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DETECTION OF AMMONIUM IN GEOLOGICAL MATERIALS BY EVOLVED GAS ANALYSIS

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The association of anomalously high levels of ammonium with both metallic and energy mineral deposits is of potential use in mineral exploration. Conventional geochemical methods for detecting NH_4 often provide only whole-rock NH_4 values and do not identify the specific minerals hosting NH_4. They may also lack sensitivity or be prone to interference. Evolved NH_3 analysis is shown to be capable of distinguishing between different NH_4-bearing minerals and can detect NH_4 values down to 120 ppm in rocks hosting silver-gold vein mineralization. Fully quantitative determination of NH_4 by this method is not possible as the NH_3 evolved from minerals during heating partially oxidised; however, amounts of evolved NH_3 do show a moderate positive linear correlation with NH_4 content determined by a modified Kjeldahl method.

Keywords: evolved gas analysis, geological materials, IR, NH_4-bearing minerals

Introduction

Interest in the distribution of ammonium in geological materials has centred on anomalously high concentrations of NH_4 associated with host rocks of precious and base-metal mineralisation [1–4], coal and oil shale deposits [5, 6], NH_4 minerals and nitrogen-rich fluid inclusions in very low-grade metamorphic rocks [7], and NH_4 as an indicator of organic maturation and hydrocarbon generation [8].

The NH_4^+ ion has a tetrahedral structure with an ionic 'radius' of 1.48 Å and similar geochemical behaviour to Group I trace elements Rb^+ and Cs^+. Because of this, it substitutes for K^+ in silicate and sulphate minerals, including NH_4-feldspar

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(buddingtonite) [5, 9– 11], NH_4-mica (tobelite) [12], NH_4-illite [2], NH_4-alunite [13] and NH_4-jarosite [14].

A number of analytical methods have been used to detect NH_4 in rocks and minerals. Infrared (IR) spectroscopy [10] is subject to potential interference from carbonates [15]; it is reported that remote sensing of NH_4 by IR is only sensitive at NH_4 concentrations > 900 ppm [16]. The Kjeldahl wet chemical method is probably the most widely used, but NH_4 values do vary depending on the dissolution procedure [17]. C–H–N analysis is used to determine total N content [1], but is considered to be suitable only for samples containing > 3000 ppm NH_4 [17].

Evolved gas analysis (EGA) has not been widely used as a geochemical technique. However, Roche *et al.* [15] demonstrated the usefulness of pyrolysis-mass spectrometry determinations of NH_4 as a lithochemical indicator of mineralisation, and Shepherd *et al.* [18] suggested that EGA has potential for identifying subtle zones of hydrothermal alteration adjacent to vein mineralisation not evident from trace element indicators.

The aims of the present investigation were to (i) examine the evolution of NH_3 induced by heating NH_4-bearing minerals and rocks; (ii) discover if NH_3 evolution peaks are diagnostic for specific ammonium host minerals, and (iii) compare the sensitivity of EGA with that of the Kjeldahl method for determining NH_4.

Samples

Four ammonium minerals were examined in which NH_4^+ has completely substituted for K^+; these minerals contain between 3.8 and 7.0% NH_4. A batch of samples adjacent to a silvergold deposit at El Cubo mine, Guanajuato, Mexico containing 120–1000 ppm NH_4, were also analysed to examine the effectiveness of the method in an exploration context.

Ammonium minerals

Buddingtonite [$NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O$]

This is the NH_4 analogue of monoclinic microcline feldspar from the type locality, Hg-bearing springs, Sulphur Bank, California [9, 10]. The sample contains minor pyrite; the ½ H_2O has been attributed to montmorillonite impurity [11].

