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Condor-94-1

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FICHE No.13407-**ANALYSIS OF SAMPLES FROM BRUNY ISLAND FOR PETROLEUM
HYDROCARBONS**

EL 1/88

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July 1995
See file EL1/88/Vol6/F28*

December 22, 1994

95-3664

Australian Science, Australia's Future

INTRODUCTION

In November 1994, as part of the on-going investigation into the possible occurrence of petroleum hydrocarbons on-shore in Tasmania, Condor Oil Investments Pty. Ltd. commenced drilling two stratigraphic boreholes on Bruny Island, named SHITTIM 1 and GILGAL 1. During the course of drilling both holes suffered an in-flow of gas and SHITTIM 1 also began to yield a hot brine at a depth of 64 metres at an estimated rate of 7000 gallons per hour. Drilling on both sites was stopped and samples taken for analyses.

SAMPLES

The following samples were delivered to the CSIRO Marine Laboratories for hydrocarbon analysis:

- Two samples of brine and a clay sample from the base of GILGAL 1
- Two samples of brine from SHITTIM 1
- Three water samples from a saw pit bubbling gas

One sample of the brine from SHITTIM 1, and the clay from GILGAL 1 were analysed for hydrocarbons. Of the samples from the saw pit, two were heavily contaminated by organic (plant) matter and so were deemed unsuitable for hydrocarbon analysis. The third sample was clear of this matter, having been "concentrated" by Mr. Bendall, and it was decided to analyse this sample.

On a subsequent trip to Bruny Island (7/12/94) Dr. Revill collected gas samples from SHITTIM 1, GILGAL 1, Johnstones well and the saw pit. These were sent to AGSO for gas analysis.

ANALYSIS

The water samples to be analysed were transferred to a separating funnel and solvent extracted with hexane (2 x 75 ml), the solvent fractions combined and reduced under vacuum to a volume of 50 μ l.

The clay sample (131 g wet weight) was extracted by ultrasonication (2 x 5 minutes, stirring in between) with 50 ml of methanol, the solvent transferred to centrifuged tubes and centrifuged at 2000 rpm for 10 minutes. The supernatant was decanted into a separating funnel containing water (milli-Q) and the sediment re-combined with the original. The extraction was then repeated with solvent mixtures of decreasing polarity (chloroform:methanol, 7:3, 4:1; chloroform) and the extracts combined. The chloroform fraction was collected, reduced under vacuum, dried by passing through anhydrous sodium sulphate and transferred to a vial and further reduced to 50 μ l. The sediment was air dried and re-weighed to obtain a dry weight.

The solvent extracts were analysed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) operating in the Selected Ion Recording (SIR) mode.

Gas samples were collected by displacing water (milli-Q) from a gas tight PET plastic bottle.

RESULTS

Gas Analyses

Results for the analysis of 4 gas samples are given in Table 1. No trace of methane was found in either SHITTIM 1 or GILGAL 1. Both the Saw Pit and Johnstones well samples contained methane and both had similar $\delta^{13}\text{C}$ isotope values of -56 ‰ and -55 ‰ respectively. Both these results are interpreted as being due to biogenic methane due to the lack of any higher homologues above C_1 and from the isotope values. The values of -55 ‰ and -56 ‰ are possibly regarded as "heavy" for biogenic samples but the environment from which they were collected (waterlogged sites with ample vegetable material) would be experiencing methane oxidation which in turn would lead to the slightly "heavy" values.

Saw Pit water sample

No evidence for hydrocarbons in this sample could be found either by GC or GC-MS (Figures 1-4).

