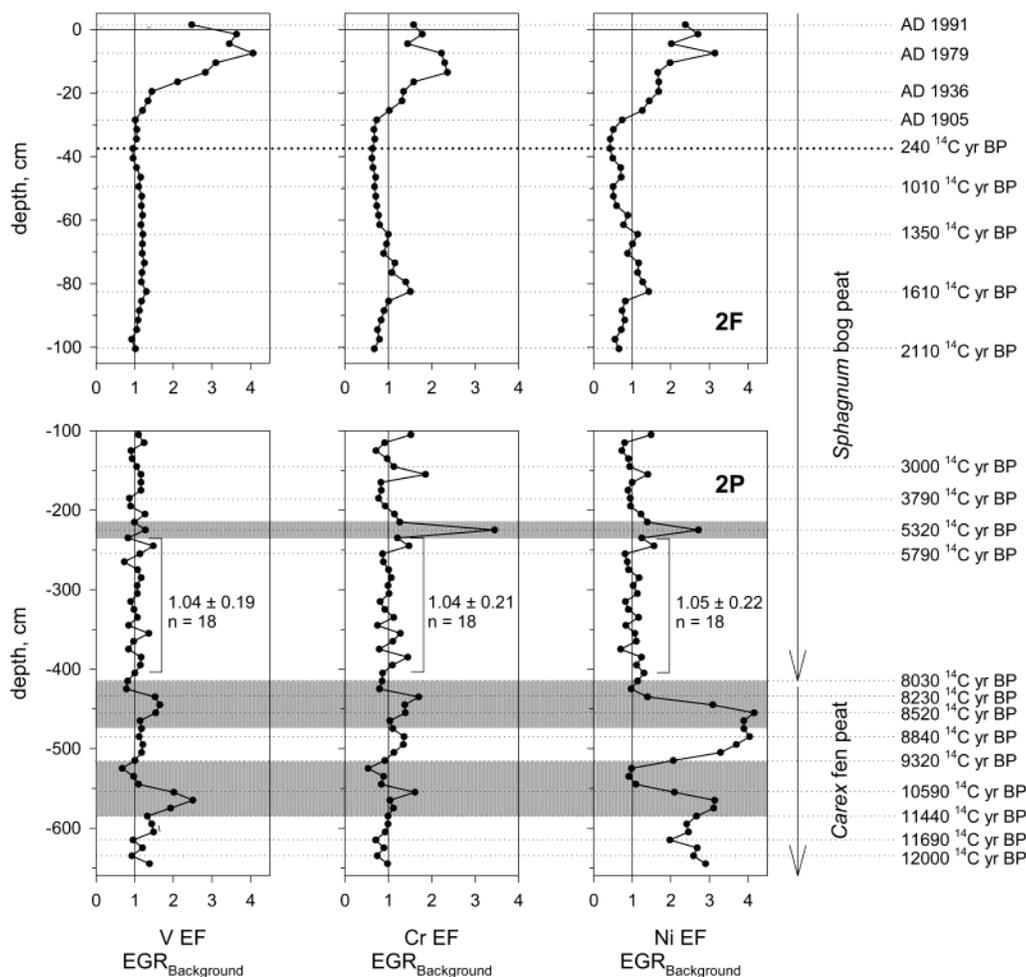
FIGURE 4. Temporal variation in EF (normalized to "natural background" values) for V, Cr, and Ni. Shaded bars in the 2P plots highlight three anomalous zones (see text for details). The solid vertical line (EF = 1) represents M/Sc values which are neither significantly enriched nor depleted, relative to crystal values.

$(r^2 = 0.820, n = 63)$. Taking 16 μg/g Sc as being representative of the Earth's Upper Crust (*41*), these regressions yield 113 μg/g V and 104 μg/g Cr, which are comparable with crustal values of 98 and 126 μg/g, respectively (*41*). In other words, not only can atmospheric soil dust (as reflected by the Sc concentrations in the peat) explain most of the variation in V and Cr, but these elements are largely present in the dust (which was deposited to the bog surface) in crustal proportions.

Explaining the Ni concentration exclusively in terms of atmospheric soil dust deposition is more problematic. The Ni/Sc ratios are elevated in all of the peat samples corresponding to the *Carex* fen peat zone (Figure 2). Even after subtracting the sample corresponding to the YD, all samples more recent than A.D. 1944, and all of the *Carex* peat samples, the linear regression yielded Ni = 2.50 [Sc] + 0.55 ($r^2 = 0.61$, $n = 57$). With respect to Ni, therefore, there appears to be more pronounced fractionation of this element taking place during chemical weathering of crustal rocks.

