

Soil gases, pathfinders for exploration of buried sulphide deposits: insights from laboratory experiments

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SUMMARY

The future of mineral resources in Australia relies on the discovery of deposits under sedimentary cover. Traditional surface geochemistry techniques are of limited use in this context, and alternative exploration tools such as the detection of soil gases are gaining increasing interest. Previous studies have highlighted the potential of soil gases, such as sulphur gases and soil gas hydrocarbons, for locating buried mineralisation. Here, we performed laboratory weathering experiments of sulphides under sterile and non-sterile conditions to gain insights into the origin of these gases.

The experiments revealed that hydrocarbon gases could not be detected, suggesting they commonly originate from microbial ecosystems in the cover and/or in the soil. In addition, equilibrium thermodynamic predictions indicate a larger range of sulphur gases than detected, which suggests the experimental system did not reach thermal equilibrium. Our results also reveal that CS₂ is the most abundant gas produced, and could be of particular interest as a pathfinder for mineral exploration through cover.

Key words: soil gas, hydrocarbon gases, sulphur gases, cover, mineral exploration

INTRODUCTION

Three-quarter of the Australian continent is blanketed by a thick sedimentary and transported cover, challenging the discovery of new mineral resources. Traditional surface geochemistry techniques may not be the most efficient to discover buried ore deposits, and novel and reliable surficial pathfinders are required to aid exploration.

Soil gases, because of their ability to move through cover, are of particular interest and are believed to hold great potential for mineral exploration in covered areas. A number of field studies have revealed a great diversity in type and abundance of soil gases –i.e. sulphur, metal and hydrocarbon gases, detected across a mineral deposit (e.g. Disnar and Gauthier, 1988; Gao

et al., 2011; Noble et al., 2018; Oakes and Hale, 1987; Wang et al., 2007).

However, these studies do not provide comparable results due to i) the diversity of gases investigated, ii) the analytical protocol (type of equipment, detection time, calibration, etc.) used for gas detection and iii) the type of deposit investigated. Importantly, the origin of the soil gases presently remains controversial. It is therefore crucial to determine whether soil gases derive from weathering of the buried orebody or from the microbial community living above it in order to improve the reliability of this technique.

This study aims to provide additional constraints on the origin of soil gases by i) producing equilibrium thermodynamic models of sulphur gas created during weathering of sulphides; ii) reproducing sulphide and ore weathering under controlled experimental conditions (sterile and non-sterile); iii) monitoring the hydrocarbon and sulphur gases produced at the end of the experiment (50 days). The results from the experiments are compared with thermodynamic predictions and seminal work on the topic (Hinkle et al., 1990; Stedman et al., 1984; Taylor et al., 1982). In addition, we revisit the potential of GC-FPD-MS technique, with improved detection limits, to detect a greater diversity of sulphur gases produced during sulphide weathering and simultaneously monitor the production of hydrocarbons.

METHODS

Laboratory experiments

Samples of pyrite, chalcopyrite, sphalerite, galena, pyrrhotite and pentlandite, as well as samples from sediment-hosted mineral deposits were selected for laboratory weathering. All samples were cut and manually ground with an agate mortar and pestle. X-ray diffraction analyses were run using a Bruker D4 ENDEAVOUR.

For each powdered mineral, two aliquots were taken and placed into two serum bottles. A litre of ultrapure water (milliQ) and a bottle of each sample were sterilised by gamma irradiation (50 kGray, using Gammacell 220 Excel) immediately before starting the experiment. Approximately 0.5 mL of sterile water was added to each serum bottle to add moisture to the system. The serum bottles were sealed and placed in a heating bath at a temperature of 50 °C for 50 days. The experiment was then

stopped and samples were left to cool down before sampling of the headspace gas. Samples were manually injected for analyses using a gas tight syringe with a shutdown valve on a Thermo Scientific Trace using splitless injection on GC 1310 that was fitted with a Flame Pulsed Detector (FPD) and a Thermo Scientific ISQ Mass Spectrometer (GC-FPD-MS). The GC was equipped with an Agilent GasPro Column (30 m x 0.325 μ m) column which using a glass y-connector was split into separate gas streams for the FPD and MS detector. The GC program to analyse the samples was as follows: column flow 2 ml a minute of helium, oven temperature program 40 °C hold for 10 minutes then warm at 25 °C/minute to a temperature of 250 °C.

To compare the relative abundances of gases produced during weathering of the different sulphide minerals, the total surface area of the dominant peak was reported to the total amount of mineral in each vial experiment. The data noted “*ab*” in table 1 for relative abundance is reported in *peak area/g mineral*.