SHITTIM 1 water sample

GC analysis of the water extract shows no detectable signs of hydrocarbons, however analysis by the much more sensitive SIR GC-MS suggests the presence of a restricted *n*-alkane profile (Figure 1) and hydrocarbon biomarkers can be detected (Figures 2-4). The presence of such a restricted *n*-alkane envelope is generally indicative of a refined petroleum product, in this case a "heavy diesel or gas oil" and the pristane/phytane ratio in this sample is commonly associated with oils derived from Bass Strait. However, the cyclic biomarker profiles contradict this and are more indicative of a mature Middle East derived oil, for example, the C_{29} hopane > C_{30} (Figure 2), low diasterane content (Figure 3) and the presence of methyl hopanes (Figure 4) generally taken to indicate a marine carbonate sourced oil. Thus in this sample there is a suggestion of a mixed source for the very low levels of hydrocarbons. These may be contamination from the drilling operations but this cannot be confirmed or eliminated unless samples of the lubricants used during the drilling operations are analysed.

GILGAL 1 clay sample

GC analysis of the total solvent extract from the clay sample (Figure 5) shows the clay to contain a slightly greater quantity of hydrocarbons than the SHITTIM 1 water, dominated by a high end unresolved complex mixture (UCM). The narrow carbon number range and GC elution time of this UCM is generally indicative of a refined product such as lubricating oils. GC analysis was unable to detect the *n*-alkane profile observed in the SHITTIM 1 water, but this may be due to material naturally present in the clay masking the signal. GC-MS analysis however does show the presence of a restricted *n*-alkane profile similar to that seen in the SHITTIM 1 water (Figure 1), with a similar pristane/phytane ratio. The cyclic biomarkers are again contradictory to the pristane/phytane ratio and similar to the SHITTIM 1 sample indicating a Middle East origin. It is reasonable to suppose in this sample that the cyclic biomarkers are associated with the UCM since these elute around the same retention time and the UCM is present in much larger quantities than the *n*-alkanes, thus the indication is that the hydrocarbons in SHITTIM 1 and GILGAL 1 share the same source(s). The inference at the present time, due to the restricted carbon number ranges of the *n*-alkanes and UCM, is that the

source is probably contamination from the drilling operations. However, we must stress that this can only be confirmed or denied by analysing samples of the actual lubricants used during the drilling operations.

It should also be pointed out that small amounts of hydrocarbons are found in most sediments. Even if the distributions found here are indigenous it may be that they have been produced by localised dolerite heating of organic matter.

CONCLUSIONS

- No methane was detected in samples from the two stratigraphic holes.
- Methane from the Saw Pit and Johnstone's well is interpreted as being biogenic in origin.
- No hydrocarbons could be detected in water from the Saw Pit and were detected in only very low amounts in water from SHITTIM 1. The clay sample from GILGAL 1 contained slightly higher levels of hydrocarbons.
- The hydrocarbons detected in both wells exhibited similar restricted *n*-alkane and biomarker profiles consistent with refined products but this cannot be confirmed without analysis of samples of lubricants and fuels used during drilling.

TABLE 1: Results of gas analysis on Bruny Island samples

Sample	Oxygen (%)	Nitrogen (%)	Carbon dioxide (%)	Methane (%)	$\delta^{13}\text{C}$ Methane (‰)
Saw Pit	1.1	37.5	7.1	54.3	-56.1
Johnstones Well	2.4	19.4	7.8	70.3	-55.2
SHITTIM 1	16.7	80.6	2.7	NIL	
GILGAL 1	21.8	77.8	0.4	NIL	

Calculated in Mole %; No C_2 to C_5 components detected.

Data provided by Dr. R. Summons, AGSO.