Synthetic NH_4-illite [ideal formula $NH_4Al_2(Si_3,Al)O_{10}(OH)_2$]

This sample has been described by Krohn & Altaner [10]. NH_4-illite has also been noted at the Lik stratiform exhalative base metal (Pb–Zn–Hg) deposit hosted in Mississipian black shales and cherts in the De Long mountains of NW Alaska [2], and in mudrocks in the anthracite/semi-anthracite coal measures of NE Pennsylvania [6], where co-existing mineral assemblages and coal rank suggest a very low-grade metamorphic environment.

NH_4-alunite [$(NH_4)_{0.92}K_{0.02}Na_{0.02}Al_{2.88}(SO_4)_{2.00}(OH)_6$]

This sample is from hot sprigs at the 'Geysers', Sonoma County, California [13].

NH_4-jarosite [ideal formula $(NH_4)Fe_3(SO_4)_2(OH)_6$]

This sample comes from solution hollows at the junction of the Upper Chalk with overlying Tertiary sediments at Newhaven, Sussex (S Kemp, pers. comm.), and was identified from its X-ray diffraction pattern which closely matches the Joint Committee for Powder Diffraction Standards (JCPDS) reference pattern 26–1014.

El Cubo mine samples

Anomalously high levels of NH_4 are associated with wall rocks adjancent to gold-silver mineralisation at El Cubo mine, Guanajuato, Mexico [16, 19]. The samples investigated were collected along subsurface traverses perpendicular to mineralised veins at 60, 110, 160 and 190 m below the surface (mine levels 0, 1, 2 and 4 respectively). The deposit is hosted by the Peregrina Intrusive (mine levels 0, 1 and 2) and Guanajuato Red Conglomerate (mine level 4). NH_4 anomalies associated with silver deposits of the region are often broader than anomalies from other major and trace element indicators, and show a more consistent relationship to the vein mineralisation [16, 19].

Methods

The full EGA system has been described previously [20]; some modifications to procedure were made for the present investigation. Samples were heated in a tube furnace at 50 deg·min^{-1} and volatiles transported by a carrier gas flowing at 300 ml·min^{-1} to non-dispersive infrared detectors for NH_3, H_2O and SO_2 arranged in series. The carrier gas was either N_2, or a 2:1 mixture of N_2 and O_2. Variations in evolved volatile concentrations in the carrier gas were continuously monitored on a multi-channel chart recorder against sample temperature. The mass of H_2O released was calculated by comparing its peak area with that of the H_2O evolution peak of sodium bicarbonate; the mass of NH_3 released was determined using an empirical method [20].

Results and discussion

Ammonium minerals

Volatile evolution profiles obtained for the pure NH_4-minerals in N_2 and mixed N_2/O_2 atmospheres are shown in Fig. 1. Theoretical decomposition mechanisms for these minerals are summarized in Table 1. Table 2 contrasts the NH_3 and H_2O contents measured by evolved gas analysis with the theoretical values. It is apparent from the data in Table 2 that the amount of NH_3 detected is less than theoretically predicted, and also that the amount of H_2O detected is greater.

