Evidence for possible zinc transport in hydrocarbon-bearing (C$_1$–C$_9$) fluids in the formation of Cobar-style deposits?

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Thermal-decrepitation mass spectrometry has revealed extended-chain hydrocarbons (C$_1$–C$_9$) in premineralisation and early syn-Zn mineralisation veins at the Elura Ag–Pb–Zn mine (NSW). Laser Raman microprobe analysis demonstrates that the *n*-alkane signatures are from primary fluid inclusions in quartz and sphalerite. One hypothesis is that the hydrocarbons may be a component of a reduced, Pb–Zn–S-bearing low- to moderate-salinity fluid. The hydrocarbon components evolved to more mature compositions (C$_1$) through time. These data may have important implications for the transport of metals in low-temperature reduced connate fluids. The study has also confirmed that two fluids with dissimilar temperatures and redox properties (and salinities) were present throughout the pre- and synmineralisation vein paragenesis, and these data support a fluid-mixing model for the formation of the Elura deposit. The ore precipitated when hot, more oxidised low-salinity basement-derived fluids mixed with reduced, lower-temperature hydrocarbon-bearing basin-derived fluids. High-strain zones provided dilational sites for localising the deposit and for basin-scale conduits that tapped fluids from within the basin and underlying basement sources.

Introduction

Organic material (and/or hydrocarbons) is associated with some sediment-hosted base-metal deposits, including the Cobar deposits (Lawrie & Hinman 1999: AGSO Journal of Australian Geology & Geophysics, 17(4), 169–187; Lawrie et al. 1999: in C.J. Stanley et al., editors, 'Mineral deposits: processes to processing — proceedings of the fifth biennial SGA meeting and the tenth quadrennial IACOD meeting, London, 22–25 August 1999', A.A. Balkema, Rotterdam, 243–246). The overall sedimentary composition appears to be an important factor in controlling the redox character of basinal brines,

and hence the capacity of these fluids to transport metals (Cooke et al. 1998: Geological Society of Australia, Abstracts, 49, 91). In basins whose sedimentary fill has buffered these brines to oxidised, near–neutral conditions, it has been proposed that metals are transported in oxidised sulphate-bearing fluids, and that redox reactions are responsible for ore precipitation (Barton 1967: Economic Geology, Monograph 3, 371–378). Metal destabilisation has been attributed to interaction with organic-rich host rocks (Hinman 1998: Geological Society of Australia, Abstracts, 49, 212; Broadbent et al. 1996: in T. Baker et al., editors, "MIC '96. New developments in metallogenic research: the McArthur–Mount Isa–Cloncurry minerals province. Extended abstracts", James Cook University of North Queensland [JCUNQ], Economic Geology Research Unit [EGRU], Contribution, 55, 24–27), or reduced sulphur at the trap site (Cooke et al. 1998: op. cit.). In those basins where reduced fluids are proposed, fluid mixing is viewed as the most likely ore-precipitation mechanism (Cooke et al. 1998: op. cit.).

Geological setting of the Cobar deposits

The Cobar deposits are structurally controlled epigenetic massive-sulphide and vein-style polymetallic Au–Cu–Ag–Pb–Zn orebodies hosted by the Late Silurian–Early Devonian Cobar Basin (NSW). This basin is an (inverted) intracontinental ramp basin filled mainly by siliciclastic marine turbidites and minor volcanics (Glen et al. 1994: Australian Journal of Earth Sciences, 41, 341–352). The deposits formed during Early Devonian inversion of the basin, and are localised within steeply dipping linear ductile high-strain zones towards its eastern margin (Glen 1985: Journal of Structural Geology, 7, 301–315). The host high-strain zones were also mixing zones and conduits for hydrothermal fluids.

The host rocks are generally metamorphosed to the chlorite grade, and, according to illite crystallinity data, reflect the transition between diagenesis and low-grade metamorphism adjacent to most deposits (Brill 1988: Australian Journal of Earth Sciences, 35, 295–302). Vitrinite reflectance data (R$_0$ 3.3–12%; Schmidt 1980: MSc thesis, Australian National University; Robertson & Taylor 1987: Journal of Geochemical Exploration, 27, 77–101) suggest that the basinal strata were exposed to temperatures of burial diagenesis, but to hotter fluids in the high-strain zones (Robertson & Taylor 1987: op. cit.). Vitrinite reflectance data also show that organic material within and adjacent to the deposits was subject to intense thermal maturation well beyond the gas-generation window. This contrasts with Mississippi Valley-type deposits, whose adjacent host-rock kerogens are usually below the oil-generation window (Gize & Barnes 1994: in 'Sediment hosted Zn–Pb ores', Springer-Verlag, New York, 13–26).

