RAMAN AND MÖSSBAUER SPECTROSCOPIC MINERALOGICAL CHARACTERISATION OF RIO TINTO AND JAROSO RAVINE MARS ANALOGUE SITES

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Exploring Mars Habitability
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MOTIVATION

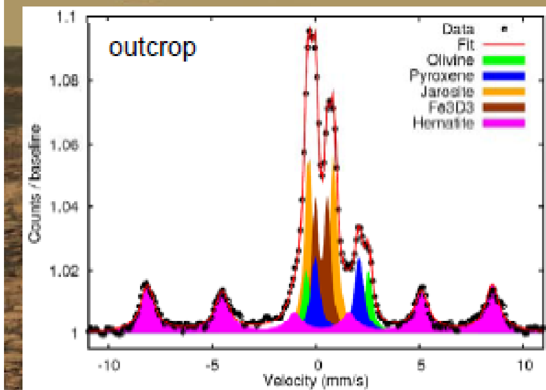
Habitability is in a great extent related with the "context description" and "context" is close-related with the mineralogy and the mineralogical processes in the area. Of particular importance are those minerals produced under water conditions.

The presence of sulphates has been observed on Mars using orbiter spectrometry and the two MER vehicles on the surface.
In particular Jarosite ($KFe_3^{3+}(SO_4)_2(OH)_6$) was unambiguously identified at Meridiani Planum on Mars by Miniaturized Mössbauer spectrometer onboard the MER´s rover Opportunity.
These results show that sulphates are of prime importance in the geological evolution of Mars.

Investigation of sulphate formation on Earth in similar conditions than those experienced in Mars in the past is of considerable interest. Work performed here is connected with the future missions and in particular with Exomars mission in which the Raman spectrometer is included as part of the Pasteur payload.

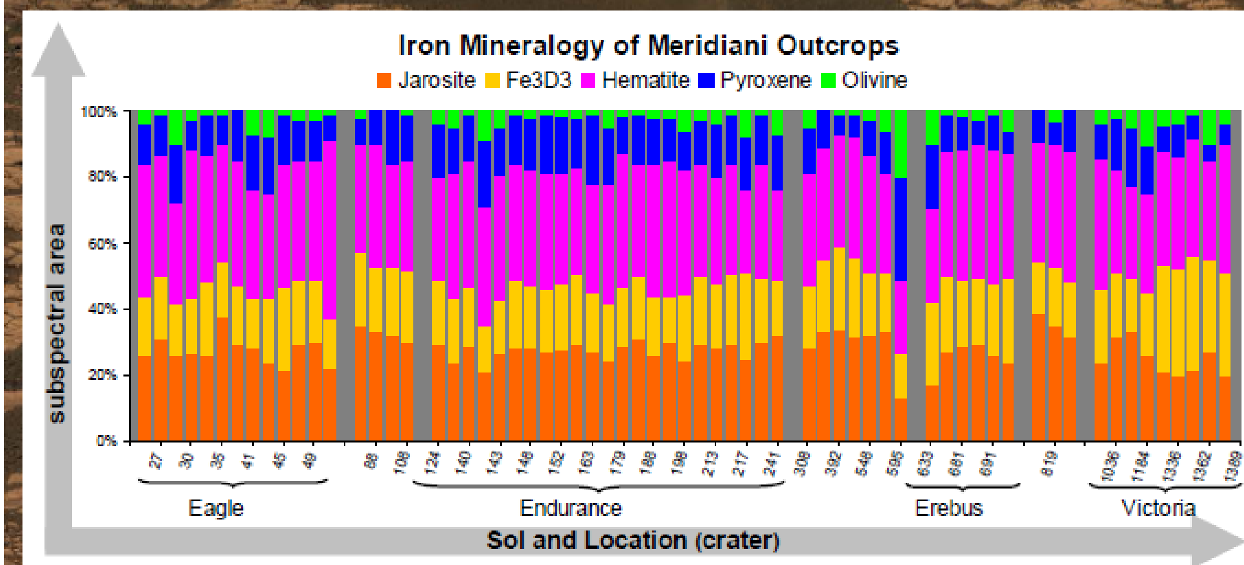
Minerals at the Mars surface from MER-Opportunity data