Enrichment Factors for V, Cr, and Ni Relative to Background Values. Normalization of the M/Sc ratios to the natural background values allows enrichment and depletions to be quantified, relative to this reference point. Enrichment factors (EF) were calculated for V, Cr, and Ni as follows:

$$EF = ([M]/[Sc])_{sample}/([M]/[Sc])_{EGR\ background} \qquad (1)$$

where [M] and [Sc] refer to the total concentration of V, Cr, or Ni and Sc in the peat sample and the background

concentrations are those cited earlier; the background value for Sc during the Holocene climate optimum is 0.08 μg/g. The EFs for V, Cr, and Ni in both peat cores relative to these background values are summarized in Figure 4.

The EFs calculated in this way give strong evidence that V and Cr are exclusively provided by the atmosphere throughout the entire peat column because the EF values for V and Cr in the deepest peat sample (just above the basal sediment) are not significantly different from the values that characterize the Holocene climate optimum. Therefore, supply of V and Cr due to mineral–water interactions in the minerogenic *Carex* fen peat or through dissolution of the sediment underlying the peat has not contributed in a measurable way to the V and Cr inventories of the peat profile. In fact, the vertical distribution of both elements follow that of Sc from the base of the profile ascending to about 240 ^{14}C yr B.P. In peat samples more recent that 240 ^{14}C yr B.P., therefore, some other source of V and Cr or some other enrichment process outside of atmospheric soil dust deposition must be invoked to explain the V and Cr EF data.

In contrast, Ni EF in deeper peat layers ranged from approximately 1 to 4, approaching unity only at the onset of the Holocene optimum. The pronounced enrichment of Ni in the minerotrophic section of the peat bog profile contrasts with V and Cr and will be discussed later. The strong depletion of Ni EF (and to a much lesser extent for V and Cr) between ca. 9320 and 10 590 ^{14}C yr B.P. is seen at a period where ASD deposition rates are at their highest values (also compare to Sc in Figure 1) (*20, 21*). This finding suggests that the soil-
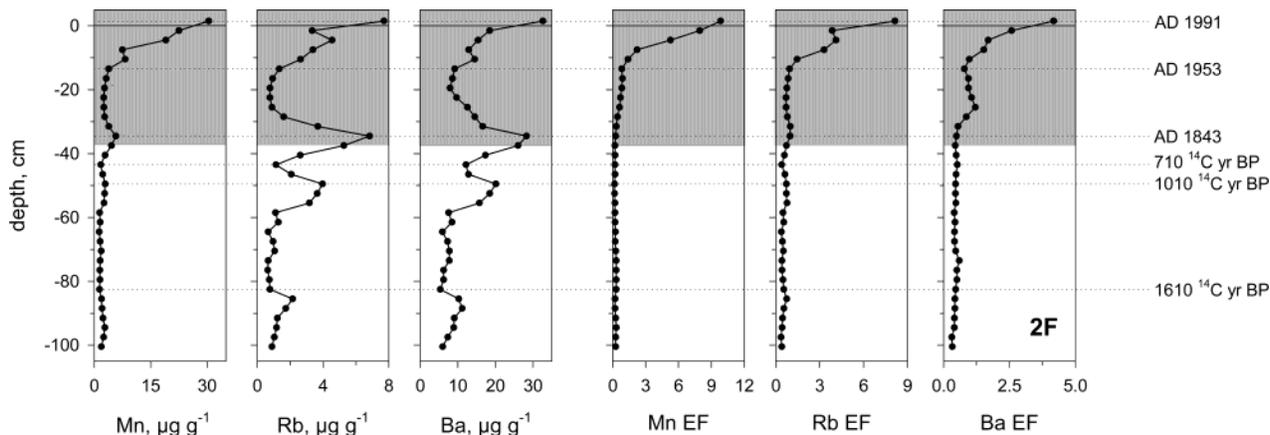
FIGURE 5. Concentrations of Mn, Rb, and Ba as well as corresponding EF in the 2F core from EGR.

derived particles supplied to the bog during the YD were predominantly coarse materials, relatively poor in trace elements, with abundant heavy minerals (20, 21). A similar depression of EF, especially for Ni, is also found between 8520 and 8030 ^{14}C yr B.P. ASD deposition rates, characterized by elevated Ti and Zr (20, 21) as well as Sc (Figure 1) concentrations, also peaked during that period. Again, larger soil dust particles with abundant heavy minerals (as revealed by enrichments of Ti, Zr, Hf, and the REE) were supplied to bog at this time, but these particles must have been relatively poor in trace elements such as Ni. These observed physical and chemical changes support our earlier arguments that this peat zone characterizes a period of climate change that lasted about 500 yr and that they are not simply the result of a single volcanic event.

