

Raman spectroscopy enables the classification of molybdenite phases in the presence of carbonaceous material from Merlin Mo-Re deposit, Australia



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ABSTRACT

A Raman band shift has been observed for the first time between the two key primary generations of molybdenite at an ore deposit. Samples were studied from Merlin, the world's highest-grade molybdenum-rhenium (Mo-Re) deposit, which is primarily hosted by metamorphosed graphitic sediments belonging to the Mt. Isa Inlier, NW Queensland, Australia. Two molybdenite textural varieties occur here; the first (molybdenite 1) contains abundant sub-nano scale inclusions of carbonaceous material, whereas the second (molybdenite 2) is relatively inclusion free. Re is found to not vary between molybdenite 1 and 2 in any systematic way. Raman spectroscopy is one of the best analytical approaches that can be used to distinguish between two molybdenite varieties and detect the presence of graphitic and other carbonaceous material at Merlin.

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1. Introduction

The Merlin molybdenum-rhenium deposit is located 145 km southeast of Mount Isa and some 700 km from the east coast of Australia. Currently it is the world's highest-grade Mo-Re deposit, with an average grade of 2.3% Mo and 34 ppm Re [1].

Molybdenite (MoS_2) is a layered transition metal dichalcogenide composed of layers of molybdenum atoms packed between sulphur atoms, with each molybdenum atom bonded to six sulphur atoms [2]. There are four first-order Raman active modes that are present in most reported MoS_2 Raman spectroscopic studies, namely, E_{1g} (286 cm^{-1}), E_{12g} (383 cm^{-1}), A_{1g} (408 cm^{-1}), and E_{22g}^2 (32 cm^{-1}) [3].

Molybdenite mineralisation at Merlin at microscopic scale is observed as predominantly of two types: an inclusion-rich (dirty) molybdenite (here termed molybdenite 1, or Mo1) and an inclusion-poor (clean) molybdenite (molybdenite 2 or Mo2) [4,5].

Previous single spot LA-ICPMS analyses of these molybdenite varieties [4] suggested that molybdenite 1 was significantly enriched in trace elements compared molybdenite 2.

Graphite has a layered, hexagonal structure. In each layer, the carbon atoms are arranged in a honeycomb lattice [6]. The most prominent features in the Raman spectra of graphitic materials are the so-called G band appearing at 1582 cm^{-1} (graphite), additional first-order bands (D bands) are located at 1355 cm^{-1} (D1 band), 1550 cm^{-1} (D3 band) and 1620 cm^{-1} (D2 band; and the second-order band at $\sim 2900\text{ cm}^{-1}$ [6]. Previous but as yet unpublished work by the authors has demonstrated that carbonaceous matter derived from the evolution of organic matter originally present in the host sedimentary rock, that is, black/carbonaceous shale, constitutes up to 10 wt. % of Merlin ore, and is lowest (0.01 wt. %) in ores that are developed away from the main orebody.

Recent analysis on molybdenite using LA-ICPMS and SEM from a wide range of ore types has shown that MoS_2 possesses a distinct trace-element geochemical composition which is locally influenced by the presence of nano- and micron-scale inclusions [4,7]. Studies on the distribution of Re in molybdenite have also been used to define the source of metal components [7]. Standard reflected light petrography and SEM techniques are not well suited to the investigation of mixture of graphite and molybdenite, which are common at Merlin, because these minerals are petrographically similar. In addition, routine carbon coating of samples for SEM analysis reduces the effectiveness of this technique for the study of graphitic matter textures. For these reasons, our study primarily employed Raman analysis and mapping.

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Several hypotheses are tested in this study to account for the difference between molybdenite 1 and 2. One hypothesis is that molybdenite 1 and 2 are separate polymorphs at Merlin and Raman analysis is appropriate for testing this, as has been demonstrated by [8]. A second hypothesis is that only a single polymorph is present, but the enhanced trace element contents in

molybdenite 1 leads to increased lattice strain, thereby producing the peak shift phenomenon.

The strategy for testing these hypotheses was to create two-dimensional hyperspectral Raman data sets of the different molybdenite phases and to compare them with SEM and LA-ICPMS mapping data of the same regions.