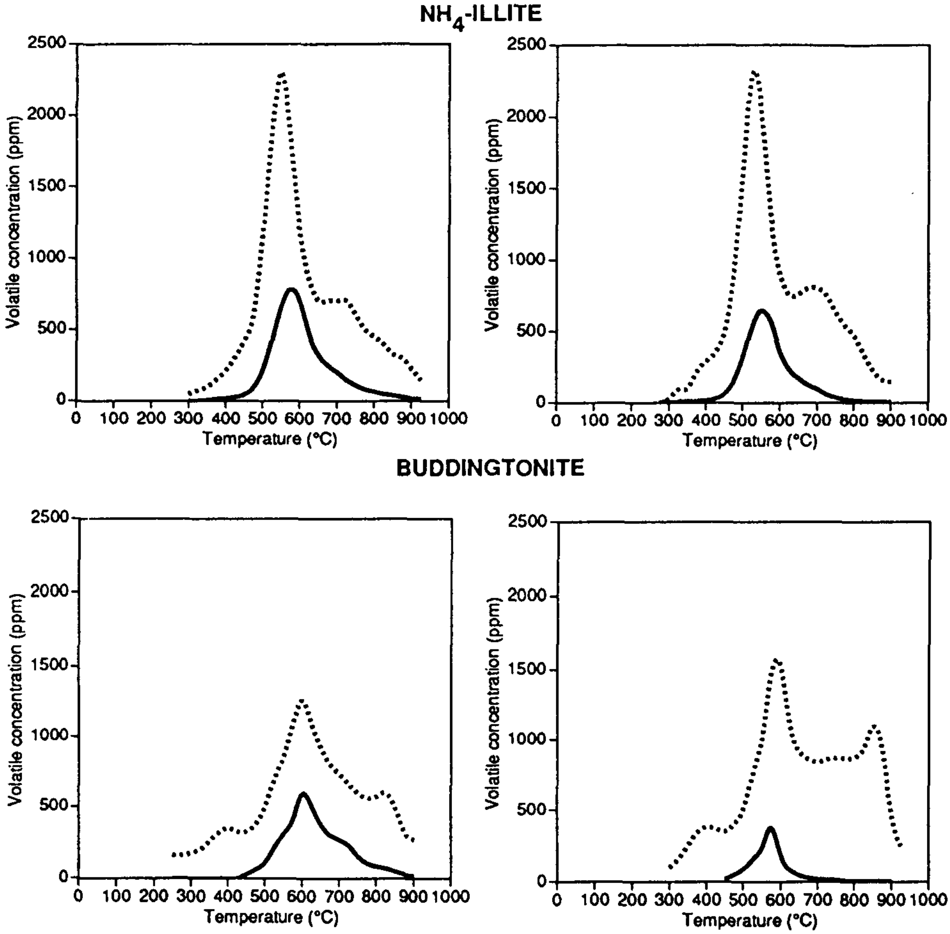

Fig. 1a Evolved gas profiles of ammonium minerals. 20 mg samples analysed in N_2 (left) and mixed N_2/O_2 atmosphere (right). Key: NH_3 - solid line, H_2O - dashed line, SO_2 - dotted line