Meridiani Planum

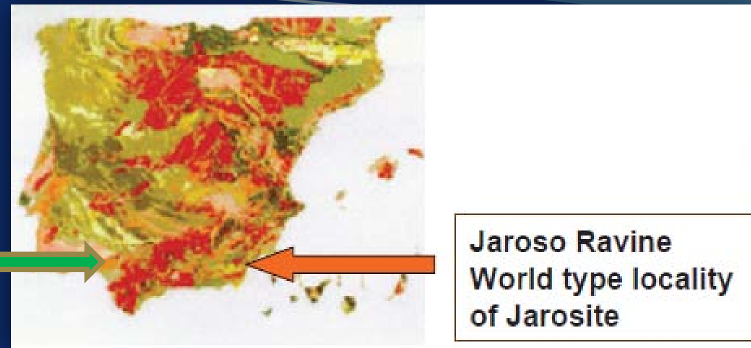


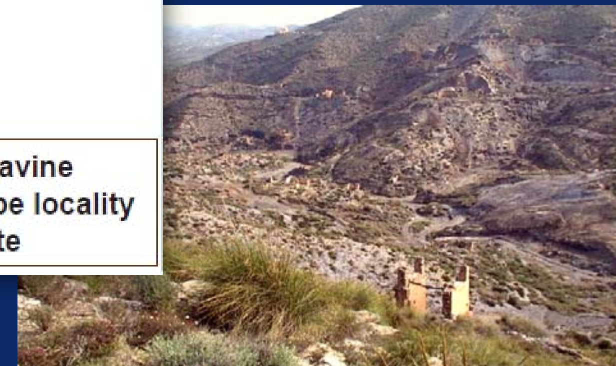
Jarosite detected in sulfate-rich outcrop rocks along Opportunity's 21- km- traverse

Jarosite $(K,Na,H_3O)(Fe,Al)(OH)_6(SO_4)_2$ forms in aqueous environment at pH ~3.5



Rio Tinto and Jaroso Ravine (SPAIN)





Río Tinto : Modern model of formation of sulfates, linked to significant acidophylic biogenic activity. Sulfates mainly come from aqueous alteration of iron-rich sulfide minerals of the Iberian Pyrite Belt (SW Spain).

(D.Fernandez-Ramolar *Planet. Space. Sci. 2004*)

1- Iron oxides and ferric sulfates, including hydronium jarosite, formed at Río Tinto under well-characterized physicochemical and biological conditions.
2- The modern drainage, where depositional processes can be observed in action, is complemented by a historical record of deposition preserved as diagenetically stabilized sedimentary rocks in terraces at several levels above the river.

Jaroso Ravine: Ancient model of formation of supergenic sulfates associated with polymetallic (Fe,Pb,Ag) sulfides and sulfosalts which are genetically linked to the calc-alkaline shoshonitic volcanism (Upper Miocene) of the SE Mediterranean margin of Spain (The Sierra Almagrera complex).

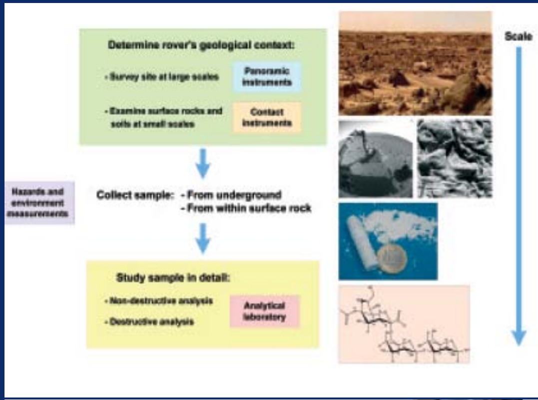
This is one of the mining districts with the greatest number of mineral species in Spain. Three new minerals jarosite ($KFe_3^{3+}(SO_4)_2(OH)_6$), almagrerite ($ZnSO_4$) and ferberite ($FeWO_4$) were described here for the first time.

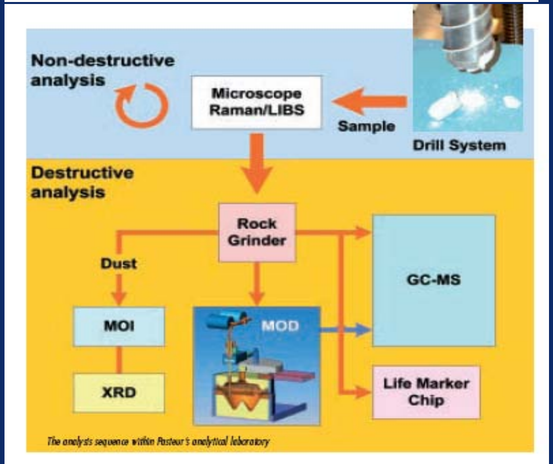
Experimental

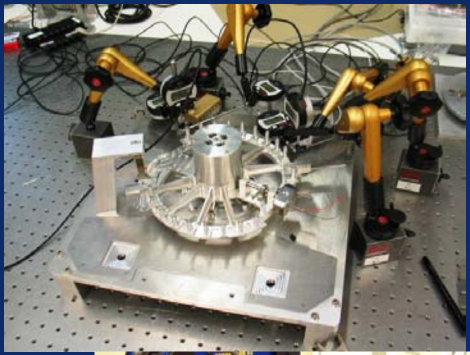
	Raman	Mössbauer
Instrument	Portable Raman based on the current design for Exomars (excitation 532nm). Other portable Raman based on commercial systems	Miniaturised Mössbauer Spectrometer MIMOS II
Sampling depths	Surface	Up to 500 μm
Spot Size	50 – 100 μm	15 mm
Analysis	Mineral grain scale	Average composition at local scale
Integration time	2 hours	Minutes / spot
Sensitivity	Large number of minerals and organic phases	Fe-bearing mineral phases, Fe oxidation states and the distribution of Fe among large number of minerals and organic phases among them

