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BIOGENIC NITROGEN FROM TERMITE MOUNDS AND THE ORIGIN OF GERHARDTITE AT THE GREAT AUSTRALIA MINE, CLONCURRY, QUEENSLAND, AUSTRALIA

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Abstract

The Great Australia deposit, near Cloncurry, Queensland, Australia, hosts an unusual enrichment in the copper nitrate mineral gerhardtite. Nitrogen isotope analyses suggest that oxidized ammonia from nearby termite mounds provides the nitrate required for gerhardtite mineralization. Groundwater δ^{15}N and [NO_3^-] show a correlated decrease with depth, suggesting a surface source of nitrogen, with $\delta^{15}N_{AIR} > +10‰$. The δ^{15}N values of gerhardtite ($\delta^{15}N_{AIR} = +13.3‰$) and local bulk termite-mound material ($\delta^{15}N_{AIR} = +13.5‰$) are virtually identical, and the remote desert location of the deposit precludes a septic or manure source of nitrogen. Similarly, remobilization of older inorganic evaporitic nitrates is an unlikely source owing to both geology and climate. Field evidence suggests that the spatial distribution of termite mounds may be a useful predictor of base-metal speciation as nitrates within the oxidation zone of base-metal deposits.

Keywords: gerhardtite, nitrogen, isotope, copper, Great Australia deposit, Australia.

Sommaire

Le gisement Great Australia, près de Cloncurry, au Queensland, en Australie, montre un enrichissement inhabituel en gerhardtite, nitrate de cuivre. D'après la proportion des isotopes d'azote, l'ammoniaque oxydé provenant des nids de termites avoisinants aurait fourni le nitrate requis pour la minéralisation en gerhardtite. Le rapport δ^{15}N et la teneur en nitrate des nappes d'eau souterraine diminuent progressivement avec la profondeur, ce qui indique une source d'azote près de la surface, avec $\delta^{15}N_{AIR} > +10‰$. Les valeurs de δ^{15}N typiques de gerhardtite ($\delta^{15}N_{AIR} = +13.3‰$) et les échantillons des amoncellements locaux construits par les termites ($\delta^{15}N_{AIR} = +13.5‰$) sont quasiment identiques, et l'emplacement isolé dans le désert écarte la possibilité d'une source de l'azote dans les fosses septiques ou le fumier. De même, la remobilisation de nitrates inorganiques anciens provenant de séquences évaporitiques serait improbable à cause du contexte géologique et du climat. D'après les relations de terrain, la distribution des nids de termites serait un indicateur fiable de la spéciation des métaux de base dans la zone d'oxydation de gisements de sulfures de ces métaux.

(Traduit par la Rédaction)

Mots-clés: gerhardtite, azote, isotope, cuivre, gisement Great Australia, Australie.

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INTRODUCTION

Cupric nitrate minerals are rarely observed in the oxidized zone of copper deposits, and may be found in both arid and temperate environments. Recognized species include gerhardtite [$Cu_2(NO_3)(OH)_3$], buttgenbachite [$Cu_{19}(Cl_4NO_3)_2(OH)_{32}\bullet 2H_2O$], likasite [$Cu_3(NO_3)(OH)_5\bullet 2H_2O$], and rouaite [$Cu_2(NO)_3(OH)_3$]. The uncommon occurrence of these minerals reflects the usual dominance of other dissolved anionic species (*e.g.*, HCO_3, SO_4, Cl) relative to aqueous species of nitrogen in natural waters. For cupric nitrate minerals to develop, aqueous nitrogen, usually speciated as nitrate (NO_3^-), must be locally present at levels that make it the dominant anion available.

Gerhardtite is perhaps the most widespread of the cupric nitrate species, with ten localities listed in Anthony *et al.* (2003). The type locality for gerhardtite is the United Verde mine at Jerome, Arizona, USA (Wells & Penfield 1885). The mineral has also been reported at other localities in the USA (*e.g.,* Lindgren & Hillebrand 1904, Williams 1961, Rosemeyer 1990), France (Sarp *et al.* 2001), Germany (Wittern 2001), Italy (Franzini & Perchiazzi 1992), Democratic Republic of Congo, and Australia (Sielecki 1988). A relatively recent discovery of gerhardtite at the Great Australia deposit in Cloncurry, Queensland, Australia (Fig. 1) has produced some of the most spectacular and rich specimens known to date, with crystal aggregates up to 2 cm. Our purpose in this study is to utilize the relative abundance of specimens from this exceptional find to perform the first quantitative geochemical study of the genesis of gerhardtite, and to determine the source of its nitrogen.