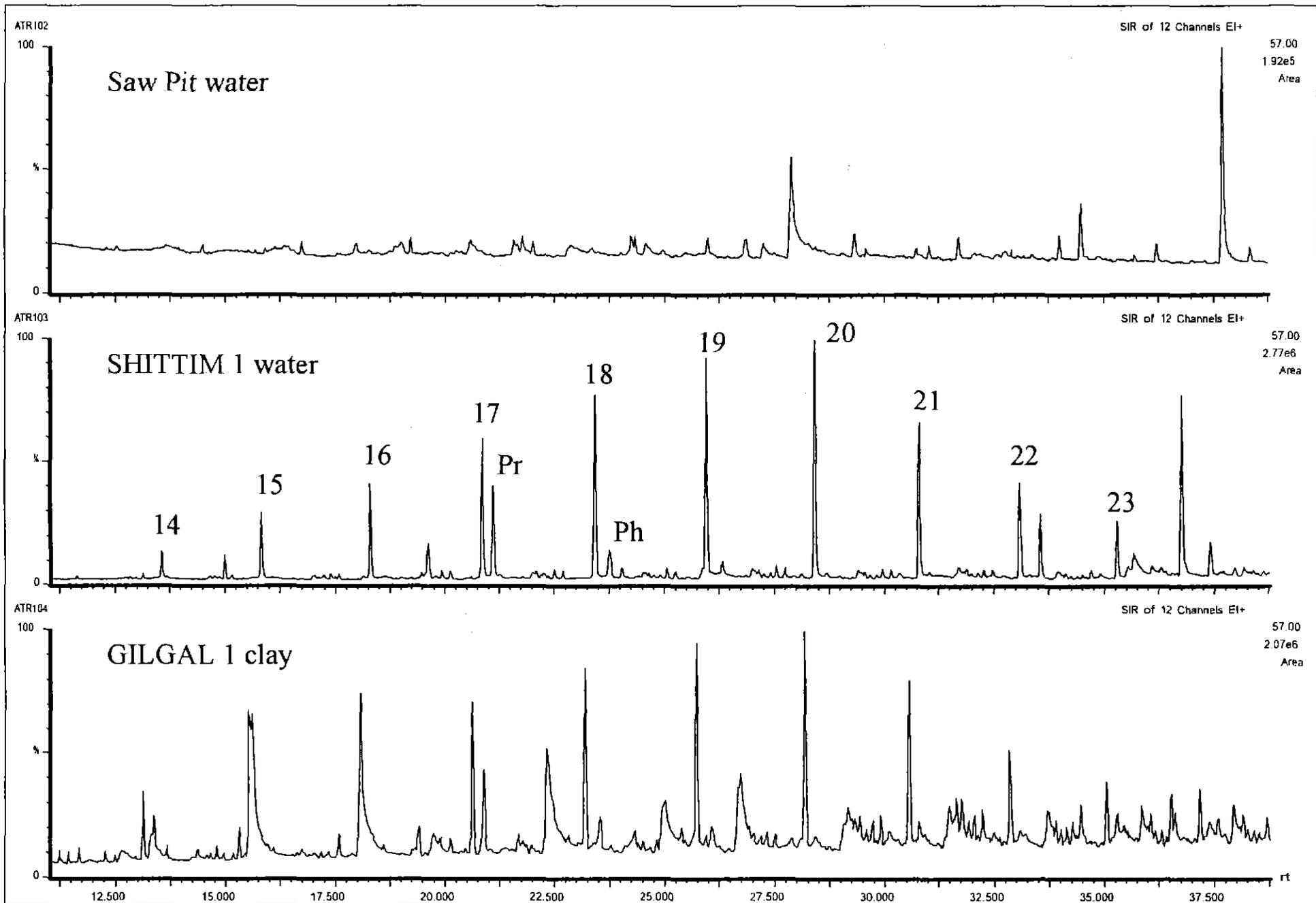


Figure 1: m/z 57 mass fragmentogram to highlight n -alkanes in the three samples analysed
 (note that the clay sample contains non-hydrocarbon material in the total extract)