Table 1. Gases detected (carbonyl sulphide: COS; carbon disulphide: CS₂; sulphur dioxide: SO₂) in moist experiments. Relative abundance (ab) of the most abundant sulphur gas -i.e. CS₂. n.d. not detected; n.a. not applicable.

	Gases detected		Relative abundance (ab)	
	Non-sterile	Sterile	Non-sterile	Sterile
pyrite	COS, CS ₂ , SO ₂	COS, CS ₂	2.6	0.2
chalcopyrite	COS, CS ₂ , SO ₂	CS ₂	304.6	94.0
sphalerite	CS ₂ , SO ₂	CS ₂	0.1	1.3
galena	CS ₂ , SO ₂	CS ₂	3.0	0.8
pyrrhotite	CS ₂ , SO ₂	n.d.	0.1	n.a.
pentlandite	n.d.	n.d.	n.a.	n.a.
Ni-Mo-PGE-sulphide ore	n.d.	n.d.	n.a.	n.a.
pyrite-rich sediment hosted ore	COS, CS ₂	CS ₂	15.6	1.3
sphalerite-rich sediment hosted ore	CS ₂	CS ₂	0.6	0.2

Equilibrium thermodynamic models

Equilibrium thermodynamic models were produced using the React module of the Geochemist's Workbench (GWB) version 12 to serve as a basis for comparison with the laboratory experiments. Gas phases produced during weathering of a specific sulphide were predicted by reacting water with the sulphide mineral at pH conditions of 7, temperature of 50°C and partial pressures of O₂ and CO₂ of 0.21 and 0.0005 atm, respectively. Thermodynamic properties used are from the Unitherm dataset provided with the software Hch (Shvarov, 1999). Thermodynamic properties for CS₂ (g), COS(g) were added from the IVTANTHERMO database (Belov et al., 1999), and CH₃SH (g) and C₂H₆S (g) from Wagman et al. (1968). The data were converted to GWB format using the K2GWB converter (Cleverly and Bastrakov, 2005).

RESULTS

Sterile experiments

Sterile experiments were conducted to determine the influence of microbes on the production of gases during sulphide weathering. Laboratory weathering of chalcopyrite produced the greater relative abundance of CS₂ compared to all other samples (ab=94.0), followed by the weathering of “pure” sphalerite and sediment-hosted pyrite-rich samples (both with ab=1.3). COS was only detected in trace amounts in the experiments involving the presence of pyrite and chalcopyrite

in the samples. Sterile experiments on other sulphides or sediment-hosted ores did not yield significant CS₂ (0.2<ab<0.8), if any. None of the gas produced from the sterile experiments contained SO₂.

Non-sterile experiments

With the exception of pure sphalerite, non-sterile experiments produced greater relative amounts of CS₂ than sterile experiments (Table 1). The non-sterile experiments commonly produced SO₂, which was not detected in sterile experiments. COS was detected as trace amounts from pyrite, pyrite-rich sediment hosted and chalcopyrite samples but not in other samples.

Hydrocarbon gases and organic sulphur compounds

In nature, organic molecules such as hydrocarbons and organic sulphur compounds can be derived from sedimentary organic matter and biological activity. As such, these compounds were not expected to form from sterile experiments. However, non-sterile weathering experiments could have witnessed the formation of hydrocarbon gases. Yet, no hydrocarbons or organic sulphur compounds were detected in any of the experiments.

Thermodynamic predictions

Equilibrium thermodynamic models indicate that the following gases are produced during weathering of sulphides: CH₄, CO₂, O₂, S₂, SO₂, H₂S, CS₂, COS, CH₃SH, and C₂H₆S. Of these, we investigated further the following gases COS, SO₂, CS₂, CH₃SH and C₂H₆S. COS is the major gas phase predicted for pyrite, chalcopyrite and pentlandite with partial pressures of 10⁻¹³, 10⁻¹⁴ and 10⁻¹⁸ respectively (Figs 1 & 2). SO₂ is predicted to be the most abundant gas phase for weathering of sphalerite and galena, followed by minor amounts for pyrite and chalcopyrite. In contrast, no SO₂ is predicted to be produced from pyrrhotite and pentlandite. Pyrrhotite is the only sulphide mineral considered here that should have produced moderate abundance of CH₃SH and C₂H₆S. Importantly, CS₂, the most abundant gas detected in the laboratory experiments is only predicted in trace amounts for weathering of pyrite and chalcopyrite (Fig. 2).