Previous studies have demonstrated that the genesis of Cobar deposits involved mixing fluids (Lawrie & Hinman 1999: op. cit.): one was moderately reduced and methane-bearing during mineralisation; another, basement-derived, was a more oxidised, CO$_2$-bearing, high-temperature, low-salinity fluid. Pb-isotope data suggest the Pb–Zn end-member of the mineralisation spectrum represents basinal-source dominance, whereas the Cu–Au mineralisation was basement-source dominant though still mixed (Lawrie & Hinman 1999: op. cit.).

The Cobar deposits are characterised by complex mineral parageneses. A six-stage paragenesis has been documented at the Elura Ag–Pb–Zn deposit in the northwest of the basin (Lawrie & Hinman 1999: op. cit., table 1a). Premineralisation veins comprise subhorizontal crack-quartz fibre veins, and anastomosing subvertical laminar and breccia quartz (± early sphalerite) veins (Fig. 23).

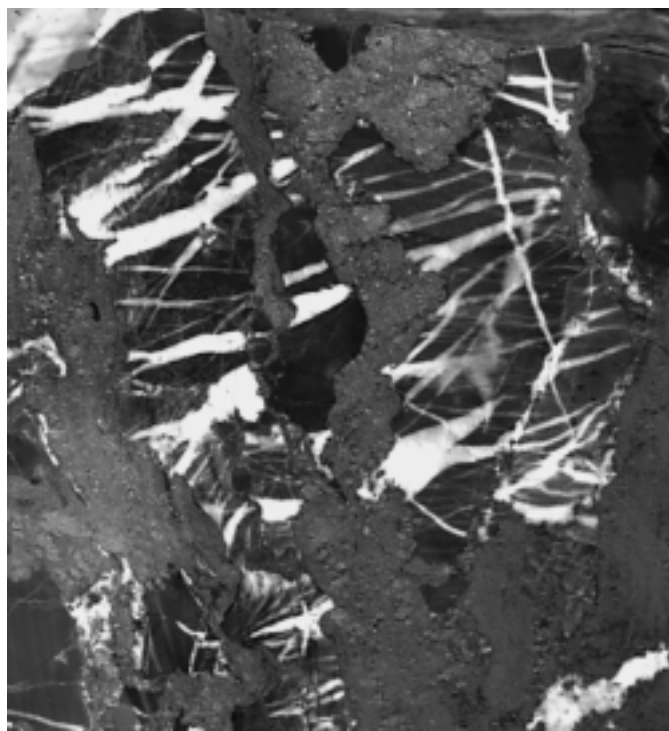**Fig. 23. An Elura hand specimen shows early crack–seal quartz (+sphalerite) veins (white) cross-cut by later sulphide-rich polymetallic veins. The host rock is silicified shale.**

New data and results

Samples from several different premineralisation crack–seal and breccia veins (the latter containing sphalerite) were collected from within 10 m of the main sulphide orebodies at '3 drill level' in the Elura mine. The samples for laboratory analysis were obtained from mapped veins. Their structural and microstructural timing, and paragenesis, were resolved before fluid-inclusion studies.

Primary and pseudosecondary fluid inclusions in low-strain domains within euhedral quartz and sphalerite grains have a wide range of homogenisation temperatures (110–230°C), highly variable liquid–vapour ratios, and low to moderate salinities (2–5 wt% NaCl equivalent; Lawrie & Hinman 1999: op. cit.).

Laser Raman microprobe data

Laser Raman analysis (Dollish et al. 1974: 'Characteristic Raman frequencies of organic compounds', Wiley, New York) of primary and pseudosecondary inclusions has revealed hydrocarbon spectra in premineralisation quartz veins. The similarity of Raman spectra within individual crack–seal veins, and contrasts reflecting different hydro-carbon compounds in adjacent veins (Fig. 24a–c), suggest that the hydrocarbons were trapped during a moderately short time, and that individual crack–seal veins were active at slightly different times.

