

Case report

A case study on the application of isotope ratio mass spectrometry (IRMS) in determining the provenance of a rock used in an alleged nickel switching incident

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Abstract

The application of isotope ratio mass spectrometry (IRMS) in forensic science to establish the provenance of a range of questioned substances including soils, drugs, explosives, currency, ivory and rhino horn has been widely documented. The present study wishes to highlight the applicability of IRMS and specifically stable carbon IRMS in determining the provenance of a carbonate rock that was switched for nickel metal exported from South Africa to Israel. The technique employed effectively argued against a South African origin for the rock whilst simultaneously supporting an Israeli origin, enabling investigators to focus their attention accordingly. The study represents the first documented instance known to the authors where IRMS has been employed in the forensic geo-location of a rock.

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1. Introduction

In a recent survey conducted by the Forensic Isotope Ratio Mass Spectrometry (FIRMS) Network [1] based at the University of Reading, it was shown that about one quarter of all isotope ratio mass spectrometry (IRMS) work conducted was performed in the field of forensic science. As such, IRMS has been shown useful in establishing the provenance of questioned substances including soils [2], drugs [3–5], explosives [3] and ivory [6], amongst others. The authors are however not aware of a single documented instance where stable IRMS has been employed in a forensic context to determine the provenance of a rock, despite references as to the use of IRMS in tracing sources of rocks in other contexts, e.g. in archaeological materials [7].

The present study was initiated by Anglo Platinum Process Investigations upon the discovery of a rock in a container filled with nickel metal that was exported from South Africa to Haifa, Israel, and from which a volume of nickel metal similar to that

of the rock in question has been removed. Apart from the monetary losses incurred as a result of the switching incident, Anglo Platinum investigators were concerned about possible security breaches at their own facilities and to address this problem needed to determine whether the rock in question originated from their facilities in South Africa, or whether the theft took place at their client's site in Israel. In order to focus the efforts of investigators, the corresponding author was tasked with establishing the provenance of the rock.

2. Background

Likely localities at which switching may have occurred as identified by investigators were Rustenburg, Johannesburg and Durban in South Africa and Haifa in Israel. X-ray diffraction analysis showed the rock to be dominantly composed of dolomite with trace amounts of calcite. This was confirmed by a petrographic study, which showed the rock to consist of a hypidiotopic mosaic of dolomite modally constituting ~97% of the rock, with the remainder being made up of calcite and opaque minerals. Having identified the rock as a finely crystalline dolomite, the study turned towards the identification of areas underlain by dolomite close to the likely localities at

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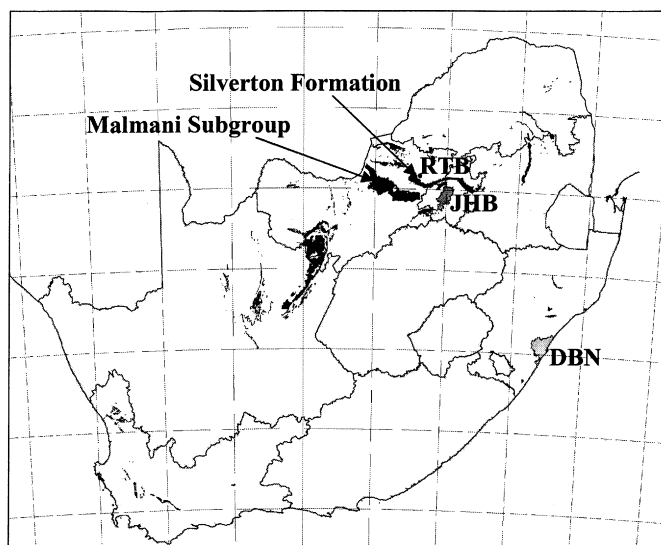


Fig. 1. The distribution of South African dolomite-bearing lithological units. RTB = Rustenburg, JHB = Johannesburg and DBN = Durban.

which switching may have occurred. Geospatial data in the possession of the Council for Geoscience (the official geological survey of South Africa and the custodians of geological information on South Africa) were queried using a GIS application to show the occurrences of dolomite in the country (Fig. 1). Durban could be excluded *ab initio* as a locality for the switching to have taken place as a result of the absence of dolomite in its vicinity. Neither Rustenburg nor Johannesburg is directly underlain by dolomite but occurrences of dolomite occur in the vicinity of both towns, therefore warranting further investigation. Geological maps of Haifa, Israel, showed the town to be directly underlain by dolomites, limestones and marls. The first part of the study therefore succeeded in limiting the original four localities at which switching may have occurred to three.