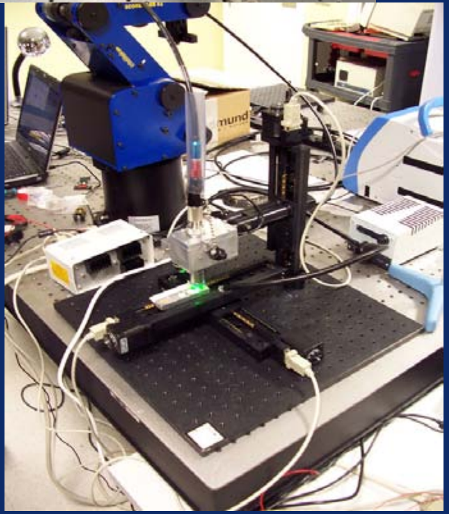
Methodology

Samples were simultaneously analysed in-situ with the two instruments without any treatment
Several samples were collected for further analysis in the laboratory using the portable instruments
These samples were also analysed with complementary techniques mainly XRD using a portable instrument

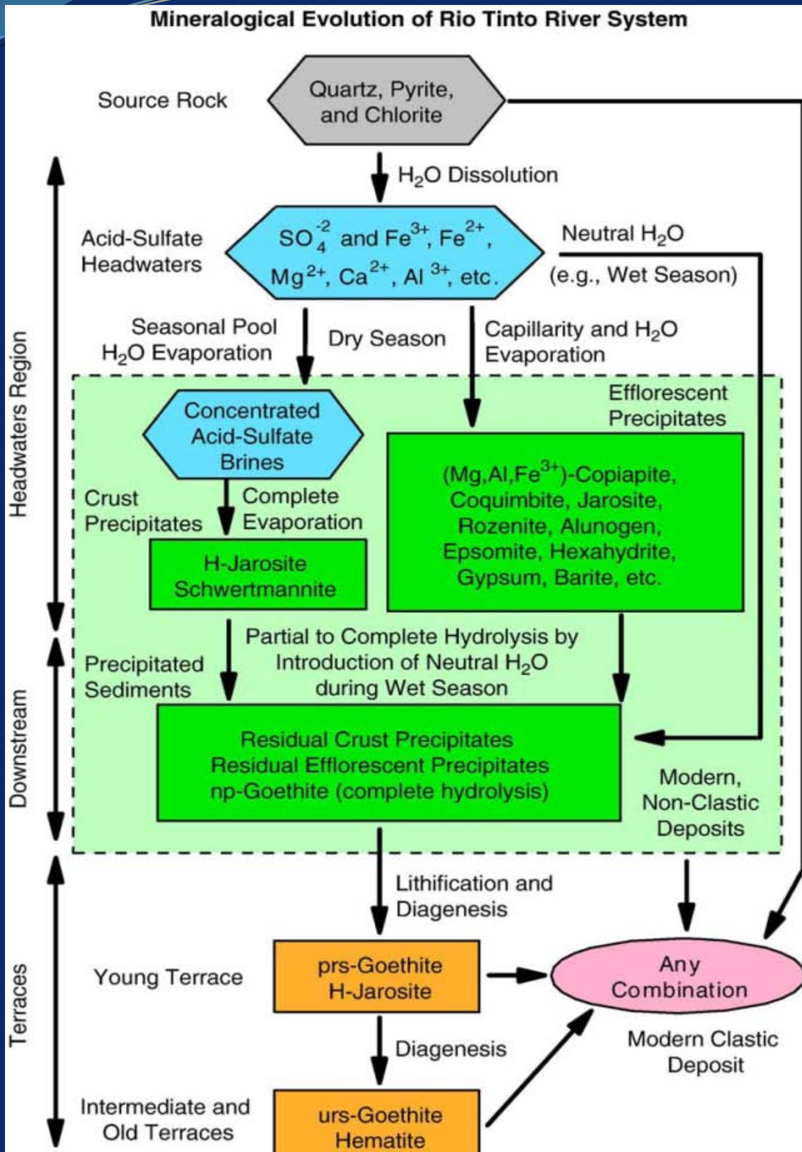






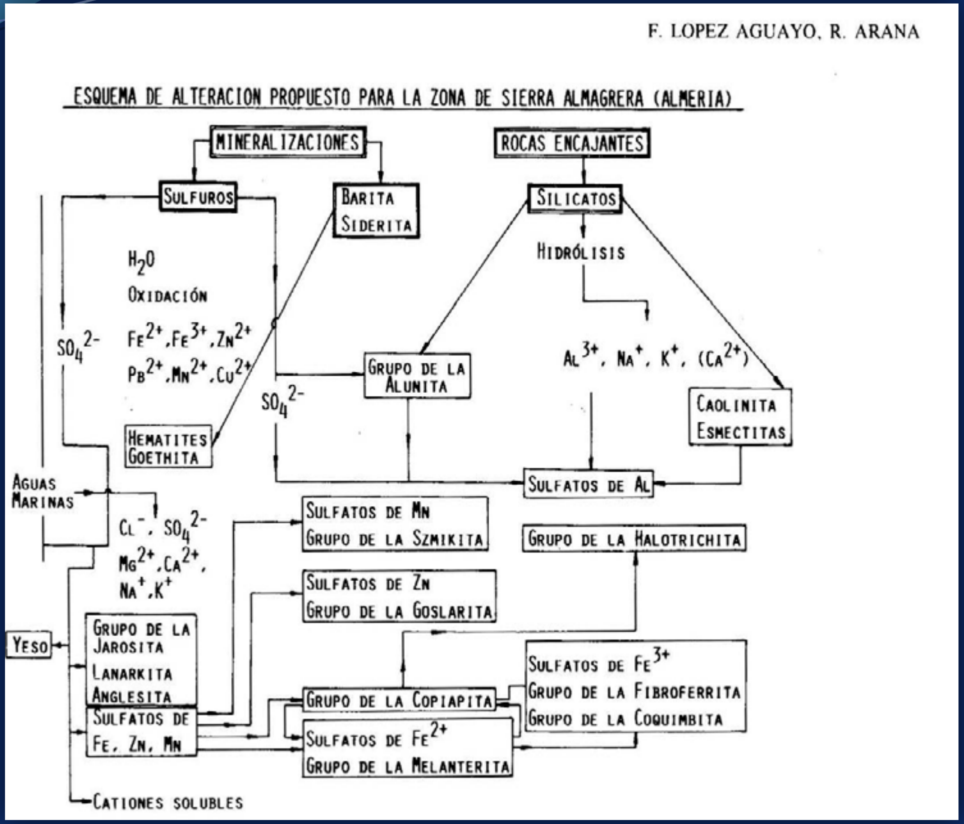


Mineralogy at Rio Tinto



D. C. Fernández-Remolar et al. (2005).

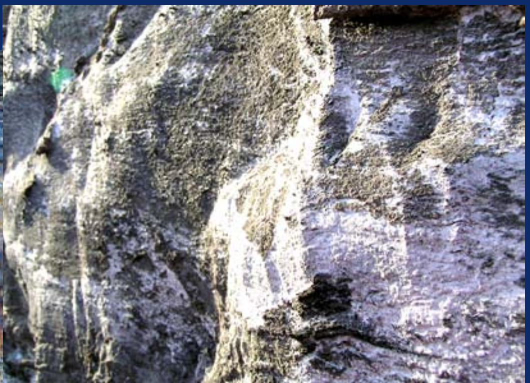
Mineralogy at the Jaroso Ravine Hydrothermal System



The SE Mediterranean margin of Spain (Jaroso Ravine) is a very interesting area of simultaneous interaction of tectonic, volcanic, evaporitic and mineralizing hydrothermal processes.