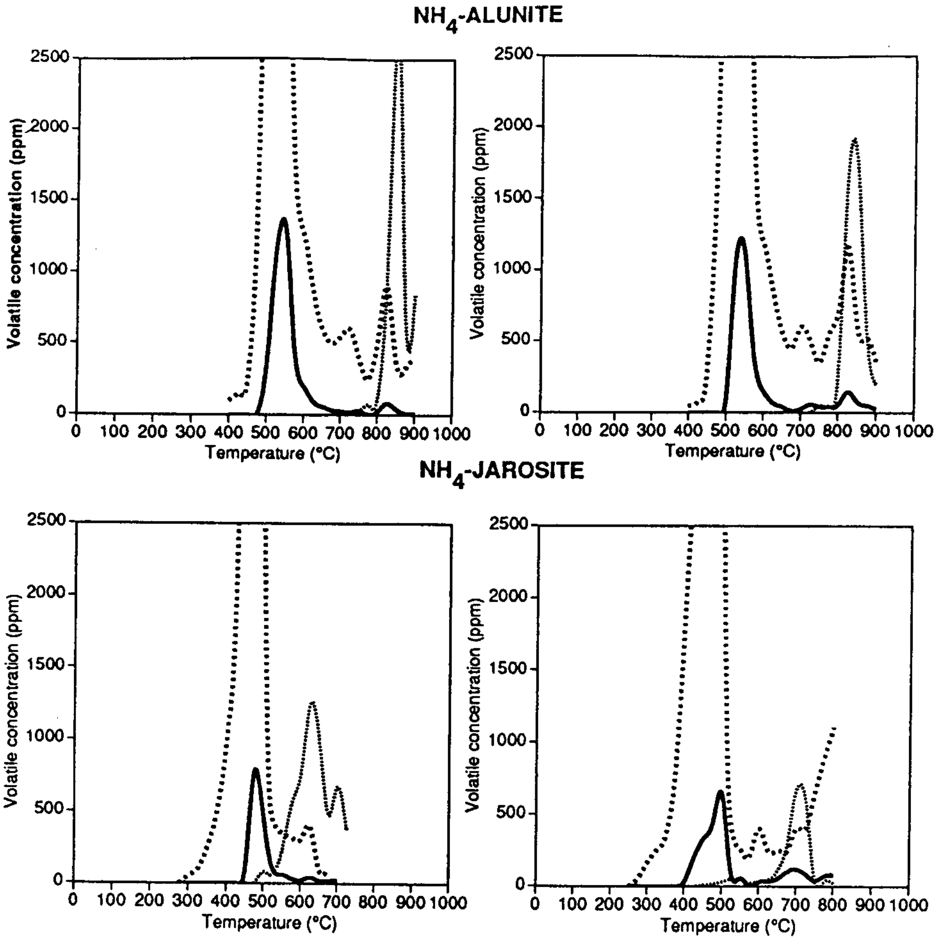

Fig. 1b Evolved gas profiles of ammonium minerals. 20 mg samples analysed in N_2 (left) and mixed N_2/O_2 atmosphere (right). Key: NH_3 - solid line, H_2O - dashed line, SO_2 - dotted line

It is likely that the partial oxidation of evolved NH_3 is responsible for these discrepancies. TGA-MS studies of NH_4VO_3 [21] indicate that above 300°C the evolved NH_3 partially decomposes to H_2O and N_2 in both oxygen and (to a lesser extent) helium atmospheres.

$2NH_3$	+	$1.5\ O_2$	$\rightarrow$	N_2	+	$3H_2O$
1M				0.5M		1.5M
1%				0.8%		1.6%

i.e. every 1% of NH_3 oxidised produces 1.6% water vapour

Table 1 Theoretical decomposition reactions for ammonium minerals indicating stoichiometry of NH_3 and H_2O evolution, assuming idealised mineral compositions

BUDDINGTONITE [22]					
Silicate-bound ammonium:	$½[(NH_4)_2–O]$	→	NH_3	+	$0.5H_2O$
Overall reaction:	$NH_4AlSi_3O_8$	→	NH_3	+	$0.5H_2O$
Molar proportions:	1M		1M		0.5M
Mass proportions / %:	(100%)		6.6		3.5
NH_4–ILLITE [22]					
Silicate-bound ammonium:	$½[(NH_4)_2–O]$	→	NH_3	+	0.5H2O
Hydroxyl water release:	$[Al_2(Si_3, Al)O_{10}(OH)_2]$	→			H_2O
Overall reaction:		→	NH_3	+	1.5H2O
Molar proportions:	1M		1M		1.5M
Mass proportions / %:	(100%)		4.5		7.2
NH_4–ALUNITE					
Assuming release of hydroxyl water is analogous to that of alunite:					
Reaction:	$NH_4Al_3(SO_4)_2(OH)_6$	→	NH_3	+	3H2O
Molar proportions:	1M		1M		3M
Mass proportions / %:	(100%)		4.6		13.8
NH_4–JAROSITE					
Assuming release of hydroxyl water is analogous to that of jarosite:					
Reaction:	$NH_4Fe_3(SO_4)_2(OH)_6$	→	NH_3	+	3H2O
Molar proportions:	1M		1M		3M
Mass proportions / %:	(100%)		3.6		11.3

If the difference between experimentally determined NH_3 and theoretical NH_3 content (NH_3 'missing' in Table 2, column G) is converted to H_2O from oxidation (column H), the value obtained corresponds closely with the difference between the experimental and theoretical H_2O content (H_2O 'excess' in column I).