Saturated hydrocarbon components were identified in spectra obtained from primary liquid-rich inclusions within sphalerite from breccia veins (Fig. 24a). These data demonstrate the coexistence of Zn-rich and hydrocarbon-bearing fluids. The low salinity (<5% NaCl equiv.) of these fluids leaves open the possibility that metal transport involved organic species. Although the Raman data confirmed the presence of long-chain hydrocarbons within individual inclusions, and the spectra represent different compounds in discrete veins, the technique could not identify the individual hydrocarbon compounds owing to the degree of band overlap.

Where the early crack–seal veins are cross-cut by later high-temperature veins, or where veins are partially preserved near high-temperature deposits, the Raman spectra indicated possible pyrobitumens (Fig. 24c). These pyrobitumens may have formed by in-situ degradation of pre-existing hydrocarbon-bearing fluid inclusions.

The main stage of mineralisation was characterised by hydrocarbon-bearing fluids that contained variable proportions of CH_4 and CO_2 (Fig. 24d) and possible minor ethane (C_2H_6). The last stage of mineralisation at Elura was characterised by aqueous fluids with no detectable CH_4 or CO_2.

Thermal-decrepitation mass spectrometry

Thermal-decrepitation mass spectrometry (Hoffmann et al. 1988: Chemical Geology, 70, 287–299), which can identify various low-molecular-weight components (e.g., water, CO_2, and hydrocarbons), was applied to analyse the same premineralisation crack–seal quartz veins and early zinc in quartz veins analysed by the laser Raman technique.

According to Figure 25a, the contents of the inclusions were released over different time–temperature intervals, and two main groups can be recognised. They include large volumes of H_2O, CO_2, N_2, and hydrocarbons up to C_5H_{12} (Fig. 25b).

The components released at lower temperatures (group 1) consist mainly of *n*-alkanes with chain lengths <C_9 and minor H_2O, CO_2, and N_2 (Fig. 26a, upper part). The absence of longer chain *n*-alkanes may be a function of the sample volume and the limitations of the tech-nique's sensitivity in detecting higher-molecular-weight hydrocarbons. The components released at higher temperatures (group 2; Fig. 26a, lower part) consist primarily of H_2O, CO_2, and N_2, and appear to lack the hydrocarbon distribution characteristic of group 1. These data are grouped together, and displayed against the data obtained from a blank sample for comparison (Fig. 26b).
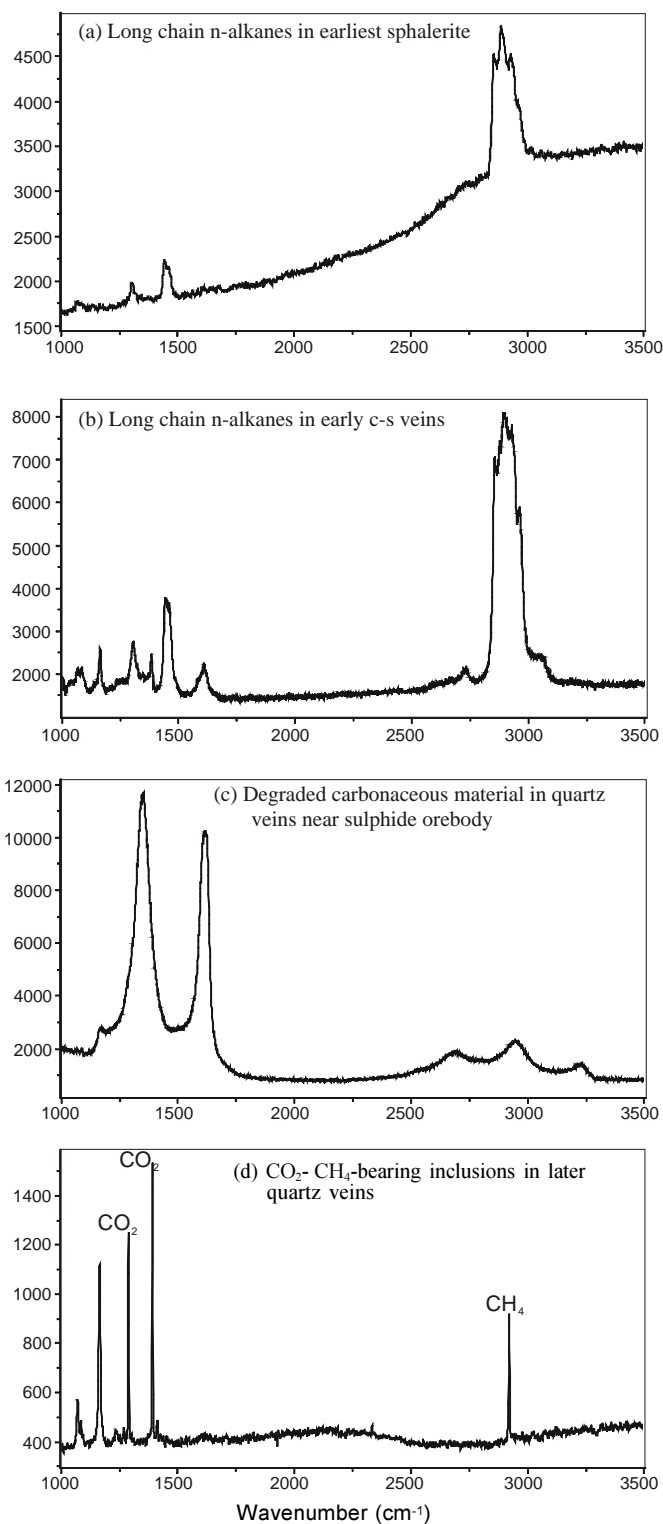