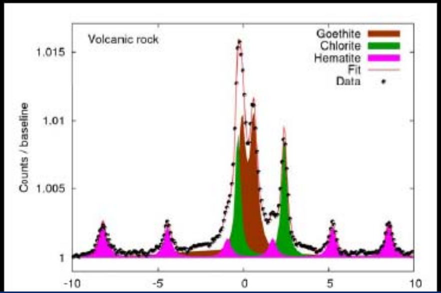
The supergenic mineral alteration processes can be separated into two stages. The first one associated with insoluble mineral precipitation (clays, oxi-hydroxide phases and alunites-jarosites) and the second associated with more soluble sulphate phases.

Martinez-Frias et al. (2004) Earth, Planets Space 56: 5-8.
Martinez-Frias et al. (2007) *Planetary & Space Science*, 55:441-448



In-situ Results : Rio Tinto

Primary volcanic rocks

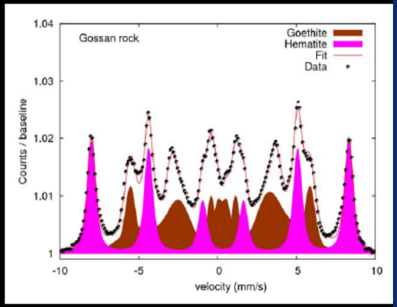


Outcrops of primary volcanic rocks investigated a few km from the river

Minor signs of weathering on the surface and along minor cracks due to water circulation (red colour)

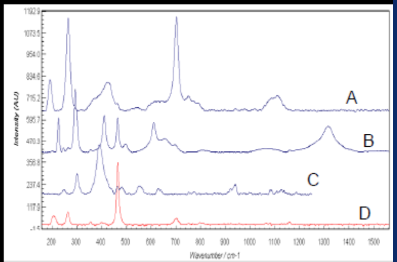
Mössbauer: chlorite, goethite, hematite
Raman: goethite, hematite, quartz,

