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TITLE: INORGANIC CONTENTS OF PEATS

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INORGANIC CONTENTS OF PEATS

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Abstract

Peat, the precursor of coal, is composed primarily of
plant components and secondarily of inorganic matter derived
from a variety of sources. The elemental, mineralogic, and
petrographic composition of a peat is controlled by a combina-
tion of both its botanical and depositional environment.
Inorganic contents of peats can vary greatly between geograph-
ically separated peat bogs as well as vertically and horizon-
tally within an individual bog. Predicting the form and
distribution of inorganic matter in a coal deposit requires
understanding the distribution and preservation of inorganic
matter in peat-forming environments and diagenetic alterations
affecting such material during late-stage peatification and
coalification processes.

Peat, the precursor of coal, is composed primarily of organic plant
components and secondarily of inorganic matter composed of crystalline
minerals, amorphous materials, exchangeable cations and metals, and non-
crystalline plant matter. The initial composition of a peat is
controlled by a combination of its botanical and depositional elements
[e.g., Cecil et al. (1), Cohen (2); Cohen and Spackman (4); Cohen et al.
(5); Raymond et al. (6), (7), (8)]. The coal resulting from this peat
is controlled by diagenetic alterations during initial peatification and
later coalification.

Inorganic compositions of coals have been related to depositional
environments [e.g., McCabe (9)], diagenetic alterations [e.g., Mackowsky
(10)], and paleoclimates [Cecil et al. (1)]. Similarly, mineralogic
associations of peats have been used to interpret geologic conditions at
the time of peat deposition [Raymond et al. (7), (8)]. However, the
mechanisms by which many inorganic elements and minerals are incorpor-
ated into peat deposits, and finally into coals following coalification,
are still open to debate [e.g., Cecil et al. (11) and Finkelman (12),
(13)]. Whatever the dominant mechanism for incorporation of inorganic
components into coals, the occurrence of minerals and inorganic matter
in recent peat deposits suggests an equivalent occurrence must have
existed in the precursors of today's coal deposits. It is therefore
important to acknowledge that peats may contain very different inorganic
components, and these differences in the starting material must be con
sidered whenever one is developing models for the occurrence of inor
ganic material in coal.

The purpose of this paper is to demonstrate the great variations that exist in mineral and inorganic element contents between and within peat deposits.

Overview

The botanical composition of peat, chemistry of interstitial peat waters, peat/fauna associations, hydrologic movements within a peat environment, and potential mineralogic and elemental sources in proximity to peat deposits represent the major factors controlling inorganic matter occurrence in peat environments.

The same hydrologic movements that control leaching of elements also control peat decay, humification, and elemental enrichment as certain elements are readily absorbed in response to the increased humification of certain peat types. Thus, mechanisms have been suggested for the transportation and emplacement in peat bogs for a large number of free elements, thereby accounting for elemental anomalies in the resulting peat deposit [Cameron and Schruben (14)]. McCarthy et al. (15) have shown that peats are able to accumulate substantial quantities of metals, possibly as a result of the concentrating abilities of bacteria [Beveridge and Fyfe (16)], incompatible with normal ion-exchange properties of the peats. Abundances of these free elements may account for much of the "amorphous humps" seen in x-ray diffraction (XRD) patterns of peat low-temperature ashes [Raymond et al. (8)]. Bacteria have also been suggested as the mechanism for the destruction of siliceous ingredients in peats [Andrejko et al. (17)], and microorganisms such as fungi and bacteria have been associated with the physical or chemical breakdown of cell components and the production of new organic substances [Cohen et al. (5)], both of which conceivably would affect the occurrence of inorganic matter in peat.