Thermodynamic models from Taylor et al. (1982) and the present study indicate a variety of sulphur gases are predicted to be produced during experimental weathering of sulphide. However, despite major development of technical capabilities over the last decades, in particular much improved detection limits and precision, the present study only revealed the occurrence of three sulphur gases, namely CS₂, COS and SO₂. CS₂ was systematically the most abundant gas detected in the experiment, in strong contrast to the thermodynamic predictions.

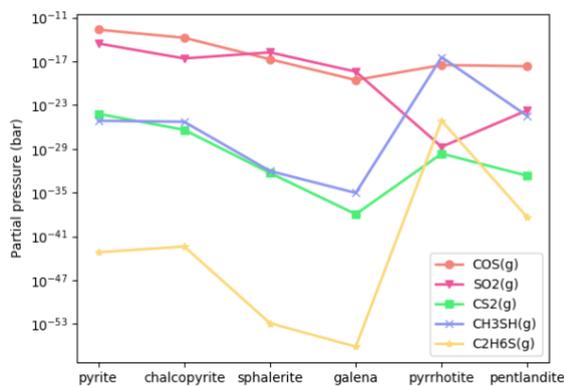


Figure 1. Partial pressure (bar) of gases predicted for the weathering of sulphide minerals.

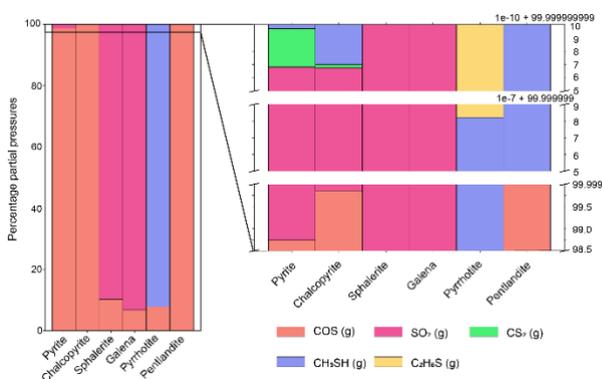


Figure 2. Percentage stacked barplot illustrating the variations of partial pressure of gases predicted for the sulphides.

DISCUSSION

These results show that despite substantial technical improvements over the last thirty years, no hydrocarbon gases and only three sulphur gas species could be detected during laboratory weathering of sulphides. The lack of hydrocarbon formation is significant because of the increasing interest in soil gas hydrocarbons for mineral exploration through cover (e.g. Disnar and Gauthier, 1988; Mulshaw, 1996; Noble et al., 2018, 2013; Rich, 2016). Our results suggest that although soil gas hydrocarbons could hold crucial information on buried mineralisation, they are probably not formed at the scale of the deposit, but rather in the overburden where microbial ecosystems are thriving.

The low diversity of sulphur gases detected is in agreement with previous reports (Hinkle et al., 1990; Stedman et al., 1984; Taylor et al., 1982). The strong contrast between the variety of gases detected and predicted by equilibrium thermodynamic modelling could be explained by the potential reaction of gases under the conditions of our experiments, which have not reached thermal equilibrium, as suggested by Taylor (1982).

Key major differences between previous experimental studies and our results are highlighted here. In our experiments, the mineral producing the greatest relative abundance of gas, in particular CS_2 , is chalcopyrite instead of pyrite (Hinkle et al., 1990; Taylor et al., 1982). In addition, our experiments only show traces of COS whereas CS_2 is largely dominant. This contradicts previous studies (Taylor et al., 1982) that reported CS_2 and COS being formed in abundance and reaching stable concentration over the duration of their experiments (12 days). In the present study the prolonged exposure of sulphide to

weathering (50 days in total versus 7 to 12 days in previous studies; Hinkle et al., 1990; Stedman et al., 1984; Taylor et al., 1982) most likely led to this discrepancy.

CONCLUSIONS

The weathering experiments of sulphides undertaken under laboratory conditions reveal that hydrocarbons and organic sulphur compounds are not produced during weathering of the ore, despite their detection in the field at the soil surface over an orebody. These organic compounds are most likely derived from the complex microbial ecosystem that is present in the overburden, concealing the deposit.

Sulphur gases, however, are produced during the laboratory weathering of sulphide minerals, and sulphide-bearing sediment hosted ore. CS_2 is particularly abundant and is likely formed by the reactions occurring during sulphide weathering but also by reactions of sulphur gases with their environment. Contradictions between laboratory experiments and equilibrium thermodynamic models suggest the laboratory experiments have not reached thermal equilibrium, and potential reaction between gases may still occur.

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