Fig. 24. Laser Raman spectra for fluid components within individual fluid inclusions: *n*-alkane spectra for liquid-rich primary inclusions within sphalerite (Fig. 24a) and quartz (Fig. 24b) from early quartz crack–seal veins; spectra for degraded carbonaceous material in quartz veins (Fig. 24c); and spectra for CO_2 and CH_4 in later quartz veins synchronous with polymetallic mineralisation (Fig. 24d).

These results are consistent with those from conventional fluid-inclusion studies (Lawrie & Hinman 1999: op. cit.), and show that two fluid components are present throughout the vein paragenesis at Elura. The data support the published fluid-mixing model containing two dissimilar fluids with contrasting temperatures and redox properties (Lawrie & Hinman 1999: op. cit; Lawrie et al. 1999: op. cit.).

Origin and role of hydrocarbons at Elura

An important question to be resolved is whether the hydrocarbons at Elura (and in the Cobar deposits generally) were externally derived from a deep basinal source, or locally produced as a result of the influx of hot metal-bearing fluids into organic-rich host-rocks. On the one hand, a deep basinal source may have offered the prospect of synchronous transport and complexing of zinc by hydrocarbons. On the other hand, a local hydrocarbon source, as proposed for the Century zinc deposit (Broadbent et al. 1996: op. cit.), may have contributed to an ore-depositional mechanism, as metal-rich fluids interacted with carbonaceous host rocks. Whereas a hydrocarbon contribution from local host rocks cannot be ruled out, evidence suggests that the hydrocarbons were largely derived from a much larger source than that in the local Cobar-deposit host-rock environment. The evidence includes:

* hydrocarbons are a component of the Cobar deposits regardless of the stratigraphic position of an ore deposit;
* individual orebodies are epigenetic, and highly discordant to the stratigraphy (e.g., the Elura deposit transects >1 km of thinly interbedded turbidites); hydrocarbons occur throughout an orebody's vertical extent and paragenesis, and neither they nor the orebodies are localised at the intersection with any lithology;
* host shear zones are narrow (<200 m at Elura) and host rocks (which include rhyolites at the nearby Peak deposit) have low TOC contents, raising doubts about their capacity to contribute the volume of fluid hydrocarbons estimated to occur in the deposits;
* host structures are basin-transecting, and contain evidence for premineralisation alteration assemblages that formed through interaction with organic acid-bearing reduced connate fluids (Robertson & Taylor 1986: op. cit.).

These observations suggest that the hydrocarbons in the premineralisation quartz veins and in the early syn-zinc mineral concentrations were not derived from local in-situ maturation of organic components, and that hydrocarbon-bearing fluids were generated on a large scale in the Cobar Basin. After the formation of the early crack–seal veins and the zinc mineralisation, small amounts of organic material in the high-strain inversion zones of the host lithologies interacted with the introduced fluids, which converted them to semi-anthracite or graphite synchronous with the later, hotter polymetallic mineralisation.