The chemistry of interstitial peat waters plays a significant role in the formation and diagenesis of the minerals present in peat deposits. As an example, clay mineralogies within peat deposits appear to relate to pH conditions at the time of their formation. The more acidic conditions resulting from the presence of greater concentrations of organic acids, which in turn appear to result from high concentrations of organic matter under continually wet conditions, favor the formation of kaolins over smectites. In a more detailed view, microscopic subenvironments of peat deposits may contain interstitial waters with characteristics very different from those of the overall deposit. As a result, minerals may exist or form in these subenvironments that are not in equilibrium with the Eh/pH conditions of the deposit as a whole.

Fauna and flora both contribute inorganic matter directly into peat depositional systems. Crystalline mineral matter has at least two documented botanical sources. Peat-producing plants, such as Nymphaea (water lilies) and Orontium ("never wet") have been shown to precipitate calcium oxalate minerals [Bardin and Bish (18); Griffin et al. (19)]. Biogenetically-derived carbonate minerals have been produced by metabolism of blue-green algae in the Everglades [Gleason (20)]. Amorphous

inorganic materials of botanical or biological origins likewise make up a large portion of the inorganic fraction of peats. Some peat-producing plants in the Everglades and Okefenokee, such as the sedges and grasses, accumulate silicon in the form of non-crystalline phytoliths [Andrejko and Upchurch (21); Andrejko and Cohen (22)]. Biogenically produced siliceous sponge spicules have been found in water lily peats in the Okefenokee Swamp [Cohen (23); Yeakel and Spackman (24); Andrejko et al. (17)] and in fluvial-deposited peats in Costa Rica [Raymond et al. (6)]. Siliceous freshwater diatom assemblages have been shown to be common in many peat forming environments [Scherer et al. (25); Scherer and Cohen (26); Raymond et al. (6)].

Other crystalline mineral matter in peats can be related directly to depositional systems and diagenetic alterations within those systems. Detrital sands and clay minerals derived from nearby streams are common in coastal peat deposits [e.g., Staub and Cohen (27), (28)]. Detrital fine-grained quartz and kaolinite have been shown to occur well away from channels within peats of the Okavango Delta, Botswana [McCarthy et al. (15)]. Sulfide and sulfate minerals (especially pyrite) have been found in brackish-water peats or peats overlain by brackish-water or marine sediments [Casagrande et al. (29), (30); Casagrande and Price (31); Cohen et al. (32); Cohen and Andrejko (33); Davies and Raymond (34); Raymond et al, (7)]. An anomalously high concentration of pyrite has been reported also within a freshwater peat environment as a result of a subterranean sulfate-enriched water source [Raymond et al. (35)]. Small quantities of fine-grained sand of probable aeolian origin have been detected in some Okefenokee peats [Cohen (23)]. It also has been demonstrated that certain short-lived minerals can be produced through natural phenomena, such as fires, [Andrejko and Upchurch (36)]. Finally, volcanic ash diagenetically altering to halloysite has been shown to be a major component of some tropical peats [Raymond et al. (6), (37)].

Variability in Inorganic Contents of Peats

As part of a previous cooperative effort between the Los Alamos National Laboratory and the Institute of Gas Technology investigating the effects of petrographic and physiochemical properties of peat on their dewatering and wet carbonization characteristics, an abundance of data on the occurrence of inorganic matter in 12 very diverse peat samples was collected [Raymond et al. (8)]. A description of these peat samples including peat type, degree of humification, location, environment of deposition, sulfur content, and proximate analysis is given in Table 1. In Tables 2 and 3, major element data as determined by x-ray fluorescence (XRF) of high-temperature ashes (HTAs) and mineralogic data as determined by XRD of low-temperature ashes (LTAs) are shown. The purpose in presenting this data is to point out the great variability that exists in inorganic contents of peat samples whether one is concerned with HTA ash contents (0.38 wt% to 30.65 wt%), elemental contents of HTAs (e.g., Si: 3.5 wt% to 42.5 wt%), or the abundance of specific minerals (whether dominated by quartz [SiO_2], bassanite [$CaSO_4 \cdot 1/2H_2O$], halite [NaCl], or amorphous material).