The peat core from EGR was found to be enriched in Ti, Zr, Hf, and the REE in a sample dating from 5320 ^{14}C yr B.P. (20). Analyses of the V, Cr, and Ni in this peat core now reveals that the aerosols supplied to the bog at this time were also enriched in both Cr and Ni by approximately 3 times but were not enriched in V (Figure 4). By analogy with Zr and REE, the relative enrichment of Cr and Ni imply that they must have been highly enriched in some comparatively dense mineral phases (e.g., Cr spinel) that became more abundant when wind strengths increased. In contrast, these particles were not enriched in V, which suggests that it has less preference for specific mineral phases and was less fractionated during chemical weathering of soils.

While there are other peaks in the Cr and Ni EF profiles (e.g., just prior to 3000 ^{14}C yr B.P.), a detailed discussion of these variations and their correlation with Holocene climate change is beyond the scope of this paper. We note further that the 2P core had been cut into 10-cm slices, which means that many of the pronounced changes in EF will have been lost by the poor temporal resolution afforded by the coarse sectioning of the core. A more detailed study of the natural enrichment of lithogenic elements such as Ti, Cr, Zr, and the REE relative to Sc may provide new insight into Holocene climate change but needs to be done using much finer sample resolution (e.g., 1-cm slices).

With the beginning of the Industrial Revolution (around 240 ^{14}C yr B.P.), atmospheric aerosols became enriched in V, Cr, and Ni again (Figure 4). The highest EF of V, Cr, and Ni (4.1, 2.4, and 3.1, respectively, relative to the background values) were found in samples dating from ca. A.D. 1950 to A.D. 1980. Subsequently, EF decreased to reach present day values. However, the EF of the three elements in the uppermost sample (living *Sphagnum* moss at the time of collection) was lower than the EF of the peat samples below. The possible effects of plant uptake on the V, Cr, and Ni concentration profiles will be discussed in more detail in the next section.

Enrichment of V, Cr, and Ni in Surface Layers by Plant Uptake. The uppermost sample (2f1, 0–3 cm) of the 2F peat core consists of *Sphagnum* moss overlying the actual peat. The concentrations of V, Cr, and Ni in this *Sphagnum* moss sample were lower than in the underlying peat, indicating no significant accumulation of the three elements by the plant material (Figure 1). As an independent check on this interpretation, concentration profiles and EF of Mn, Rb, and Ba (normalized to natural background values at EGR) in the 2F core have been summarized in Figure 5. The concentration profiles of Rb and Ba are similar to those of V, Cr, and Ni with the concentration profiles of the three elements largely following that of Sc. However, the EF data show that Mn, Rb, and Ba are more enriched in the uppermost samples (9.8, 8.1, and 4.2 times, respectively) than the much smaller enrichments of V, Cr, and Ni. Thus, the enrichments of V, Cr, and Ni were most probably exclusively caused by the enrichment of these metals in the aerosols supplied to the bog surface and are not governed by plant bioaccumulation. In other words, these enrichments appear to have been caused by processes external to the bog and not by some internal geochemical or biogeochemical process.

The enrichment of Mn in the topmost layers of peat bog profiles is characteristic of this element in ombrotrophic peat. Aaby and Jacobsen (27), for example, showed that the greatest Mn concentrations were found in the uppermost samples of two peat cores, postulating a transport of Mn to the surface layers from below. While it certainly is plausible that Mn(II) may diffuse from anoxic pore waters up into the oxic zone, with the subsequent precipitation of MnO_2, advective flow of the pore fluids takes place in the other direction. A second possibility, given the resemblance between the distribution of K and that of Mn, is that the Mn enrichment at the bog surface is due to plant bioaccumulation (26). At this time, we cannot distinguish between Mn enrichment due to redox processes and those due to plant bioaccumulation. The behavior of Rb and Ba, however, can only be explained by plant uptake as these elements have only one oxidation state. Because of similar ionic radii, Rb can substitute for Na and K and Ba can substitute for Ca in biological systems leading to enrichments of both elements in the more recent peat layers. The declining EF of V, Cr, and Ni in the moss sample as compared to the underlying peat in contrast with the increasing EF of Mn, Rb, and Ba suggests that plant uptake and recycling have not had an important effect on the distribution and enrichment of V, Cr, and Ni in the topmost layers of the peat profile.