Hydrothermally altered volcanic rocks



Mössbauer:
crystalline and superparamagnetic goethite, hematite with different degrees of crystallinity, ferrous silicates

Raman:
A: Muscovite, B: Hematite,
C: Goethite, D: Quartz



River bedrock

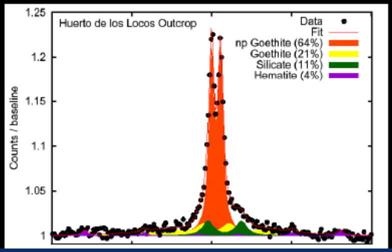
conglomeratic, cemented materials with clast sizes in the range up to ~3cm

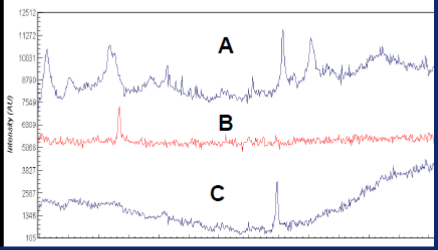
rock surfaces are visibly affected by the acidic water and exhibit a dark crust

River bedrock

Mössbauer:
Goethite*, ferrous silicate and hematite
*confirmed by XRD

Raman:
A: Jarosite+Hematite(+Goethite)
B: Quartz
C: Rozenite





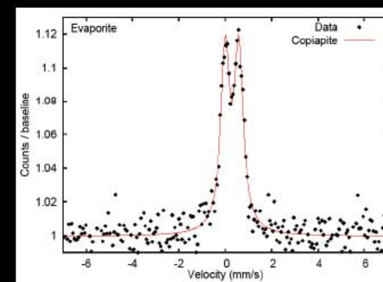
Evaporite minerals

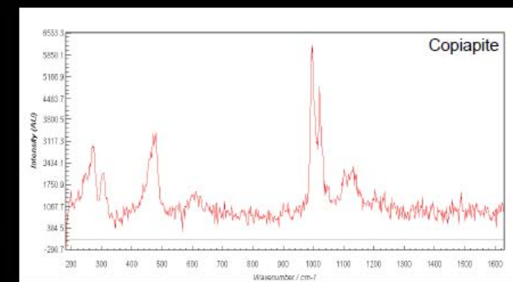
Efflorescent precipitates and evaporite crusts:
seasonal deposits close to the stream margin

precipitates with "popcorn"-like texture a few cm in diameter very common, white and different shades of yellow

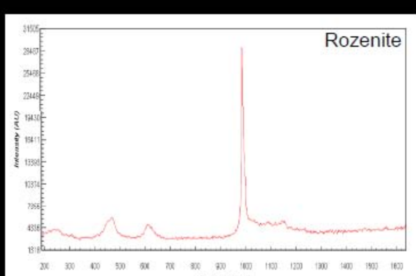
Loose crusts ~5mm thick and a few cm in diameter on some rocks close to the water,
variety of colors including white and different shades of green and blue.

popcorn texture evaporites

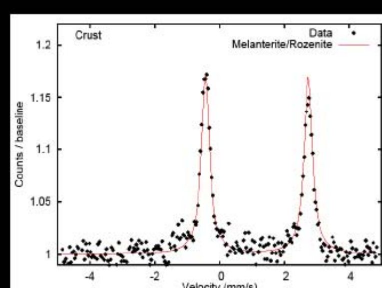




white crust

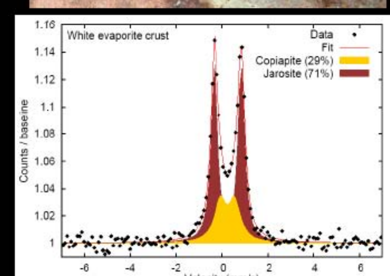


Raman:

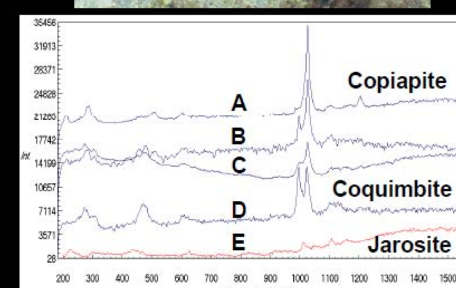


Mössbauer: Rozenite or

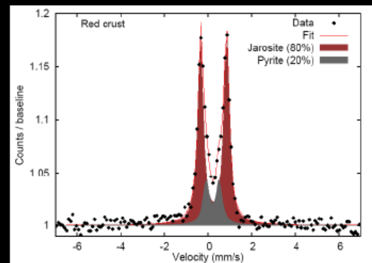
White and yellow crust on red substrate



Substrate: jarosite KFe (SO) (OH)