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TABLE 1: WELL-CHARACTERIZED PEATS

Sample	Peat Type	Humification	Location	Environment
#94	Sphagnum	Fibric	Minnesota	Raised Bog
#95	Spruce, Woody Dicot	Sapric	Minnesota	Swamp-Forest
#96	Woody Dicot, Spruce, Grass	Hemic	Minnesota	Swamp-Forest
#97	Sphagnum	Fibric	Maine	Raised Bog
#98	Nymphaea	Fibric	Loxahatchee, FL	Marsh
#99	Sawgrass	Hemic	Loxahatchee, FL	Marsh
#100	Sawgrass	Sapric	Tamiami, FL	Marsh
#101	Rhizophora	Hemic	Everglades, FL	Brackish, intertidal
#102	Taxodium	Sapric	Okefenokee, FL	Swamp-Forest
#103	Nymphaea	Hemic	Okefenokee, FL	Marsh
#104	Persea, Woody Dicot, Grass, Fern	Sapric	North Carolina	Swamp-Forest
#105	Woody Dicot, Spruce, Fern	Sapric	New York	Swamp-Forest

Sample	% S	% Residual Moisture	% Volatiles	% Fixed Carbon	% Ash
#94	0.05	8.75	74.14	24.04	1.82
#95	0.22	7.59	61.31	28.38	10.31
#96	0.24	7.19	53.92	19.63	26.45
#97	0.08	8.14	70.82	28.80	0.38
#98	0.66	7.65	67.61	25.90	6.49
#99	0.76	9.09	61.16	32.53	6.31
#100	0.62	9.26	59.67	29.32	11.01
#101	2.38	9.12	47.76	21.59	30.65
#102	0.28	6.55	59.20	26.38	14.42
#103	0.29	6.63	61.06	26.95	11.99
#104	0.13	4.52	60.92	37.92	1.16
#105	0.50	10.19	58.65	28.44	12.91

NOTE: After Raymond et al. (8).

Modeling the Occurrence of Inorganic Materials in Peats

No simple explanation exists for variations in the inorganic matter of peat deposits. When considered separately, neither plant type, HTA content, LTA mineralogy, surrounding geology, nor specific contents of certain elements will uniquely define the inorganic contents of a peat deposit. However, geologic models for bog development that consider plant types, depositional environments, and surrounding geology may be used to account for the inorganic contents seen in peats. The peats described in Tables 1 through 3 represent a variety of different peat types from many different depositional settings. Thus they illustrate variations in botanical, mineralogic, elemental, and ash compositions as great as commonly observed in all peats. However, similar variations in peat characteristics may occur within individual bog/marsh complexes.

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TABLE 2. MAJOR ELEMENT COMPOSITION OF HTA BY XRF

Element	Uncer.	# 94	# 95	# 96	# 97	# 98	# 99
Si %	0.1	28.8	25.3	27.9	7.8	11.8	6.6
Ti %	0.01	0.43	0.46	0.43	0.27	0.20	0.14
Al %	0.2	6.2	7.2	6.3	5.6	3.2	2.3
Fe %	0.4	3.4	3.6	7.2	3.3	6.0	2.8
Mn %	0.01	0.09	0.05	0.39	0.03	0.02	0.06
Mg %	0.3	1.7	2.0	0.96	20.3	2.0	4.1
Ca %	0.15	6.8	10.8	5.9	8.8	27.7	34.4
Na %	0.03	0.55	0.42	0.56	1.7	0.77	0.56
K %	0.04	1.2	1.4	1.6	0.79	0.34	0.24
P %	0.04	0.85	0.51	0.51	1.8	0.28	0.34

Element	Uncer.	# 100	# 101	# 102	# 103	# 104	#105
Si %	0.1	3.5	15.9	41.9	42.5	25.5	10.3
Ti %	0.01	0.12	0.35	0.16	0.03	0.74	0.21
Al %	0.2	2.9	6.2	2.6	1.8	7.2	3.1
Fe %	0.4	12.6	2.4	0.87	1.7	5.5	3.4
Mn %	0.01	0.02	0.01	0.01	0.01	0.02	0.18
Mg %	0.3	1.4	4.3	0.17	0.29	5.8	3.1
Ca %	0.15	33.5	3.8	0.16	0.2	1.8	33.8
Na %	0.03	0.34	10.7	0.16	0.19	1.1	0.24
K %	0.04	0.15	1.2	0.26	0.20	0.63	0.74
P %	0.04	0.25	0.27	0.37	0.17	0.64	0.59

NOTE: After R .,amond et al. (8).