Anthropogenic Enrichment of V, Cr, and Ni since the Industrial Revolution. The EF data show that the greatest change in Cr and Ni enrichment began ca. A.D. 1905 and for V was in A.D. 1936 (Figure 4). We know of no other complete time series of atmospheric deposition of V, Cr, and Ni in the

TABLE 2. Concentrations of V, Cr, and Ni ($\mu g \ g^{-1}$) in the Deepest Peat Samples as Well as in Sediment Underlying the Peat at EGR

element	deepest peat sample (2p55), $n = 4$	sediment underlying sample 2p55, $n = 7$
V	11.4 ± 0.7	79.0 ± 4.5
Cr	11.2 ± 0.1	100 ± 3
Ni	20.0 ± 3.1	41.1 ± 4.1

contemporary literature. A recent paper (*42*) on Ni and V in ice and snow from Mont Blanc provides some data for the period ca. 1960–1990, but this site lies at an elevation of 4250 m, well above the planetary boundary layer, and the results cannot easily be compared with the peat bog record from EGR that lies at 1005 m. The snow and ice data, with near weekly temporal resolution, show extremely variable concentrations with V varying by up to 300× and Ni varying up to 100×. Comparison with Al concentrations and crustal abundance suggests that 10–100% of the V and Ni may be derived from crustal sources with the rest predominantly anthropogenic. Comparison of the two data sets suggests that it would be worthwhile to measure Cr in addition to V and Ni in deeper, older ice layers for comparison with the samples dating from 1960 to 1990 to try to quantify the natural background concentrations, fluxes, and enrichments of these metals in alpine ice.

Enrichment of V, Cr, and Ni in Basal Layers Due to Sediment Dissolution. The botanical "bog/fen limit" at EGR is found in the 2P core at 420 cm. The peat cores consist of *Sphagnum* bog peat above this limit, whereas underlying zones are dominated by *Carex* fen peat. Previous studies revealed that the peat at EGR consists of not more than 150 cm of truly ombrotrophic peat and that the underlying peat layers become increasingly minerogenic with increasing depth (*20*). For example, elements such as Ca, Mg, Sr, Fe, and S are released by chemical weathering of the carbonate fraction of the basal sediment and migrate vertically upward (*21*). While this process does not impact elements such as Pb, Cu, Cd, and Sb (*20, 21*), it certainly has affected Ni. While V and Cr are nearly 10 times more abundant in the sediment as compared to the basal peat layer (Table 2), for Ni the concentration gradient between the sediment and peat sample 2p55 is only a factor of 2. Descending vertically downward through the peat profile, already the peak at 435 cm, which is clearly visible for V and Cr, is hardly recognizable in the case of Ni (Figure 1, insert). Below this depth (8230 ^{14}C yr B.P. until the end of the YD), Ni concentrations distinctly increase out of portion with Sc, which clearly documents an addition of Ni to the peat profile inventory from chemical weathering. In contrast, chemical weathering of the basal sediment has not had a measurable effect on the V and Cr inventories of the peat core. Therefore, while the peat bog at EGR has yielded a record of atmospheric V and Cr accumulation since 12 370 ^{14}C yr B.P., the record of atmospheric Ni deposition extends back only ca. 8000 ^{14}C yr: in older peat samples, the atmospheric Ni signature cannot be distinguished from the Ni added by chemical weathering of the basal sediment.