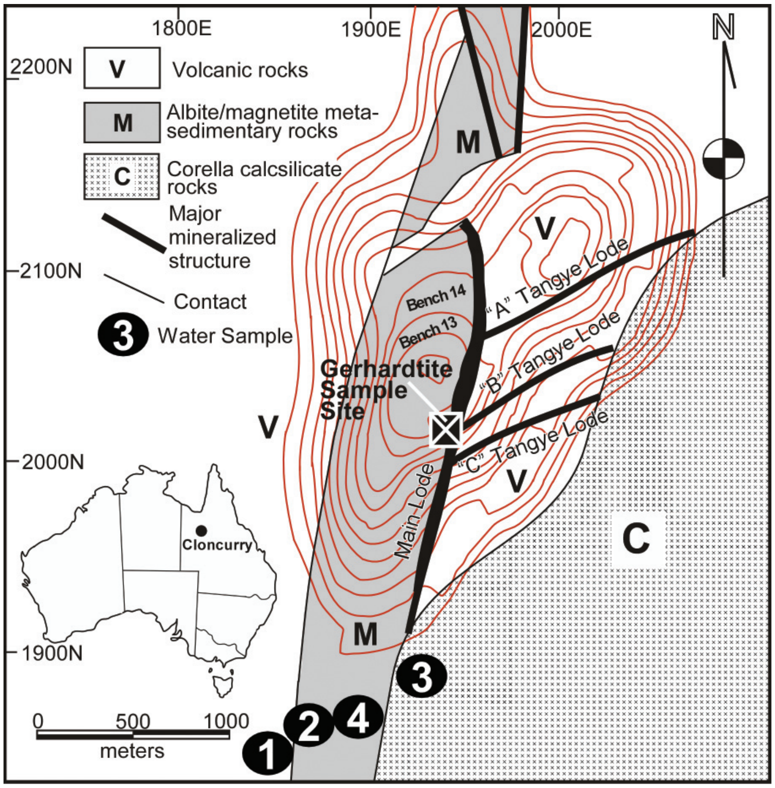

FIG. 1. Map of the main portion of the Great Australia deposit, Cloncurry, Queensland, Australia, showing open cut and geology. Mine grid is in meters, and open cut contours (benches) are on 5-meter intervals. The gerhardtite samples analyzed in this study are from the area of the crossed box, at the intersection of the B Tangye and Main lodes on benches 13 and 14. The location of water samples analyzed in this study are shown as black circles with numbers corresponding to the numbers in Table 1. Information on geology, structure, and open cut are taken from Cannell & Davidson (1998), Melchiorre & Williams (2001), and unpublished results of mapping by P.A. Williams.

BACKGROUND INFORMATION

Atmospheric nitrogen may be fixed by a number of mechanisms, including lightning strikes and biological processes, and nitrogen isotope signatures can be used to distinguish each of these sources (*e.g.,* Clark & Fritz 1997). With the exception of the large nitrate deposits found in extremely arid environments, localized enrichments in nitrate are most commonly biogenic in origin (*e.g.,* bat guano in caves and abandoned mines, cattle manure, and excretions from termite mounds). In the remote desert of central Queensland, where the Great Australia Deposit is located, it is unlikely that either bat guano or manure would provide much fixed nitrogen to the total budget, as the local abundance of these materials is quite low. It is possible that lightning may produce some fixed nitrogen in this region during summer monsoon storms, but certainly not at the same scale or conditions favorable for preservation as within the hyperarid deserts of northern Chile and southern California, where this mechanism has been demonstrated to be a significant source of nitrogen (Ericksen 1981, Ericksen *et al.* 1988, Böhlke *et al.* 1997). However, it has been demonstrated that termite mounds are significant source of nitrogen in arid portions of Australia (*e.g.,* Barnes *et al.* 1992).