Mineral	# 94	# 95	# 96	# 97	# 98	# 99
Quartz	A	A	A	A	M	M
Corundum	M	P	P	A	P	P
Bassannite	M	P		A	A	A
Alkali Feids.	M	M	M			
Muscovite	P	M	P		P	
Kaolinite		P	P	P	P	P
Smectite			P			P
Halite (w/Sodium Perchlorate)						
Pyrite						M
Amorphous	A	M	A	A	A	A
Ash %	1.8	9.1	27.5	0.6	5.8	5.8
Location	MN	MN	MN	ME	FL	FL

Mineral	# 100	# 101	# 102	# 103	# 104	# 105
Quartz	P	A	M	M	A	A
Corundum			P	P	M	P
Bassannite	P	M				P
Alkali Felds.						P
Muscovite			P	P		
Kaolinite		P		P	P	
Smectite		P				
Halite (w/Socium Perchlorate)		A				
Pyrite		P				
Amorphous	A	M	A	A	A	A
Ash %	11.2	31.9	15.0	15.6	1.3	12.8
Location	FL	FL	GA	GA	NC	NY

A - Abundant M - Minor P - Present.

NOTE: After Raymond et al. (8).

Such an occurrence has been described for the Great Heath of Little Cranberry Island, Maine, by Raymond et al. (7).

The Great Heath of Little Cranberry Island contains three major peat types within 1 km². The majority of the Heath is a Sphagnum moss-dominated raised bog, composed of similar materials to peats #94 and 97 (Table 1). Surrounding the raised bog is a swamp/marsh complex containing grass, sedge, Sphagnum moss, alder, tamarack, and skunk cabbage. Swamp/marsh-deposited peat occurs both around the margins of The Heath and under Sphagnum-dominated peat. Similar swamp/marsh communities exist at the collection sites of peats #95, 96, and 104 (Table 1). A third type, dominated by herbaceous aquatics, is present underlying all swamp-marsh dominated peat but is present only as a minor botanical community of The Heath. Similar herbaceous aquatic communities are represented by peats #98 and 103 (Table 1), although ash contents of the herbaceous aquatic peats of Cranberry Island are much higher. The three peat types of The Great Heath have major differences in petrographic characteristics, HTA contents, and associated mineralogies. In Figure 1 the relative mineralogic associations of the three peat types are shown for three vertical sections of the deposit located along a transect from the center of the deposit to its margin situated behind a cobble beach berm. Mineral species become more numerous in the peat deposit both approaching its margin and bottom. High ash contents and diverse mineralogies are the result of the geometry of the depositional basin and the proximity of surrounding mineralogic sources. Botanical variations in turn reflect alterations in nutrient levels necessary to support ecologic communities within the maturing bog. High ash contents near the margin irrespective of peat type are the result of a very proximal sediment source. Sulfur contents range from a low of 0.19 wt% within the raised bog to a high of 4.44 wt% behind the beach berm where the peat was infiltrated by marine waters.