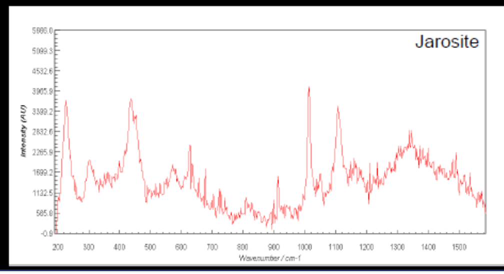


Red crust on dark substrate

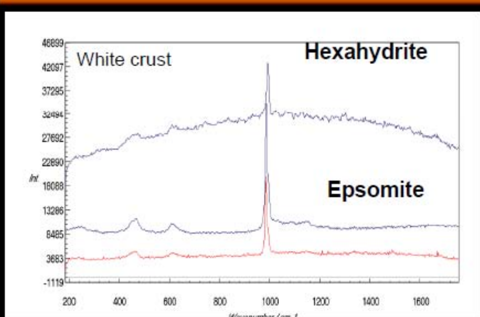


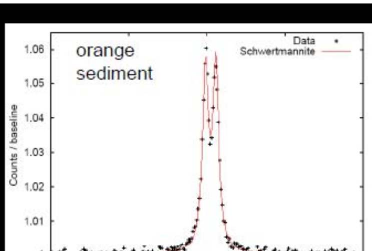
Mössbauer: jarosite crust on pyrite substrate