THE GREAT AUSTRALIA DEPOSIT

The Great Australia deposit is located within the northern portion of the eastern succession of the Proterozoic Mount Isa inlier, about 1 km south of Cloncurry, Queensland (Figs. 1, 2). The Mount Isa inlier consists of metasedimentary and metavolcanic rocks associated with multiple episodes of rifting and granite emplacement between 1900 to 1600 Ma (Blake 1987). The Great Australia deposit is considered to be one of the largest examples of "Mount-Freda-style" vein-replacement mineralization in Australia, and consists of distinctive vein- and replacement-type Cu–Co mineralization (*e.g.,* Davidson 1998, Cannell & Davidson 1998). Occurring within a dilatational jog in a major splay of the Cloncurry fault, this deposit is hosted by the Proterozoic Toole Creek Volcanic Suite of the Soldiers Cap Group and metasedimentary Corella Formation of the Mary Kathleen Group (Fig. 1). Both units have undergone brittle deformation, and have strongly brecciated zones associated with NE–SW-trending faults.

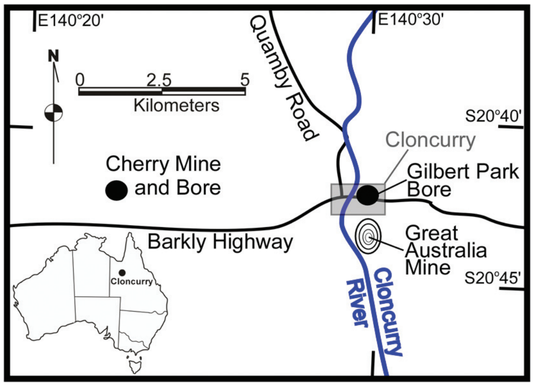

FIG. 2. Map of the Cloncurry area, showing the location of the Great Australia mine and additional samples of water analyzed in this study.

Supergene mineralization of the ore zones consists of surficial breccia cemented by oxides of Fe and Cu, highly silicified in places, and deeper horizons of malachite, azurite, chrysocolla, cuprite, native copper, atacamite, connellite, and abundant copper phosphate species (Day & Beyer 1995, Sharpe 1998). At and beneath the current water-table, near the junction of the Main and B Tangye lodes, a coarsely crystallized assemblage of chalcocite and djurleite forms a sulfide-enriched zone. The products of hypogene mineralization observed during limited mining of high-grade zones and in drill-core material consist solely of chalcopyrite within brecciated fault-veins grading up to 8% Cu, 1g/t Au, and 0.35% Co (Cannell & Davidson 1998). The two largest economically mineralized zones are called the Main Lode and the B Tangye Lode (Orphan Lode).

ELEVATED [NO_3^-] AND ^{15}N IN AUSTRALIAN GROUNDWATERS DUE TO NITROGEN FIXATION BY TERMITES

Symbiotic bacteria associated with termites are known to fix nitrogen and to produce nitrogen isotope signatures characteristic of diet groups such as wood feeders, soil feeders, and fungus growers (*e.g.,* Sleaford *et al.* 1996, Tayasu *et al.* 1997, Tayasu 1998). Wood-feeding termites and fungus-growing termites typically have $\delta^{15}N_{AIR}$ of +2 to +5‰, whereas soil-feeders have $\delta^{15}N_{AIR}$ of +10 to +16‰ (*e.g.,* Tayasu *et al.* 1997). The more positive $\delta^{15}N_{AIR}$ values for soil feeders are mainly attributed to diet, as soil-feeders ingest partially decomposed organic matter that has previously experienced ammonia volatilization and denitrification enrichments (*e.g.,* Mariotti *et al.* 1982, Wada *et al.* 1984, Högberg 1990). The ratio of nitrogen assimilated from plant sources *versus* intestinal microbe sources in termites is also considered to determine $\delta^{15}N_{AIR}$ values of termites (Tayasu *et al.* 1997). Other investigators suggested that termites may have $\delta^{15}N_{AIR}$ values that are further enriched by diets of certain C3 (woody) and C4 (grasses) plants (Virginia *et al.* 1989, Cormie & Schwarcz 1996) in arid desert environments such as central Queensland.