The distinctive NH_3 release patterns obtained from EGA can be used to identify different NH_4- minerals (Fig. 2), but the determination of NH_4 content is only semi-quantitative due to partial oxidation of evolved NH_3 to N_2 and H_2O. However, detection of NH_3 is enhanced by analysis in an N_2 atmosphere as this generally suppresses NH_3 oxidation.

Table 3 El Cubo samples: mineralogy, evolved NH_3 peak area and NH_4 content by a modified Kjeldahl method

El Cubo mine level	Sample code	XRD analysis: (1) Major mineral phases	XRD analysis: (2) Minor mineral phases	Evolved NH_3 peak area / area units	Kjeldahl NH_4 content /ppm
0	90:2A	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	505	202
0	90:4A	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	1217	448
1	90:1A	Quartz, K-feldspar, Plag.feldspar	Mica	921	298
1	8	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	96	157
1	13	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	114	121
1	18	Quartz, plag. feldspar, K-feldspar	Mica	114	174
1	25	Quartz, plag. feldspar, K-feldspar	Mica, ?calcite	347	286
1	26	Quartz, plag. feldspar, K-feldspar	Mica	759	619
1	29	Quartz, K-feldspar, plag.feldspar	Mica, chlorite	1639	1110
1	31	Quartz, plag. feldspar, K-feldspar	Mica, chlorite	607	722
2	90: 4A	Quartz, plag. feldspar, K-feldspar	Mica	65	105
2	90: 8A	Quartz, plag. feldspar, K-feldspar	Mica, chlorite	355	316
2	90:13A	Quartz, plag. feldspar, K-feldspar	Mica, chlorite	630	644
2	3	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	435	342
2	4	Quartz, plag. feldspar, K-feldspar	Mica	597	224
2	12	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	87	122
2	23	Quartz, plag. feldspar, K-feldspar	Chlorite, mica	396	309
4	90: 3A	Quartz, plag. feldspar	Chlorite	63	215
4	90:12A	Quartz, plag. feldspar	Chlorite, mica	805	322
4	90:15A	Quartz, plag. feldspar	Chlorite	523	154
4	90:23A	Quartz, plag. feldspar	Chlorite, mica	348	263
?	VV: 2	Quartz, plag. feldspar, K-feldspar	Smectite, mica	723	287
?	VV:14	Quartz, plag. feldspar, K-feldspar	Mica	482	214
?	VV:16	Quartz, plag. feldspar, K-feldspar	Smectite, mica	382	354

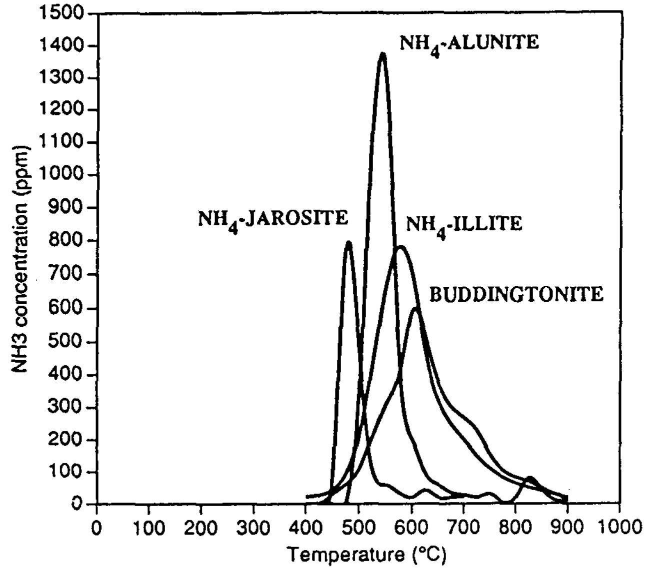

Fig. 2 NH_3 evolution profiles of ammonium minerals. 20 mg samples analysed in N_2 atmosphere

El Cubo mine samples

Evolved NH_3 profiles of the El Cubo samples are shown in Fig. 3. Most of the samples evolve NH_3 as a sharp near-symmetric peak between 650° and 785°C; several samples also evolve NH_3 below 600°C (marked in bold in Fig. 3).