Raman: pure jarosite

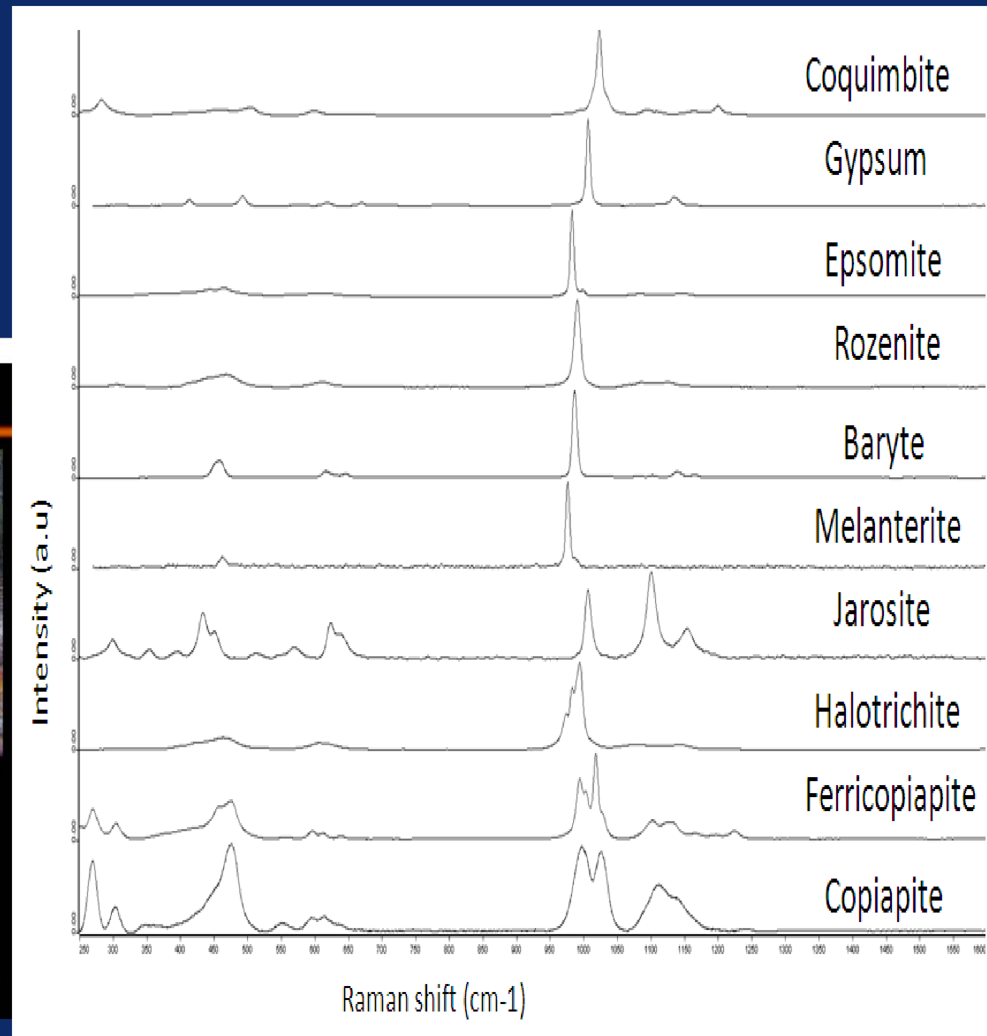


Crust and sediment from less acidic stream





Raman Summary
Sulfates from collected samples



Minerals identified at Rio Tinto in-situ and verified on collected samples

	T. BUCKBY, S. BLACK ET AL. (2003)	D. C. FERNÁNDEZ-REMOLAR ET AL. (2005)	This work Raman	This work Mössbauer
PRIMARY MINERALS OF PYRITE BELT		Quartz Pyrite Chlorite	Quartz Pyrite Chlorite	Pyrite Fe-silicates
SECONDARY MINERALS			Hematite Goethite	Hematite Goethite Fe-silicates
PRECIPITATION (SEDIMENTS)		H-Jarosite Schwertmannite	Goethite Hematite Jarosite Schwertmannite	Goethite Hematite Jarosite Schwertmannite
PRECIPITATION (EFFLORESCENCE)	Aluminocopiapite Alunogen Baryte Botryogen Chalcanthite Copiapite Coquimbite Epsomite Ferricopiapite Goslarite Gypsum Halotrichite Hexahydrite* Magnesiocopiapite Mallardite Melanterite Parabutlerite Rhomboclase* Rozenite* Szomolnokite* Voltaite	Copiapite Coquimbite Jarosite Rozenite Alunogen Epsomite Hexahydrite Gypsum Barite	Ferricopiapite Copiapite Coquimbite Rozenite Jarosite Epsomite Barite Gypsum Halotrichite Melanterite Hexahydrite Szomolnokite	Copiapite Coquimbite Rozenite Jarosite Epsomite Melanterite Hexahydrite

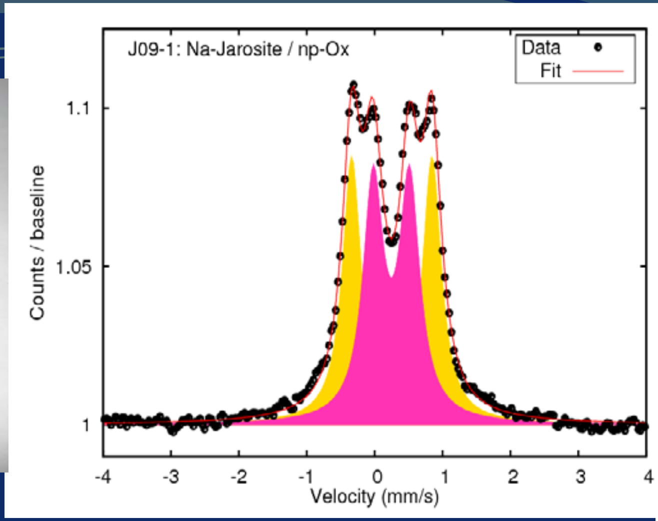
In-situ Analysis: Jaroso Ravine and Hydrothermal Areas