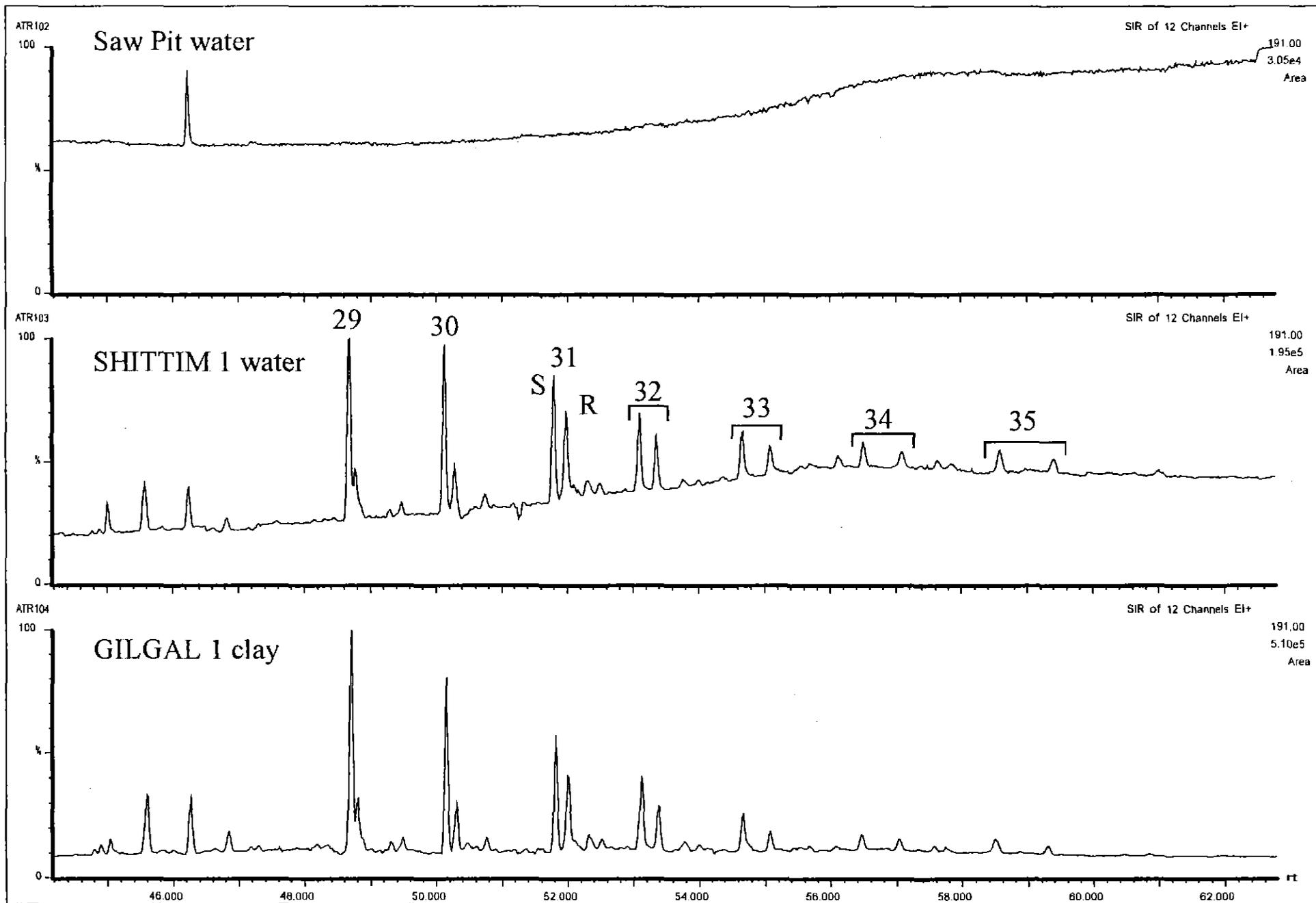


Figure 2: m/z 191 mass fragmentogram to show distribution of hopanes in the three samples analysed