The biological fixation of nitrogen typically produces ammonia within a termite mound, which in turn is bacterially oxidized to form nitrate. The nitrate is leached out of the termite mound by capillary action, so that the highest concentration of nitrate is within the outer shell of the mound (*e.g.*, Barnes *et al.* 1992). Rainfall may then leach nitrate out of the mound and through the vadose zone to the groundwater as seasonally elevated nitrate recharge with a distinctive positive $\delta^{15}N_{AIR}$ value. Nitrogen fixed by mound-building, soil-feeding, social termites and their symbiotic microorganisms of arid central Queensland should have a distinctive and positive $\delta^{15}N_{AIR}$ value.

Elevated levels of nitrate, to 75 mg/L, are common in groundwater from the arid regions of Australia, including central Queensland (*e.g.*, Jacobson *et al.* 1991, Barnes *et al.* 1992). In many cases, these waters meet all drinking water standards except the nitrate limit. Data on bore-water geochemistry indicate a correlation of high-nitrate groundwaters with shallow unconfined aquifers; Barnes *et al.* (1992) have attributed elevated levels of nitrate to termite-generated nitrate.

Methods

Gerhardtite, termite mound material, and groundwaters from the Great Australia deposit and surrounding area were collected and analyzed for $\delta^{15}N_{AIR}$ values (Figs. 1, 2). A pure concentrate of gerhardtite was prepared by hand-picking small (<2 mm) cleavage fragments of gerhardtite from a coarsely crushed gossan matrix containing cuprite, native copper, and atacamite. Purity was checked by optical examination, and confirmed by the consistent stoichiometric yield of nitrogen gas from combustion for isotope analyses. Samples of termite mounds were collected as small fragments chipped from the shell of active termite mounds. Mineral and termite-mound samples were analyzed by combustion using an in-line element analyzer and stable-isotope-ratio mass spectrometer at the Environmental Isotope Laboratory at the University of Waterloo, Canada.

Groundwater nitrate samples were collected in the field by passing water samples through ion-exchange resin columns. A Hach test kit NI–12, utilizing cadmium reduction and a color-wheel comparator, was used for field determinations of $[NO_3^-]$. Following collection, the columns were kept on ice or refrigerated prior to analysis. The nitrate was subsequently stripped from the ion-exchange columns at the Environmental Isotope Laboratory at the University of Waterloo, and converted into $AgNO_3$ salt. Combustion within an in-line element analyzer was employed to convert $AgNO_3$ into nitrogen gas for nitrogen isotope analysis (*e.g.*, Silva *et al.* 2000). Standard deviation for replicate sample for $\delta^{15}N_{AIR}$ analysis is generally better than ±0.3‰ for both water and mineral samples.

Oxygen isotope analysis of groundwater nitrate was performed using the graphite combustion method (*e.g.*, Silva *et al.* 2000). The standard deviation for replicate $\delta^{18}O_{VSMOW}$ analyses is generally better than ±0.4‰. Results of nitrogen and oxygen isotope analyses are reported in the usual manner, as ‰ deviations from AIR and VSMOW standards.

Results

The $\delta^{15}N_{AIR}$ value of gerhardtite from the Great Australia deposit averages 13‰ (±0.3‰), based upon replicate analyses (Table 1). Termite-mound material from the edge of the open pit of the Great Australia deposit has $\delta^{15}N_{AIR}$ values that vary from 13 to 12‰ (±0.9‰) (Table 1). The $\delta^{18}O_{VSMOW}$ values of gerhardtite and termite-mound material were not determined. Gerhardtite contains oxygen in both nitrate and hydroxyl groups, and the isotopic partitioning between

TABLE 1. VALUES OF $\delta^{18}O_{VSMOW}$, $\delta^{15}N_{AIR}$, NO_3^- (ppm), TOTAL DISSOLVED SOLIDS (mg/L), AND SAMPLING DEPTH FOR GROUNDWATER SAMPLES, AND VALUES OF $\delta^{15}{}_{AIR}$ FOR GERHARDTITE AND TERMITE- MOUND MATERIAL