The Peat-to-Coal Transition

An important question is whether variations in inorganic matter that occur in recent peat deposits continue to persist in coal deposits. The dissolution of certain silica-rich materials, such as sponge spicules and phytoliths, has been shown to be commonplace in underlying peats of the Okefenokee Swamp [Andrejko et al. (17)] suggesting that some inorganic components of peats are removed during peatification. On the other hand, free silica recrystallizes to quartz through epigenetic processes during coalification [Ruppert et al. (38)]. There is little doubt that major transformations in inorganic matter occur during the peat-to-coal transition. However, certain relationships between inorganic matter in peats and coals can be shown to persist. For example, both Recent peat and Miocene lignite deposits of Costa Rica exhibit mineralogic traits that suggest similar weathering processes must have affected the mineral-rich horizons in the lignites that are now affecting mineral-rich horizons in recently deposited peats (Figure 2). Furthermore, relationships in sulfur contents of coals [e.g., Burk et al. (39) and Raymond (40)] have been shown to correlate well with hypothesized influence of marine waters during deposition of the coals, as do sulfur occurrences in recent peats (see previous discussion).
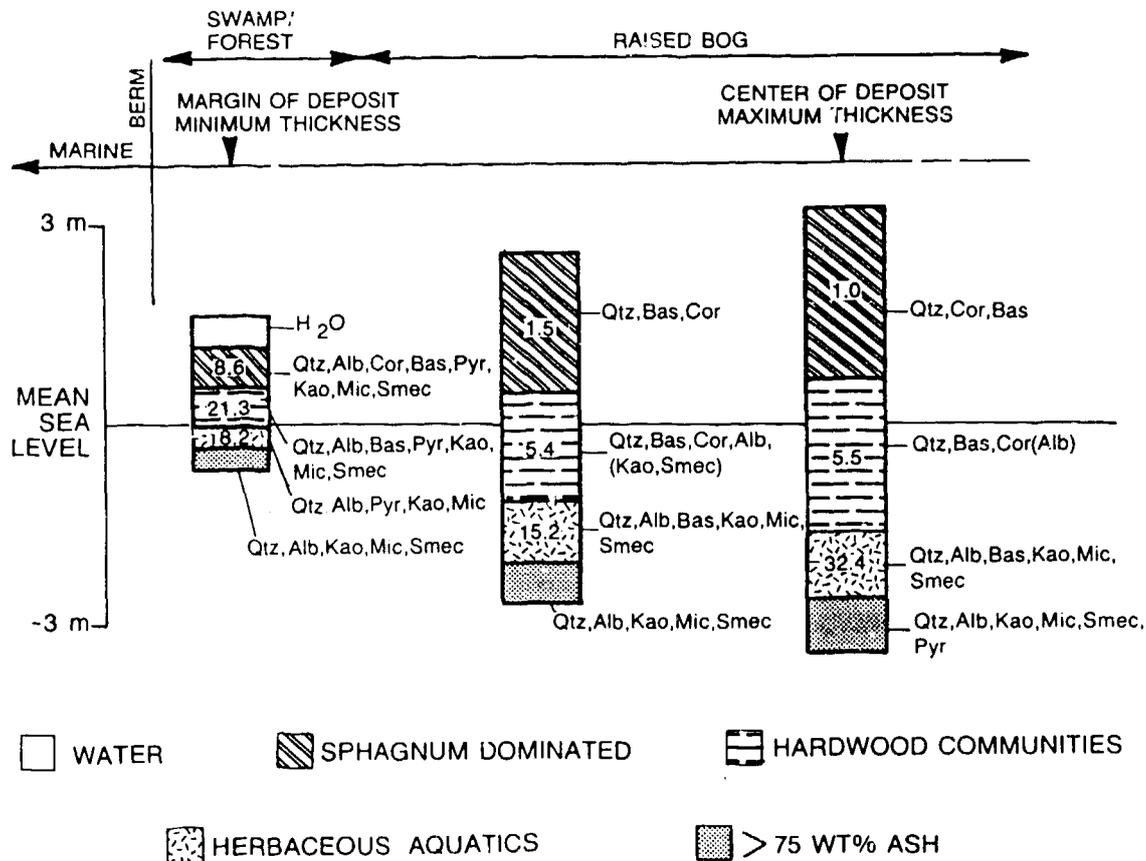
7

Figure 1: Association between mineral occurrence, peat type, HTA content, and location within the raised-bog/swamp-forest complex of the Great Heath, Cranberry Island, ME, for three vertical peat sections. HTA contents appear on the vertical sections. Qtz = quartz, Alb = albite feldspar, Cor = corundum, Bas = bassanite, Pyr = pyrite, Kao = kaolinite, Mic = mica, and Smec = smectite [after Raymond et al. (7)].