Calculating "Excess" V, Cr, and Ni in the Peat Profile. Using the natural background M/Sc ratio from the middle of the Holocene (summarized earlier), it is possible to use the Sc concentration profile to calculate the "lithogenic" component of the metal profiles as

$$[M]_{lithogenic} = [Sc]_{sample} \times [M/Sc]_{EGR \ background} \quad (2)$$

In essence, this calculation provides an estimate of the atmospheric soil dust inputs to the peat profile. Subtracting

the lithogenic component from the total concentrations allows the excess concentration of each element to be calculated as

$$[M]_{excess} = [M]_{total} - [M]_{lithogenic} \quad (3)$$

The results of these calculations, presented in Figure 6, indicate that there is very little excess V, Cr, and Ni found in the peat profile. In fact, most of the metal is lithogenic, and the supply of this component can be explained by the deposition of atmospheric soil dust. Excess V, Cr, and Ni are restricted to the top, most-recent peat samples and the YD (centered at 10 590 ^{14}C yr B.P.). In addition, there is an excess of Ni in the peat samples below and above the YD that can be explained by chemical weathering (as described earlier). On the basis of the data and arguments presented elsewhere in this paper, we interpret the excess V, Cr, and Ni for the topmost, recent samples from anthropogenic contributions. In contrast, peaks in excess V, Cr, and Ni centered around the YD indicated that the soil dust deposited during this period had a different chemical composition and was richer in these three metals as compared to samples from the middle of the Holocene.

Comparison to Results from Ice Cores. As ice cores can be also utilized as archives of atmospheric metal deposition, we compared the results of the present study to those obtained from ice cores. To the best of our knowledge, only one study (*43*) reports on a time series of several elements (including V, Cr, Mn, and Ba) in a single ice core. This particular study, however, did not include the elements Ni and Rb and provides only data since the mid-19th century to recent times.

A direct comparison between EF calculated from the results of the analysis of trace elements in ice cores from Antarctica and peat bogs from Central Europe is difficult; therefore, such a comparison should be made very carefully and with great caution. Mineral dust deposited at continental and polar sites, for example, largely differs in size representing long- and short-range transport of particles. Nevertheless, a comparison of time series in ice cores and peat bogs is useful to assess global and local contamination with particular elements of environmental concern.

Table 3 summarizes the EF for V and Cr calculated from the corresponding elemental concentrations in ice (*43*) and peat cores, respectively, averaged over extended periods. Mn and Ba were not included in this comparison because the two elements are so dynamic in peat that they cannot be compared with ice archives. Elemental EF from the ice core were calculated using Al as reference element (*43*). For a better comparison of the data, our EFs, which refer to Sc as the reference element, have been recalculated considering Al as tracer element. As reported earlier (*20*), however, Al tends generally to be slightly enriched in aerosols derived from soils relative to Sc in crustal rocks. Therefore, EF values based on Al are often about 20% lower than those using Sc as the reference element (*20*).