	Location	1	2	3	4	5	6	7
1	Great Australia mine Bore #1	42	810	5	7.36	7.47	7.4	7.2
2	Great Australia mine Bore #2	42	800	7	7.96	8.01	8.0	6.9
3	Great Australia mine Bore #3	48	660	8	8.03	-	8.0	7.3
4	Great Australia Mine Bore #4	42	760	6	7.90	7.98	7.9	6.9
5	Gilbert Park Bore, Cloncurry, QLD	100	780	2.5	6.67	-	6.7	6.4
6	Cherry mine Bore, Chumvale, QLD	20	770	12	9.61	-	9.6	9.3
	Gerhardtite mineral separate				13.07	13.54	13.31	
	Great Australia termite mound #1				13.46	13.57	13.52	
	Great Australia termite mound #2				12.88	12.76	12.82	

Column headings: 1: Depth to the water table (m), 2: total dissolved solids (mg/L), 3: NO_3^- content (mg N per L), 4: nitrate $\delta^{15}N_{AIR}$, 5: nitrate $\delta^{15}N_{AIR}$ (repeat measurement), 6: nitrate $\delta^{15}N_{AIR}$ (average), 7: nitrate $\delta^{18}O_{VSMOW}$.

these two sites is unknown. The $\delta^{15}N_{AIR}$ values of groundwater nitrate range from 6 to 9‰, whereas nitrate $\delta^{18}O_{VSMOW}$ values also range from 6 to 9‰ (Table 1). Nitrate concentrations of groundwater measured [total nitrogen/L] in the field range from 2.5 to 12 mg (Table 1).

DISCUSSION

Values of $\delta^{15}N_{AIR}$ have been measured in many natural materials over the past 20 years (*e.g.,* Létolle 1980, Amberger & Schmidt 1987, Böttcher *et al*. 1990, Mizutani *et al*. 1992, Tayasu 1998, Holloway & Dahlgren 2002). This knowledge of the distribution of $\delta^{15}N_{AIR}$ values allows for the comparison of our data with many potential sources of nitrogen (Fig. 3). The $\delta^{15}N_{AIR}$ value for gerhardtite overlaps with the $\delta^{15}N_{AIR}$ values for manure and septic sources and soil-feeding termites (Fig. 3). The remote desert of central Queensland is sparsely inhabited and has very low density of cattle, restricted to only the most recent 100 years. As the gerhardtite is commonly found completely encased deep within compact cuprite nodules that generally have well-formed crystals of cuprite, it is likely that the gerhardtite mineralization formed prior to the past 100 years. There is no formal or anecdotal record of cattle-grazing activities on the site of the present open-pit mine. It is unlikely that the gerhardtite mineralization is the result of nitrogen from cattle ranching or other historical activities.

Dissolution of pre-existing evaporite or lightning-fixed nitrate minerals are not considered a likely source for the Great Australia gerhardtite. First, there is no record of any such evaporite units within the igneous intrusions or high-grade metamorphic rocks of the region. Second, the tropical savannah of the region has seasonal monsoon rains and accompanying floods that would significantly minimize both the accumulation and preservation of evaporite or lightning-fixed nitrate minerals. Lastly, the isotope values reported for these inorganic nitrate minerals from the Atacama Desert of Chile are 7 to 10‰ lighter in ^{15}N than gerhardtite (Fig. 3).

Conversely, the local abundance of soil-feeding termites (Fig. 4) and the similarity of the $\delta^{15}N_{AIR}$ values of their mound material with that of gerhardtite suggest that termites may have provided a majority of the nitrogen responsible for gerhardtite development at this location. The authors have observed a spatial distribution of termite mounds amounting to over 100 individual mounds per hectare (Fig. 4a). At approximately 0.5 kg of termites per mound (the senior author's estimate), a hectare would contain at least 50 kg of termites. Estimates of nitrogen production by termites, based upon CH_4/N_2O values (Khalil *et al*. 1990, Galbally *et al*. 1992) and species-specific measurements (Sugimoto *et al*. 1998), indicate a nitrogen production of 4.3×10^{-3} mol N_2O/gram of termite/year. It is reasonable to conclude that for areas of high termite-mound density, over 950 kg of fixed nitrogen is produced per year by the termites within one square kilometer. Over geological time, the total amount of fixed nitrogen is quite significant.