Whole-rock X-ray diffraction (XRD) analysis indicated that the samples are composed predominantly of quartz, K-feldspar and plagioclase feldspar, with minor chlorite and mica (Table 3). Possible host minerals for NH_4 are K-feldspar (XRD main line at 3.24 Å) and mica (XRD d_{001} at 10 Å). Statistical analysis indicated a weak positive correlation between NH_4 concentration and 3.24 Å XRD intensity (correlation coefficient 0.32), and also with 10 Å XRD intensity (correlation coefficient 0.46), but did not conclusively indicate which mineral was hosting NH_4.

A graph of 'evolved NH_3 peak area' *vs.* 'NH_4 content by a modified Kjeldahl method' is shown in Fig. 4. A moderate positive linear correlation is evident (correlation coefficient 0.66). This suggest that the EGA data are sufficiently sensitive to differences in NH_4 content for semi-quantitative classification of samples.

Table 2 Evolved gas analysis results compared to theoretical volatile contents for ammonium minerals

A	B	C	D	E	F	G	H	I
Mineral	Atmos.	Theoretical NH_3 content / %	EGA NH_3 content / %	Theoretical H_2O content / %	EGA H_2O content / %	[= C–D] NH_3 'Missing' / %	[= G× 1.6] Equivalent H_2O / %	[= F–E] H_2O 'Excess' / %
Buddingtonite	N_2	6.6	2.2	3.5	6.8	3.0	4.8	3.3
Buddingtonite	N_2/O_2	6.6	0.7	3.5	10.1	4.5	7.2	6.6
NH_4-illite	N_2	4.5	2.5	7.2	11.4	2.0	3.2	4.2
NH_4-illite	N_2/O_2	4.5	1.9	7.2	12.4	2.6	4.2	5.2
NH_4-alunite	N_2	4.6	1.8	13.8	17.7	2.8	4.5	3.9
NH_4-alunite	N_2/O_2	4.6	1.6	13.8	17.7	3.0	4.8	3.9
NH_4-jarosite	N_2	3,6	0.9	11.3	15.3	2.7	4.3	4.0
NH_4-jarosite	N_2/O_2	3.6	0.9	11.3	16.3	2.7	4.3	4.9

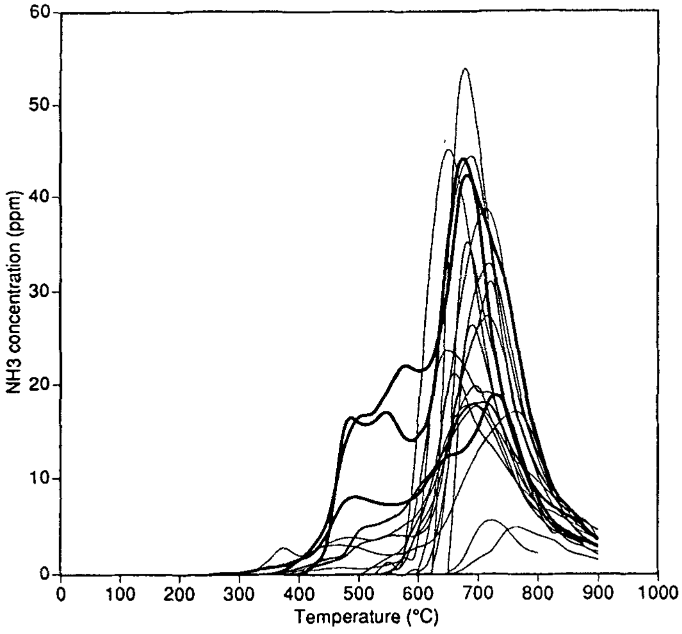

Fig. 3 Evolved NH_3 profiles of El Cubo mine samples, Guanajuato, Mexico. 300 mg samples analysed in N_2 atmosphere