Etang de la Gruère, the site where the peat cores have been collected, represents a rural area in mid-Europe. Antarctica, in turn, is a remote region without any relevant local emissions. Therefore, only aerosol depositions of global influence are preserved in the ice core from Antarctica. This implies that EFs obtained from ice cores should be lower than or at most equal to EFs calculated from peat cores in the middle of Europe. This assumption holds true for V (Table 3), but the EF for Cr in peat is distinctly lower than that calculated for Cr in ice cores. As mentioned before, dust from the Antarctic predominantly consists of very fine particles (<5 μm). The reason for the high enrichment of Cr at the South Pole may be found in this fine fraction of dust, which partly consists of clay that is enriched in Cr. Dust
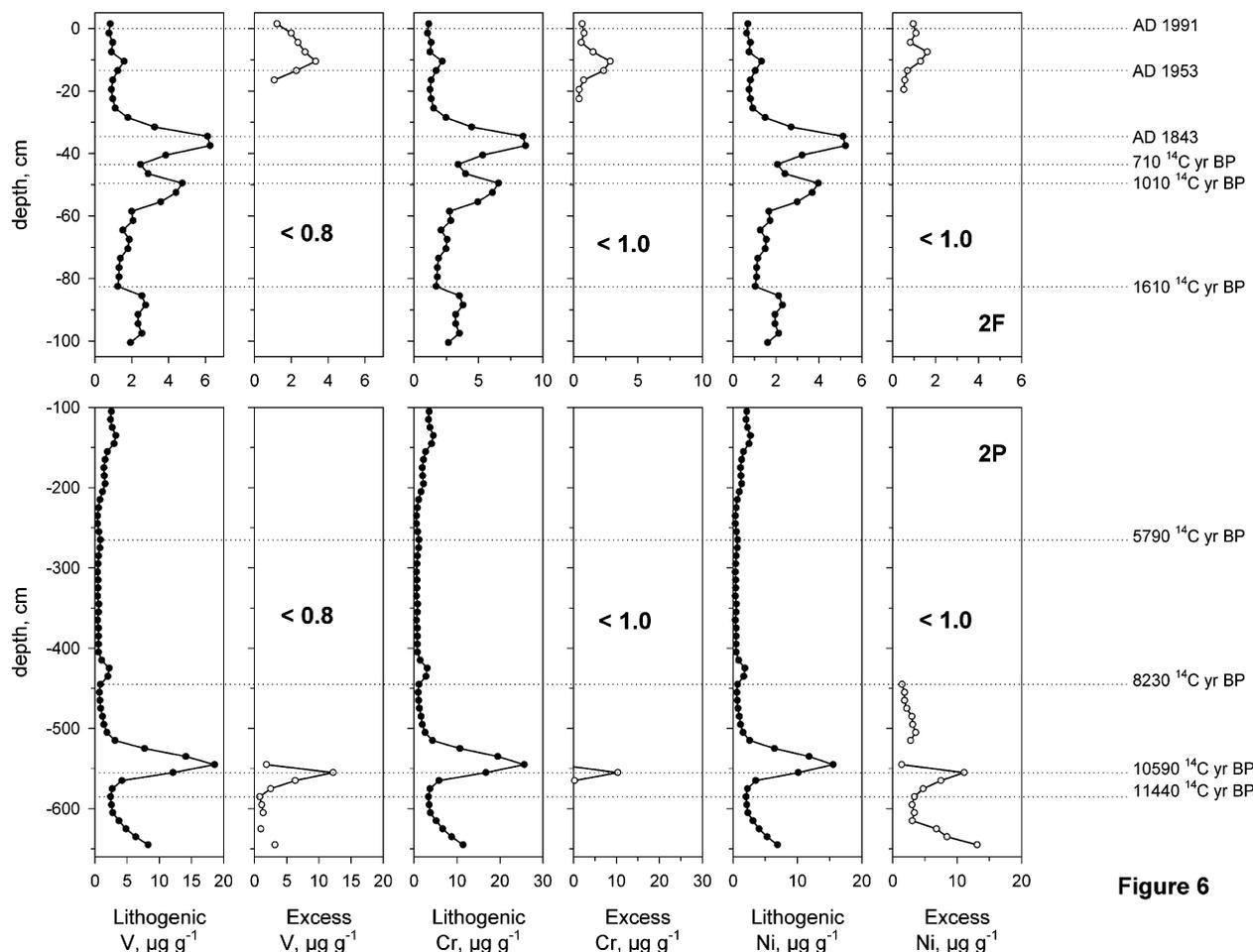
FIGURE 6. Concentrations of V, Cr, and Ni from atmospherically derived soil dust (lithogenic) and excess contributions (anthropogenic, sediment dissolution) normalized to "natural background" values. Details and calculations are given in the text.

TABLE 3. Comparison of Mean Crustal Enrichment Factors for V, Cr, Mn, and Ba for Various Time Periods Using Peat and Ice Cores[a]

	vanadium			chromium		
	peat		ice	peat		ice
time period	EF_{Sc}	EF_{Al}	EF_{Al}	EF_{Sc}	EF_{Al}	EF_{Al}
1830–1888	1.2	0.9	0.7	0.8	0.6	4
1895–1923	1.3	1.0	0.6	1.2	1.0	6
1940–1951	2.4	2.0	0.9	2.1	1.7	6
1959–1990	4.0	3.1	1.3	2.3	1.9	16

[a] Time periods and elemental EF from ice cores have been taken from ref *30*. EF calculated from elemental concentrations in peat have been averaged to match the given time intervals (*30*) as closely as possible as follows: 1830–1888, peat sample 2f12–2f13; 1895–1923, peat sample 2f9–2f11; 1940–1951, peat sample 2f6–2f8; 1959–1990, peat sample 2f2–2f5.

particles from EGR, in contrast, are "diluted" with local particles, which are comparatively large and poor in Cr.

The collection of ice cores, in general, requires substantial financial support and a highly sophisticated logistic infrastructure. Sampling, transport, and decontamination of the frozen ice cores as well as subsequent trace element determination is time-consuming and a delicate task. Peat cores, in turn, are easily accessible at much lower cost; elemental concentrations are higher by orders of magnitudes, facilitating analysis, and also provide valuable information regarding atmospheric metal deposition. Considering the advantages

peat bogs offer for studies of ancient and recent atmospheric metal deposition, these archives should be more intensively exploited for this purpose. In this context, the peat bog at EGR may serve as an excellent reference for V, Cr, and Ni in modern European aerosols.

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