It is important, however, that investigators of coal properties that aid or prohibit certain economic uses of coals need be wary when utilizing data from peat studies. For instance, whether peat investigators analyze mineralogic contents of LTAs or HTAs will provide very different results (Figure 3). Even though HTA studies provide more information concerning the slagging effects of resulting ashes, LTA studies of peat's provide more information on which minerals might eventually end up as inorganic components of coals. Furthermore, we have discovered that analytical procedures developed both for proximate analysis of higher rank coal [ASTM D 3172 (41)] and for moisture, ash, and organic matter of peat materials [ASTM D 2974 (42)] appear to have poor reproducibility for proximate analysis (moisture, ash, volatiles, and fixed carbon) of peats [Raymond et al. (43)]. For example, determination of moisture evolution at 105°C can vary greatly depending upon peat sample size and humidity of the ambient gases (Figure 4), which in turn will cause erroneous results with respect to volatile, fixed carbon, and HTA contents.
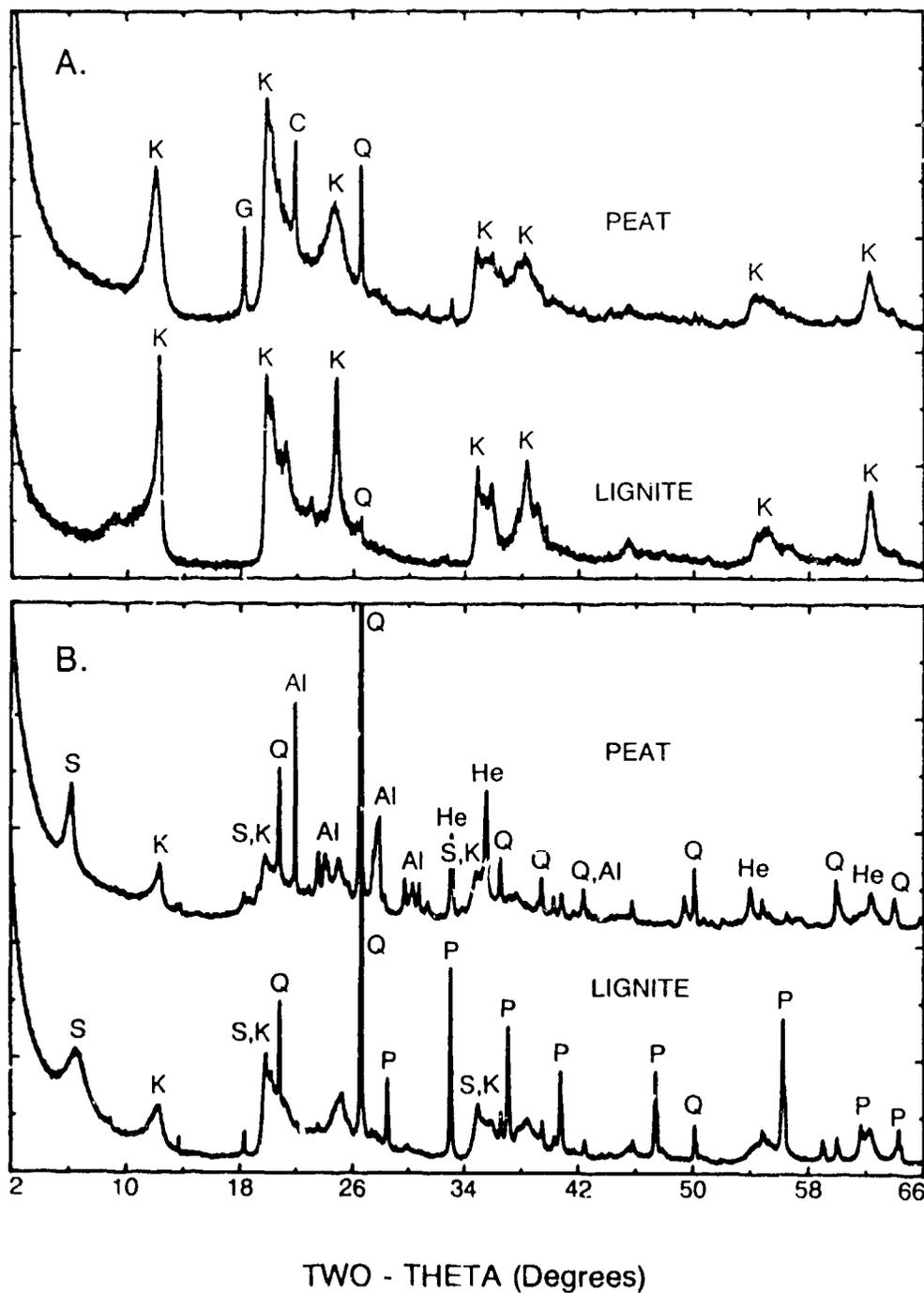
TWO - THETA (Degrees)