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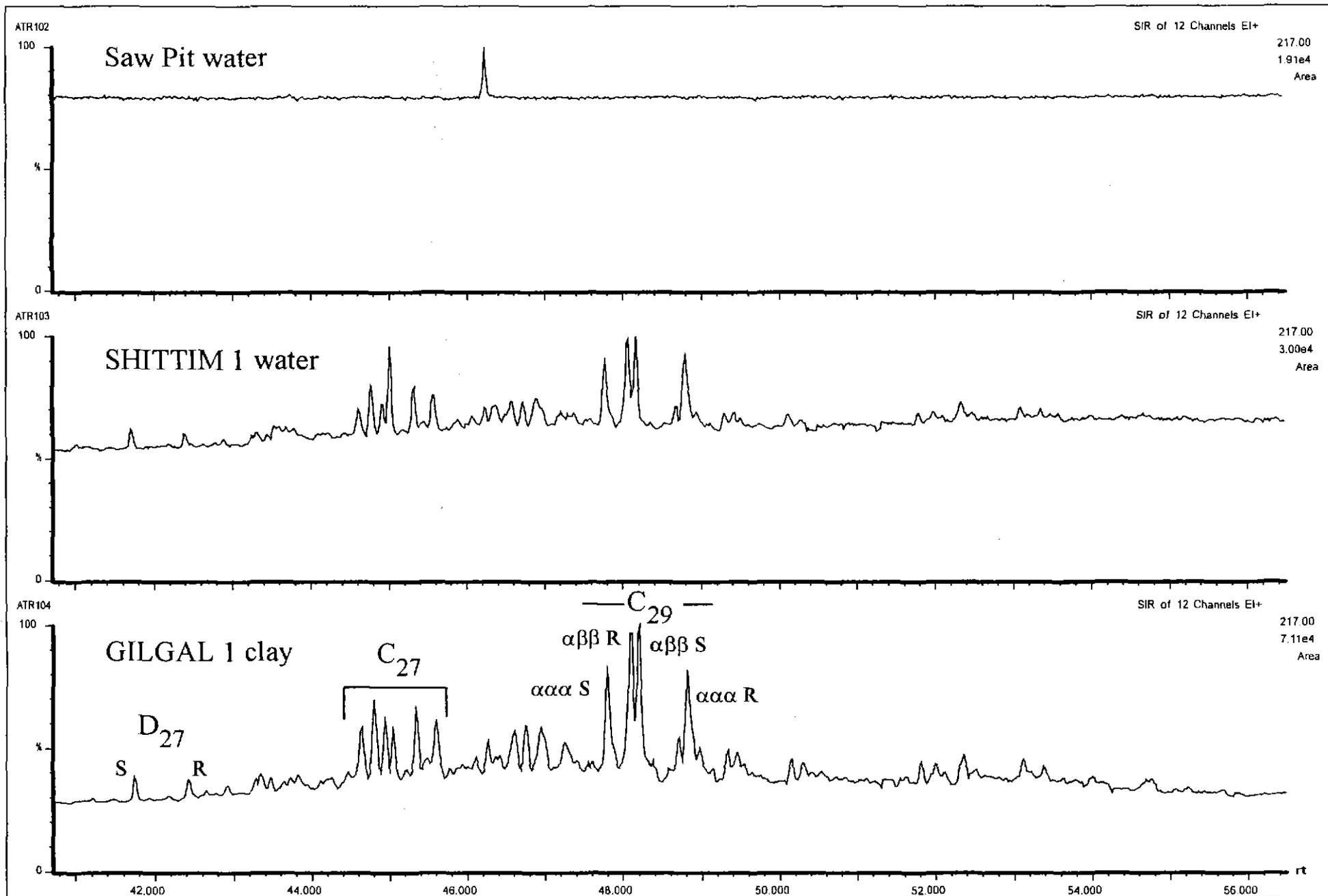


Figure 3: m/z 217 mass fragmentogram showing the sterane profiles for the three samples analysed (numbers refer to carbon number, D = diasteranes, alpha and beta refer to stereochemistry at carbons 5, 14 and 17)