3. Regional geological setting

Dolomite in the vicinities of Rustenburg and Johannesburg are confined to the Silverton Formation and Malmani Subgroup of the Late Archaean–Early Proterozoic Transvaal Sequence. The former is described as “thick, monotonous laminated mudrocks” with significant volcanics, commonly carbonaceous mudrocks and subordinate chert, sandstone and dolomite lenses, with carbonates confined mainly to the north of the Transvaal basin [8]. Mapping conducted in the vicinity of Rustenburg however made no mention of the presence of carbonates in the Silverton Formation [9] thereby effectively excluding the Silverton Formation as a source for the rock in question.

The Malmani Subgroup on the other hand is composed largely of dolomite, with subordinate interlayered chert and mudrocks [8] and was therefore considered a likely source for the rock in question. The limestones, dolomites and marls underlying large parts of Haifa belong to the Judea Group, with

a Cenomanian-Turonian age and the rock in question may therefore also have originated from Haifa.

4. Literature review

The next part of the study involved a thorough study of the available literature on the dolomites of the Malmani Subgroup and the Judea Group in order to decide on suitable analytical methods to employ in generating data that could be compared with data from the literature as a basis for discrimination. A large number of papers on the geochemistry and geology of the Malmani dolomites were found, three of which contained data on the stable carbon isotopic composition of the dolomites [10–12].

The literature on the Judea Group proved to be much scarcer and only a single reference was found that fortuitously contained reference to the stable carbon isotope composition of the Cenomanian dolomites of Israel [13]. At this stage it became obvious that the stable carbon isotopic composition of the dolomites were markedly different ($\delta^{13}\text{C} = -0.9 \pm 0.7\text{‰}$ for the Malmani dolomites versus $+1.2\text{‰}$ for the Cenomanian dolomites of Israel, both relative to PDB).¹ Additional literature suggested that the difference between the stable carbon isotopic composition of the Malmani dolomites and the Judean dolomites might be even more pronounced as a result of a $\sim 2\text{‰}$ positive excursion in the carbon isotopic composition of carbonates that is recognized to have taken place at the boundary between the Cenomanian and Turonian stages [14], effectively arguing for $\delta^{13}\text{C}$ -values of up to $+3\text{‰}$ PDB in the Judea Group. High positive $\delta^{13}\text{C}$ -values are known for metamorphosed carbonates of the Transvaal Sequence [12], but these carbonates are mineralogically dissimilar from the rock studied here and could therefore be excluded as a source for the rock.

5. Analytical technique

A milled portion of the sample was weighed into a tin capsule and loaded into an auto-sampler carousel on the ANCA-GSL (automated nitrogen and carbon analysis for gases, solids and liquids) sample preparation system connected to a GEO 20-20 mass spectrometer at the Environmental Isotope Group of iThemba Labs Gauteng. The samples were then dropped into a furnace held at 1000 °C where they were combusted in the presence of oxygen and converted to CO_2 . The combusted gases were swept in a helium stream over a combustion and reduction catalyst to purify the gas to carbon dioxide. Water was removed by a magnesium perchlorate chemical trap and the CO_2 separated from nitrogen and other unwanted gasses by a gas chromatograph. The resultant chromatographic peak of CO_2 entered the ion source of the continuous-flow isotope ratio mass spectrometer (CF-IRMS)

¹ PDB and VPDB are essentially numerically equivalent. In this paper, both PDB and VPDB are used, depending on how the data were reported in the references cited.

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