As the spatial density of termite mounds within the Cloncurry area is highly variable, and as it has been demonstrated that individual termite mounds may be occupied for at least 100 years (Sprent 1987), it is possible that present-day termite-mound distribution might predict which deposits will host nitrate mineral species. Detailed aerial photos may be useful in identification of these targets.

The relationship between $\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$ values and nitrate concentrations have been used to illustrate the mechanism of denitrification of groundwater (*e.g.,* Böttcher *et al*. 1990, Clark & Fritz 1997, Kendall & McDonnell 1998). The denitrification mechanism, whereby aqueous NO_3^- is converted to N_2 gas by the bacteria *Thiobacillus denitrificans*, produces an increase in $\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$ values in residual groundwater nitrate, whereas concentrations of nitrate decrease. In the groundwaters in the Cloncurry area of central Queensland, the $\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$ values of groundwater nitrate show a reasonably good correlation (Fig. 5), but the concentrations of nitrate are observed to increase (rather than decrease) with increasing $\delta^{15}N_{AIR}$ and $\delta^{18}O_{VSMOW}$ values (Table 1, Fig. 6). Moreover, this relationship shows a good

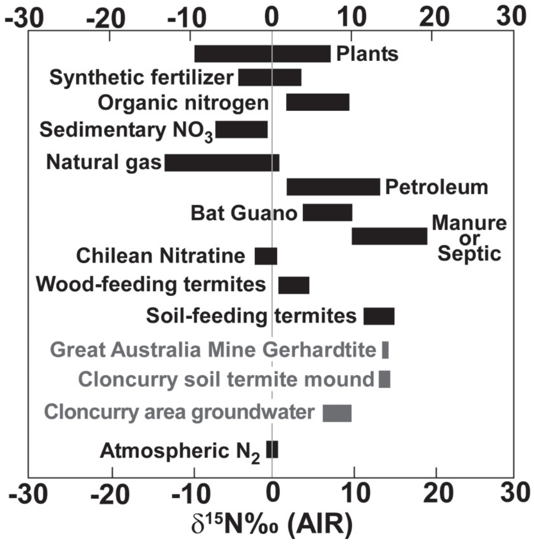

FIG. 3. Distribution of $\delta^{15}N$ values of various substances. Data in black from Tayasu (1998), Mizutani *et al*. (1992), Böttcher *et al*. (1990), Amberger & Schmidt (1987), and Létolle (1980). Data on Chilean nitratine are from Böhlke *et al*. (1997) and unpublished information from authors EBM and TPR. Data from this study are shown in gray.