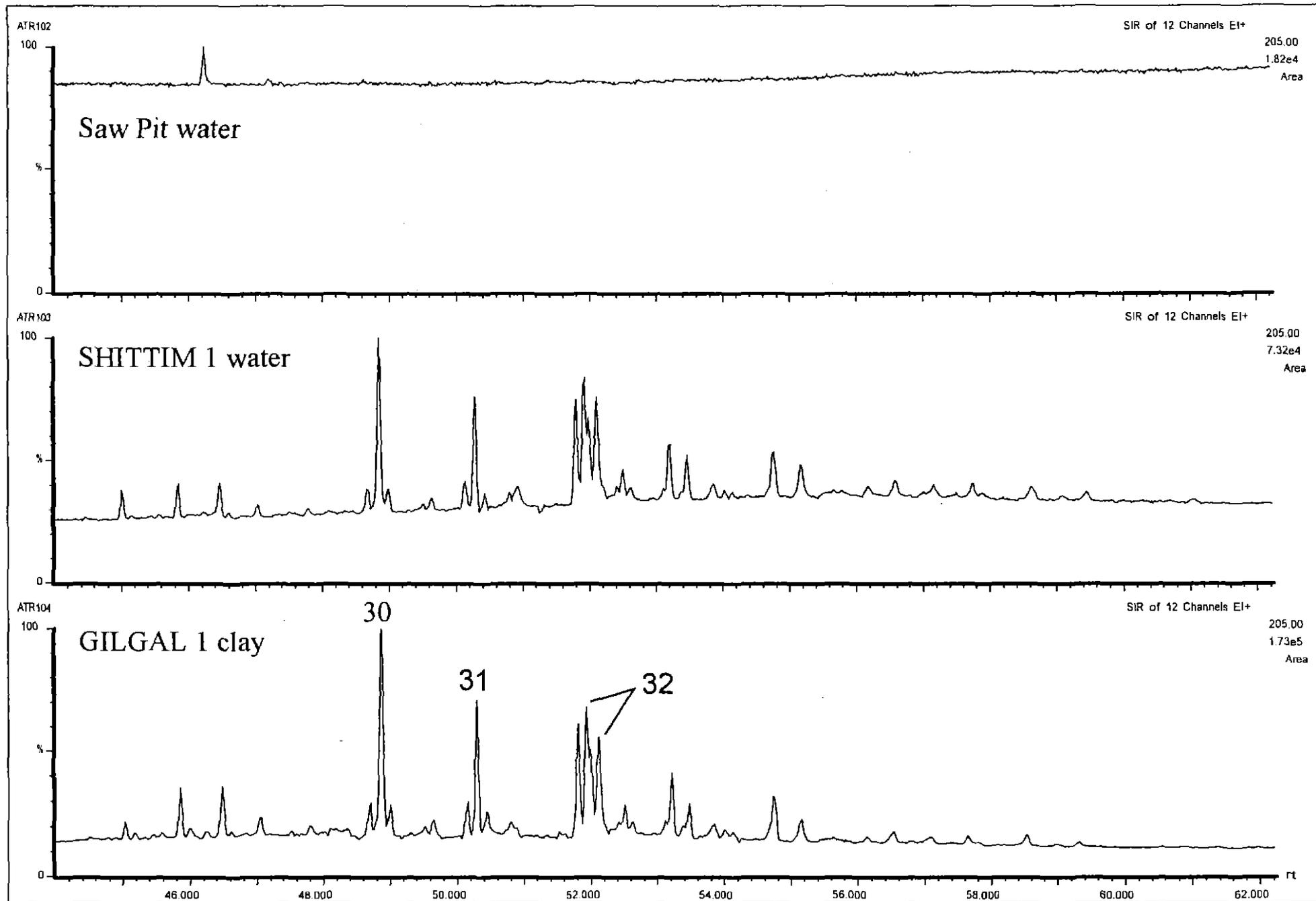


Figure 4: m/z 205 mass fragmentogram showing methyl hopanes in the three samples analysed (numbers refer to carbon number of methyl hopanes)