The data presented above suggest that the hydrocarbons are a component of a fluid expelled from deep within the basin. At all stages in deposit paragenesis, liquid:vapour ratios are highly variable within individual quartz grains, and a wide range of homogenisation temperatures, CO_2:CH_4 ratios, and salinities are apparent (Lawrie & Hinman 1999: op. cit.). Pb-isotope data (Lawrie & Hinman 1999: op. cit.) also suggest the presence of basinal- and basement-derived fluids carrying sulphur (Seccombe 1990: Mineralium Deposita, 25, 304–313; Sun & Seccombe 1998: Geological Society of Australia, Abstracts, 49, 433) and Pb–Zn components (Hinman 1992: PhD thesis, JCUNQ) derived from the host basin.

Host structures acted as basin-scale conduits that tapped fluids from both within the basin and from underlying basement sources (Seccombe 1990: op. cit.; Lawrie & Hinman 1999: op. cit.). The same structures acted as mixing zones for these contrasting fluids, and provided a focus for localising ore precipitation at dilational sites where basement heterogeneities permitted marked extension in high-strain volumes. The formation of the Cobar deposits links the physical effects of basin inversion (expressed as brittle–ductile deformation in restricted high-strain zones), the telescoping of geotherms, and the mixing of fluids from within the basin with those derived externally from the basement (Lawrie 1991: in 'Base metals symposium', JCUNQ, EGRU, Contribution, 38, 137–143; Hinman 1991: in 'Base metals symposium', JCUNQ, EGRU, Contribution, 38, 144–166).

Conclusions

This study has demonstrated the presence of *n*-alkanes (C_1–C_9) in premineralisation quartz veins and in early Zn-rich mineral concentrations at Elura. The preservation of free hydrocarbons in inclusions in veins, while carbonaceous matter in adjacent host rocks was degraded, is consistent with calculated stabilities which indicate that hydrocarbons may survive low-grade metamorphism (Mango 1991: Nature, 352, 146). Similar relationships have been noted in rocks metamorphosed to the prehnite–pumpellyite facies (Brocks et al. 1999: Science, 285, 103).
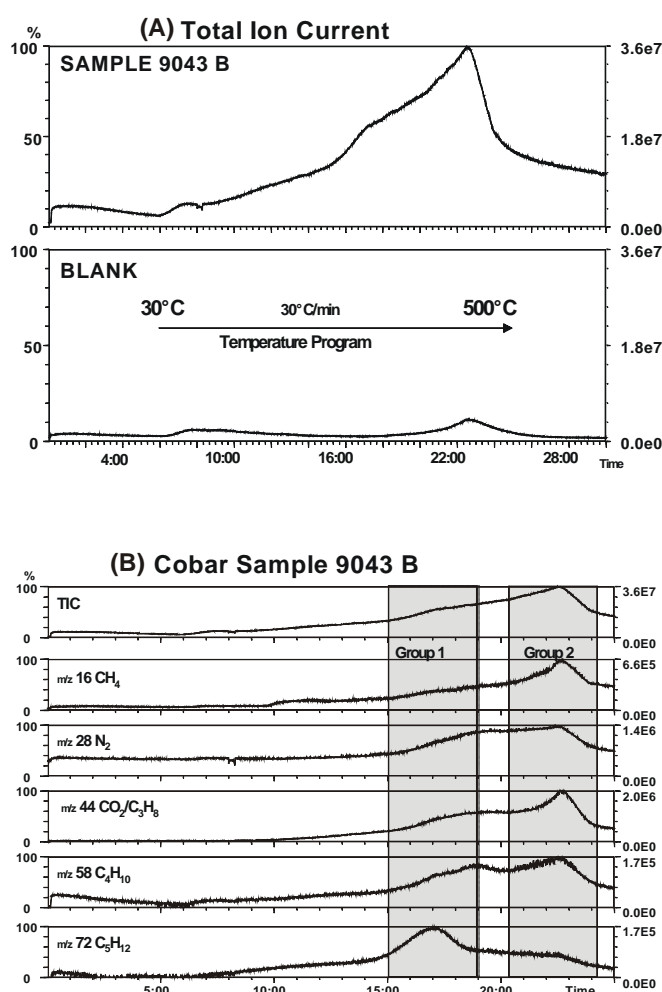

Fig. 25. Thermal-decrepitation mass spectrometry results for a quartz crack–seal vein. (A) Contents released from inclusions over different time–temperature intervals (top graph), and the output from a sample blank shown for comparison (lower graph). (B) Analysis of these data reveals two main groups, of which individual components (released during progressive heating) comprise large volumes of H_2O, CO_2, N_2, and hydrocarbons up to C_5H_{12}.