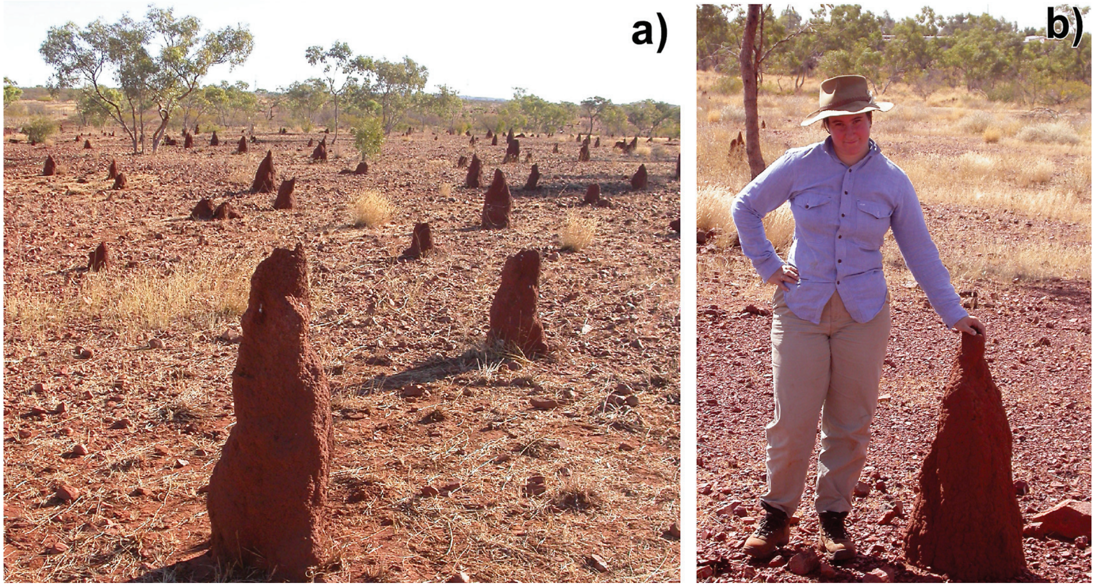

FIG. 4. Photographs from the Great Australia mine lease showing: a) *Amitermes vitiosus* termite mounds with a spatial density of over 100 mounds per hectare, and b) size of a typical *Amitermes vitiosus* termite mound (biologist is 1.7 m tall).

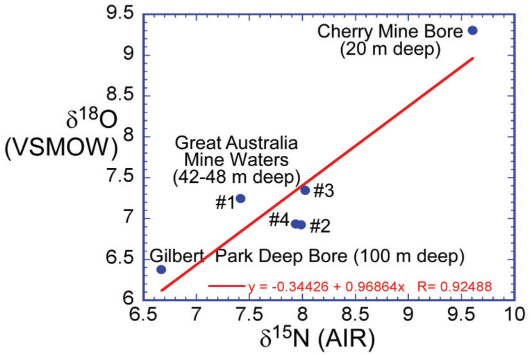

FIG. 5. Plot of $\delta^{18}O_{VSMOW}$ *versus* $\delta^{15}N_{AIR}$ for groundwater samples from the Cloncurry area. Depths of groundwater sampling are shown in brackets.

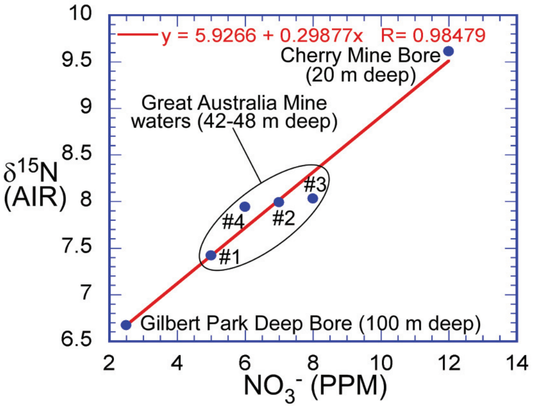

FIG. 6. Plot of $\delta^{15}N_{AIR}$ *versus* NO_3^- (ppm) for groundwater samples from the Cloncurry area. Depths of groundwater sampling are shown in brackets.

correlation with depth, wherein the highest NO_3 and stable isotope values occur closest to the surface, and the lowest values occur at the deepest levels. This relationship is interpreted as evidence for the production of nitrate by oxidation of ammonia in the termite mounds.

The dominant species of termite in the Cloncurry region is *Amitermes vitiosus*. Within habitation mounds of these soil-feeding termites, significant quantities of uric acid are produced by nitrogen bioaccumulation, ultimately resulting from the unusual social and reproductive behavior of termites. The food sources of termites, including the humus consumed by soil-feeding termites, contain little nitrogen. What nitrogen there is, termites and their symbiotic gut microbes bioaccumulate through several mechanisms (Sprent 1987, Tayasu 1998). Within individual termites, uric acid ($C_5H_4N_4O_3$), usually formed as a waste product, is stored and re-used when nitrogen supply is low. Further-more, the complex social organization of termite colonies, wherein most individuals are very closely related, non-reproductive, and divided into task-oriented castes (Bartz 1979), leads to controlled cannibalism under a range of circumstances. These include limited availability of nitrogen, overproduction of particular social castes, and necrophage (consumption of dead colony mates; Cook & Scott 1933, Hendee 1934, Moore 1969). Cannibalism and necrophage cause nitrogen recycling throughout the life of the colony, in many instances more than 100 years (Sprent 1987). This constant bioaccumulation and recycling may account not only for the high concentration of nitrogen in the mounds, but may also contribute to the enrichment of ^{15}N.