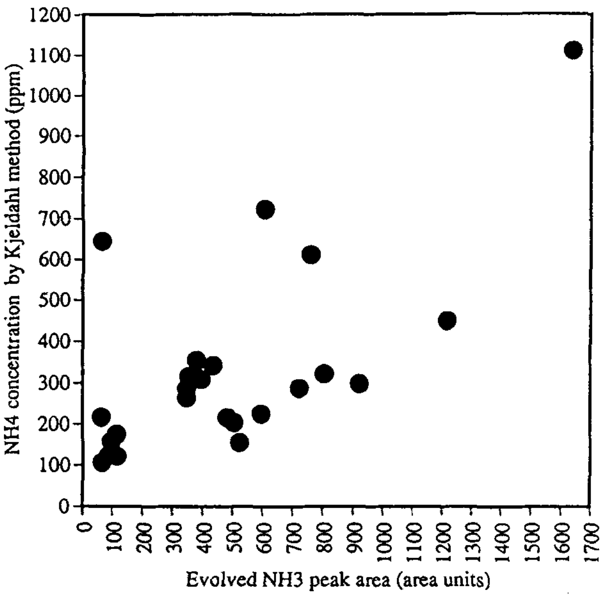

Fig. 4 Evolved NH_3 peak area *vs.* NH_4 concentration determined by Kjeldahl method for samples from El Cubo mine, Guanajuato, Mexico

Conclusions

Recent developments in NH_4 geochemistry have focused on the association of anomalously high concentrations of NH_4 with metallic and energy mineral deposits and very low-grade metamorphic rocks. The credibility of using NH_4 geochemistry in mineral exploration depends on understanding the factors controlling enrichment of NH_4. At present, many studies utilise methods which: (i) provide only whole-rock NH_4 contents; (ii) can not identify NH_4 host minerals (e.g. Kjeldahl method); (iii) may lack sensitivity (e.g. C–H–N analysis); (iv) are prone to interference from other minerals (e.g. infrared spectroscopy). The present investigation demonstrates that evolved NH_3 analysis is capable of distinguishing between several NH_4 minerals (buddingtonite, NH_4-illite, NH_4-alunite and NH_4-jarosite) normally associated with hydrothermal activity and mineralisation, and is sensitive to low-to-trace concentrations of NH_4 (1110–120 ppm levels) in the host rocks of a gold-silver deposit. The method is not fully quantitative because evolved NH_3 partially oxidises to N_2 and H_2O; however, amounts of NH_3 evolved do show a moderate positive linear correlation with NH_4 content determined by a modified Kjeldahl method.

* * *

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Zusammenfassung — Die Assoziation von ungewöhnlich hohen Ammoniakpegeln mit sowohl Metall- als auch Energiemineralllagerstätten ist ein potentielles Mittel bei der Mineralerforschung. Übliche geochemische Methoden zur Detektion von NH_4 liefern oft nur Vollgestein NH_4 Werte und identifizieren nicht die einzelnen NH_4 Wirtsminerale. Es fehlt ihnen auch an Empfindlichkeit oder sie neigen zu Überlappung. Es wurde gezeigt, daß die Bestimmung freigesetzten Ammoniaks die Unterscheidung verschiedener NH_4-haltiger Minerale ermöglicht und in Gestein mit Silber-Goldadermineralisation NH_4-Werte bis hinab zu 120 ppm bestimmen kann. Ein vollquantitative Bestimmung von NH_4 ist mit Hilfe dieser Methode nicht möglich, da ein Teil des aus dem Mineral freigesetztem NH_3 beim Erhitzen oxidiert wird; auf alle Fälle zeigt die freigesetzte NH_3-Menge eine mäßige positive Korrelation mit dem mit Hilfe einer modifizierten Kjeldahl-Methode bestimmten NH_4-Gehalt.