Preliminary calculations suggest that this early paragenetic association could represent organic complexing of zinc at low temperatures (D. Huston, AGSO, personal communication 1999). Furthermore, a genetic link between organo-sulphur compounds, and oilfield- and base-metal-deposit-forming (reduced) fluids has been suggested by some researchers (Sverjensky 1984: Economic Geology, 79, 23–37; Giordano 1985: in Geological Society of London, Special Publication 78, 175–202; Sicree & Barnes 1996: Ore Geology Reviews, 11, 105–131; Kharaka et al. 1998: Reviews in Economic Geology, 9). An alternative hypothesis is that the early mineralisation resulted from the mixing of pulses of zinc-rich fluids and cooler hydrocarbon-bearing fluids generated at different depths in the basin.

A progressive (or episodic) shift to higher methane and C_2 hydrocarbon contents with increasing salinity and temperature (in the reduced fluid component) is apparent through time. This is consistent with a connate source for the hydrocarbon-bearing fluid, which was expelled from the basin in response to tectonic inversion and prograde thermal maturation of the basin sediments. Similar hydrocarbon-bearing fluids have been reported in epigenetic Zn-rich mineralisation in the Coeur d'Alene base- and precious-metal veins in the USA (Leach et al. 1988: Geology, 16, 122–125).

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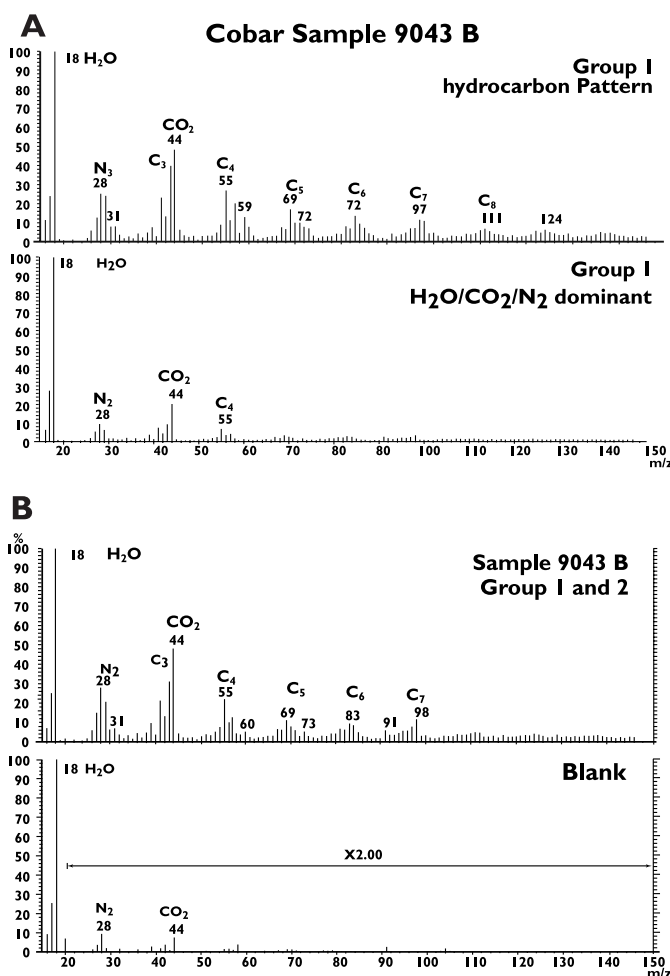
Fig. 26. Further thermal-decrepitation mass spectrometry results for the same quartz crack–seal vein. The group 1 components (released at low temperatures; A, top graph) are mainly hydrocarbons with chain lengths $<C_9$ and minor H_2O, CO_2, and N_2. The components released at higher temperatures (group 2; A, lower graph) consist primarily of H_2O, CO_2, and N_2. Data from groups 1 and 2 are combined (B, top graph), and compared with the components from a sample blank, which provides a baseline comparison (B, lower graph).