Figure 2: XRD patterns of mineral-rich horizons in peats and lignites of Costa Rica resulting from: (A.) ash falls being deposited directly into peat systems where alteration occurs within a low pH, reducing environment and (B.) ash falls deposited outside of the peat systems and transported to the peat deposits by fluvial means. K = kaolinite, G = gibbsite, C = cristobalite, Q = quartz, S = smectite, Al = albite feldspar, He = hematite, and P = pyrite.
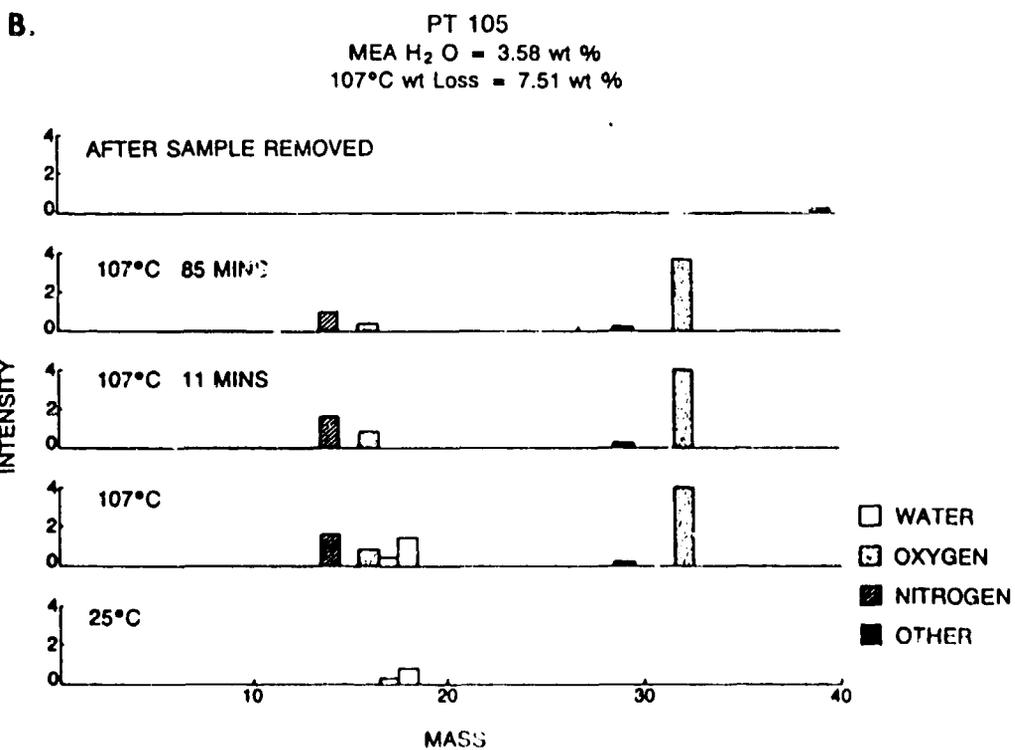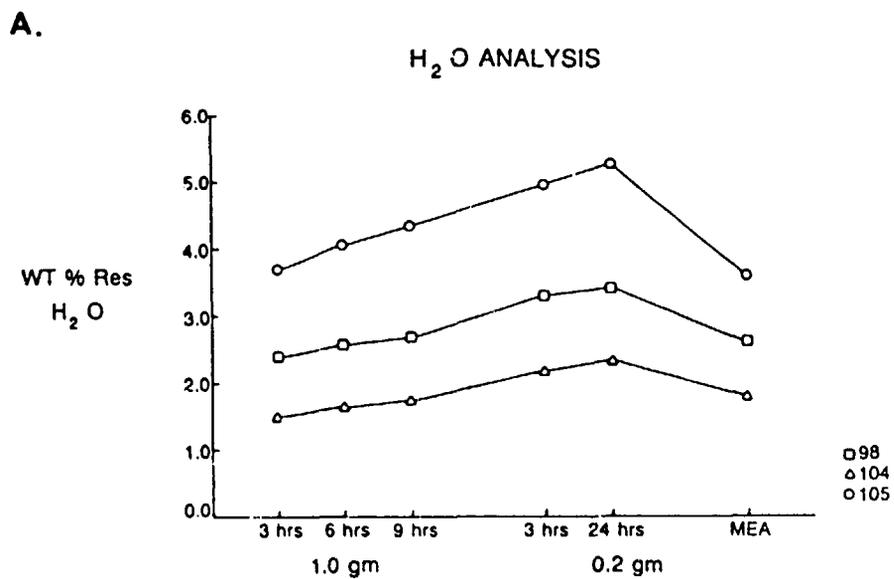
Figure 3: Differences in mineral occurrence between LTA and HTA of a Sphagnum peat (PT#94). M = mica, K = kaolinite, B = bassanite, Q = quartz, Al = albite feldspar, Co = corundum, and An = Anhydrite.