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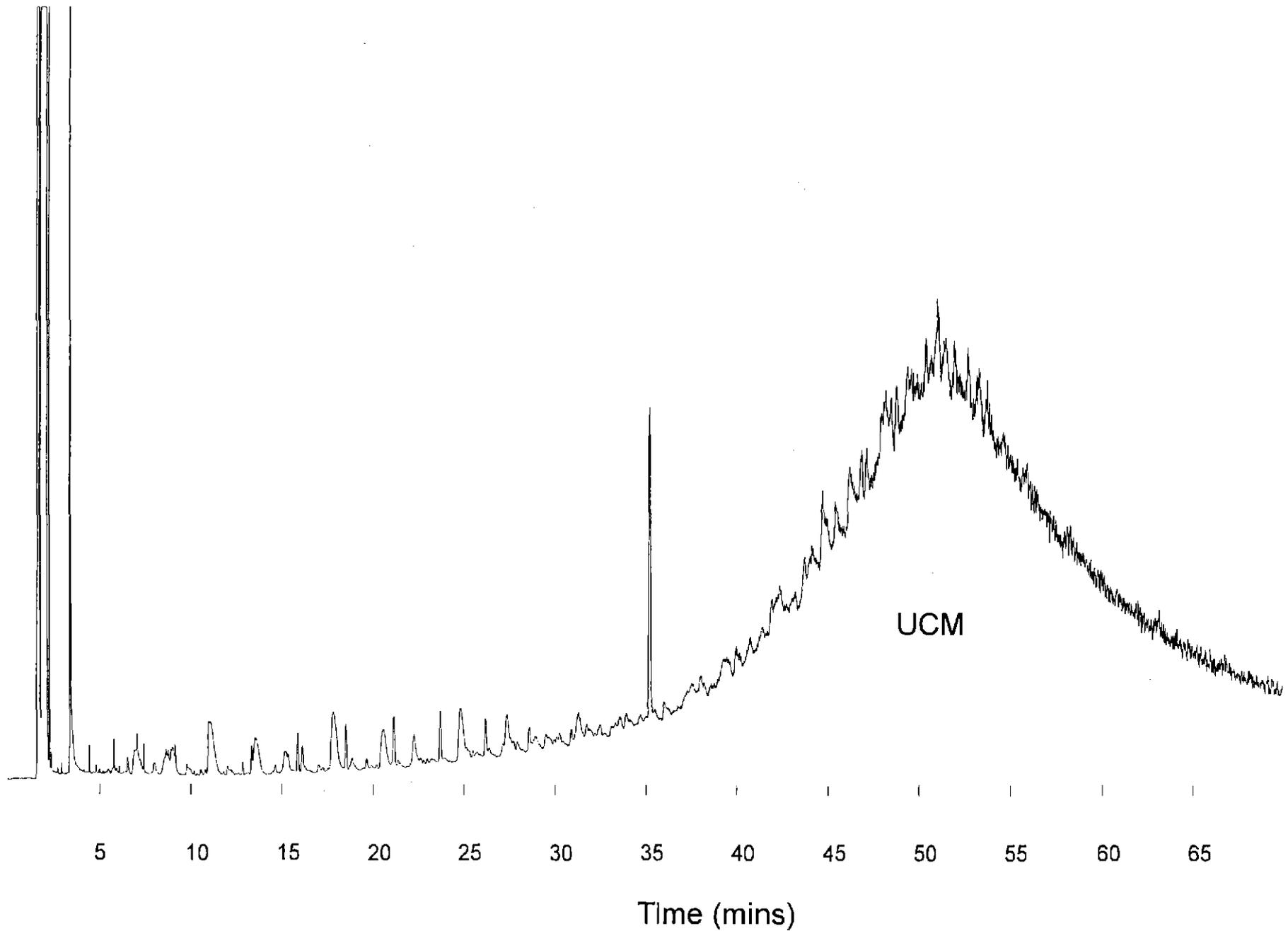


Figure 5: GC chromatogram of the total solvent extract from the GILGAL 1 clay sample

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