Nitrogen concentrated by termites eventually gets excreted in termite feces as uric acid (Moore 1969). Whereas other colony members consume some of the feces to recover the nitrogen, some feces are used to build the mound, decreasing the C:N ratio (Sprent 1987). Some ammonia is partially lost to the atmosphere through volatilization, but significant quantities are trapped within the termite mound and oxidized by nitrification to nitrate. Nitrate is leached out of the termite mound by capillary action, which produces an elevated concentration of nitrate within the outer shell of the mound (*e.g.*, Barnes *et al.* 1992). Rainfall will then leach nitrate out of the mound and through the vadose zone to the groundwater as seasonally elevated nitrate recharge with a distinctive positive $\delta^{15}N_{AIR}$ value. A greater influx of nitrate to the substrate and groundwater results from degradation of the termite mounds when the colony dies (Sprent 1987). Termites can provide a substantial portion of the total nitrogen turnover; for example, in the Chihuahuan Desert ecosystem, as much as 10% of N in soil results from the action of termites (Schaefer & Whitford 1981, Schlesinger 1997).

In the Cloncurry area, this process of nitrification appears to be producing groundwater that has $\delta^{15}N_{AIR}$ values 6.9 to 3.2‰ lighter than the initial measurements at the termite mound (Table 1). We believe that this is the result of ammonia–nitrate fractionation, which has been measured to be up to 10‰, with nitrate being more depleted than starting ammonia (Minagawa & Wada 1984).

The depth of the groundwater correlates with nitrate isotope values and concentration, with increasing concentrations of nitrate and heavier nitrogen and oxygen isotope values measured in the more shallow wells (Figs. 5, 6). The source of the majority of the nitrate is thus at the surface, with elevated, positive values of nitrogen and oxygen isotope ratios consistent with a termite-mound source. Deep wells such as the Gilbert Park deep bore (Fig. 2), which taps a confined aquifer, show the lowest isotope values and nitrate levels. The decrease in both NO_3 concentrations and isotopic values with increasing depth (Figs. 5, 6) may therefore reflect a mixing relationship between the locally derived nitrate from termite mounds and the lower background-concentration of nitrate in the groundwater. The oxygen and nitrogen isotope values of the deep, protected, Gilbert Park bore (Fig. 5), and the y-intercept of the nitrate concentration *versus* $\delta^{15}N_{AIR}$ trend (Fig. 6) suggest a second, but volumetrically much less significant source of nitrate, which is consistent with soil-generated organic matter (*e.g.,* Clark & Fritz 1997, Kendall & McDonnell 1998).

It is notable that the close correspondence between the $\delta^{15}N$ value of the gerhardtite and the termite-mound material suggests that the isotopic composition of the mineral-forming nitrate is not appreciably modified during transport in the vadose zone. Gerhardtite probably forms episodically owing to the action of sporadic episodes of heavy rainfall that leach a large amount of nitrate from the outer shell of the termite mounds in a short time. This nitrate is transported tens of meters downward to the oxidation zone of the Great Australia orebody, where it reacts with other secondary copper minerals to form gerhardtite.

CONCLUSIONS

Nitrogen and oxygen stable isotope values from groundwater, termite mounds, and gerhardtite samples suggest that oxidized termite-mound ammonia is ultimately the probable source of both elevated nitrate in groundwater and gerhardtite mineralization at the Great Australia Deposit, Australia. The correlated decrease in groundwater $\delta^{15}N$ and $[NO_3^-]$ values with increasing depth suggests a surface source of nitrogen with a $\delta^{15}N_{AIR}$ value similar to that of local termite-mound material ($\delta^{15}N_{AIR}$ = +13.5‰). The close correspondence between the nitrogen isotope composition of the termite mounds and the gerhardtite ($\delta^{15}N_{AIR}$ = +13.3‰) suggests that termite mound nitrate is directly incorporated into the structure of gerhardtite with little or no isotopic modification during transport within the vadose zone.

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