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A.

H$_2$O ANALYSIS

B.

PT 105
MEA H$_2$O = 3.58 wt %
107°C wt Loss = 7.51 wt %

Figure 4. A. Weight % of residual water evolving from three peat samples using 1.0 and 0.2 gm sample sizes vs. drying times compared to water content determined using a moisture evolution analyzer (MEA). B. Analysis of gases evolving from a woody peat (PT#105) at room temperature and after extended drying periods at 107°C. The sample was heated in a thermogravimetric analyzer and evolving gases were analyzed in a quadrupole mass spectrometer. Note, oxygen and nitrogen evolution cease after sample was removed.

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Conclusions

Inorganic contents of peats can vary greatly in response to changes in depositional/ecological environments. These variations can occur both vertically and horizontally withi.. an individual peat bog, as well as between geographically separated peat bogs. Even though specific characteristics existing within peats may or may not survive coalification, understanding the occurrence, form, and distribution of inorganic matter in peats is a b .:inning to understanding similar occurrences in coals.

Prediction of the f. rm and distr.)ution of inorganic matter in a coal deposit, however, requires more than just an understanding of the distribution and preservation of inorganic matter in various peat types and peat-forr :.g environments. Such predictions require an understanding of the diagenetic alterations of inorganic components of peats during late-stage peatification and coalification processes. Comparative studies across the peat-to-lignite transition, including mineralogic analyses, chemical analyses, geologic settings, and the effects of microorganisms will provide an insight into the genesis, alteration, and variable distribution of inorganic matter in higher rank coals.

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