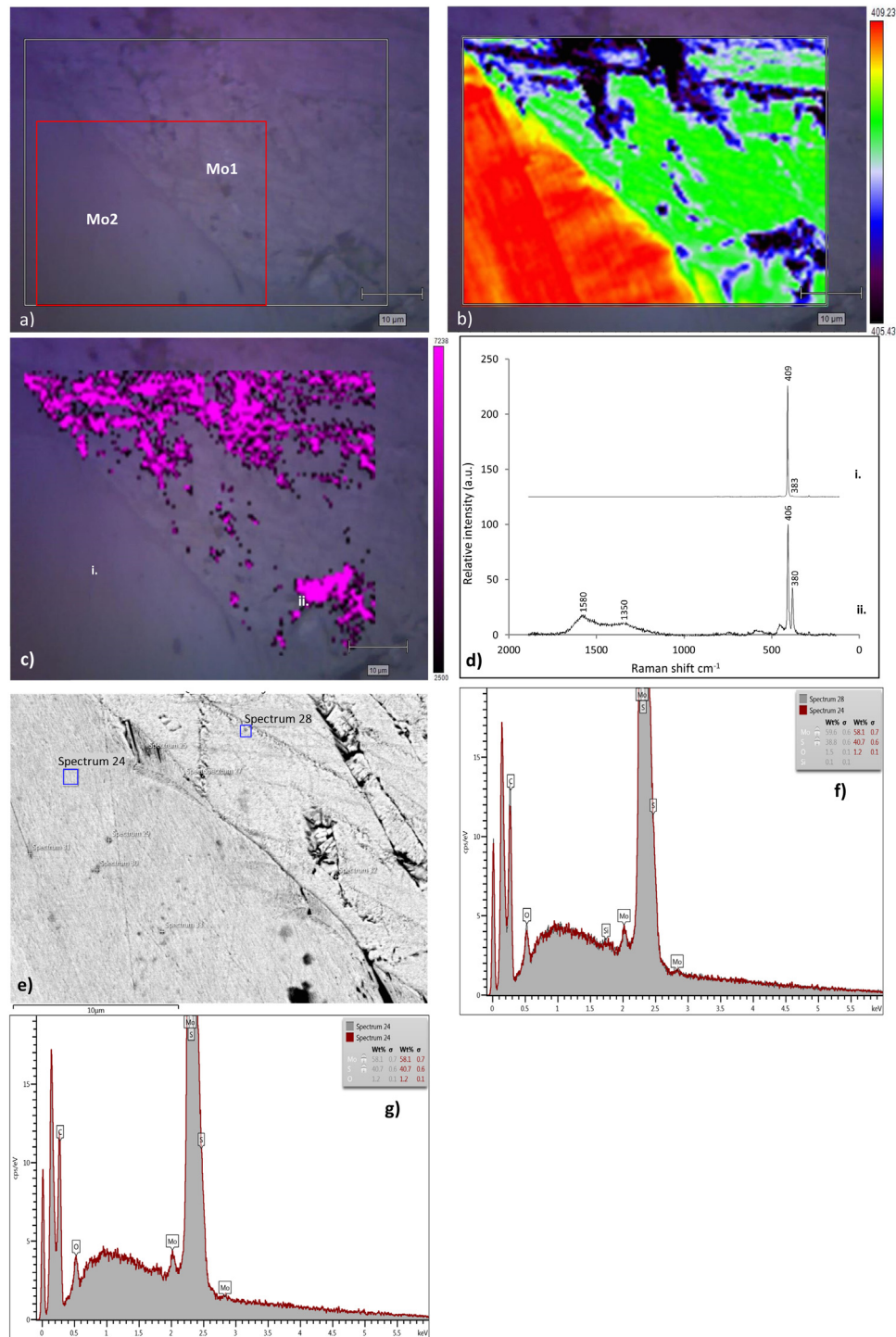


Fig. 1. (a) Optical image using 100 times objective of MDQ0119- 343.40 m (sample ID given by Chinova Resources) showing Mo 1 and 2; the Raman measurement area (white) and SEM measurement area (red) (b) False colour map showing Raman peak position [cm^{-1}] of A_{1g} mode of molybdenite. (c) CM inclusions in magenta using integration value from 1490 to 1660 cm^{-1} . (d) Raman spectra of (c) i. Mo 2 and (c) ii. Mo 1. (e) FESEM image. (f) EDS spectrum 28. (g) EDS spectrum 24. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Mo = Molybdenite, CM = Carbonaceous material, FESEM = Field Emission Scanning Electron Microscope and EDS = Energy Dispersive spectrum.

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