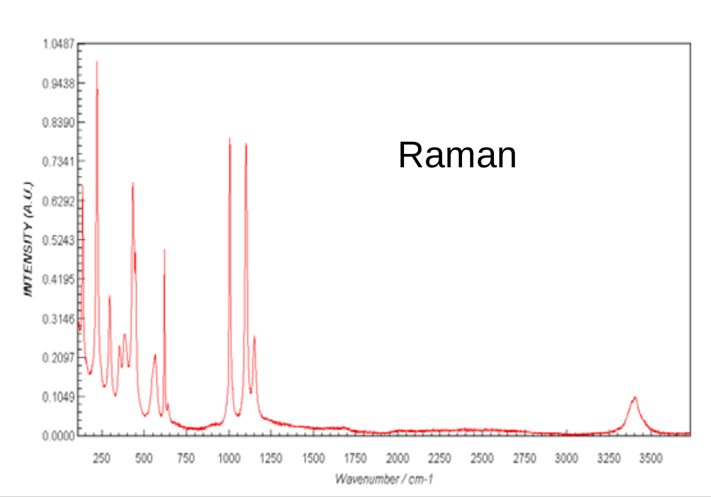


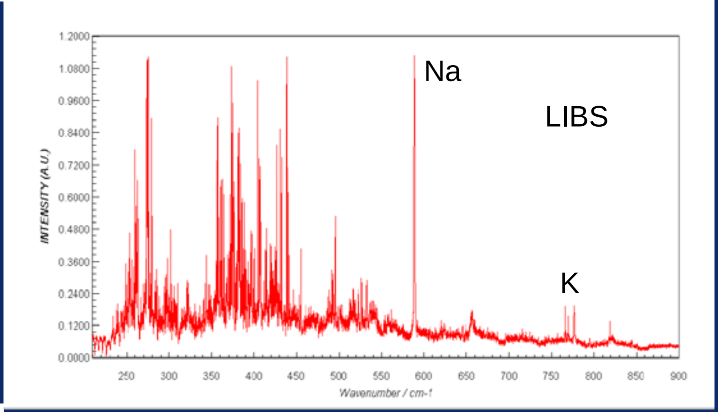


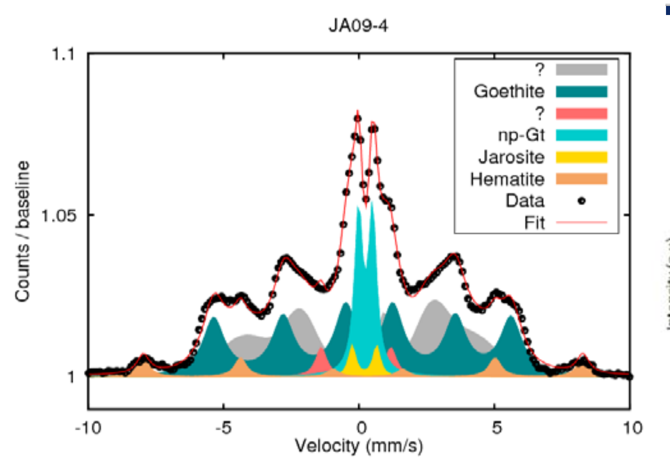


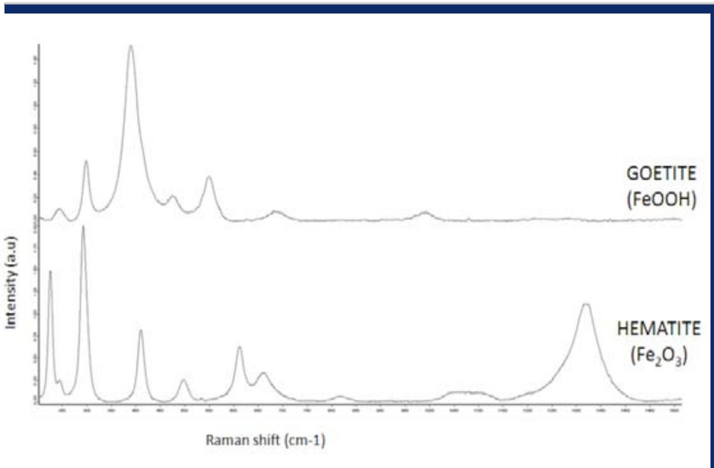

Spectra were performed in-situ along the ravine and in the areas around hydrothermal vents (Martínez Frías et al. 1992) and samples were collected at the same places.


J09-1: Na-Jarosite / np-Ox
Data
Fit
Counts / baseline
Velocity (mm/s)


Raman
INTENSITY (A.U.)
Wavenumber / cm-1

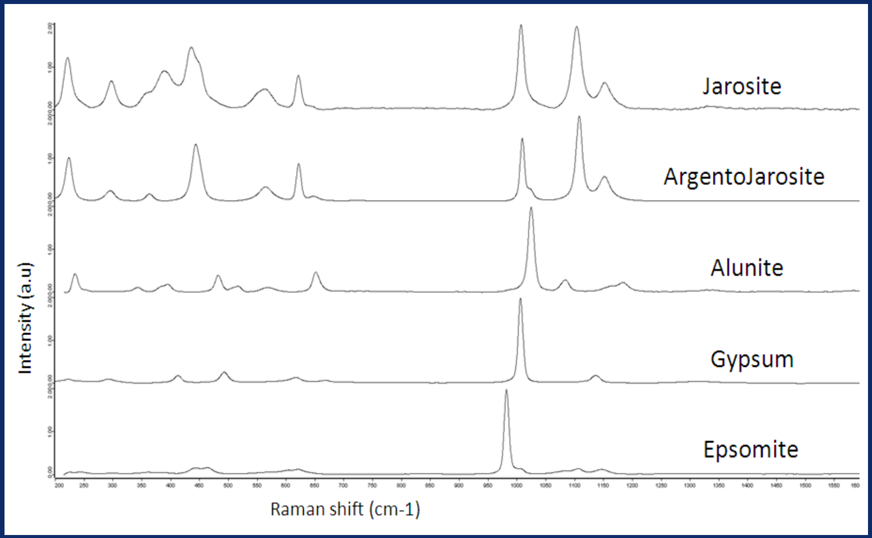

Na
LIBS
K
INTENSITY (A.U.)
Wavenumber / cm-1


JA09-4
?
Goethite
?
np-Gt
Jarosite
Hematite
Data
Fit
Counts / baseline
Velocity (mm/s)

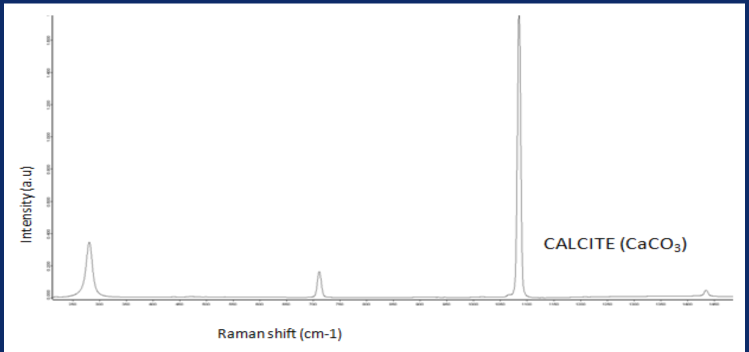

GOETITE
(FeOOH)
HEMATITE
(Fe_2O_3)
Intensity (a.u)
Raman shift (cm-1)

Summary of the RAMAN results as product of hydrothermal alteration at Jaroso Ravine

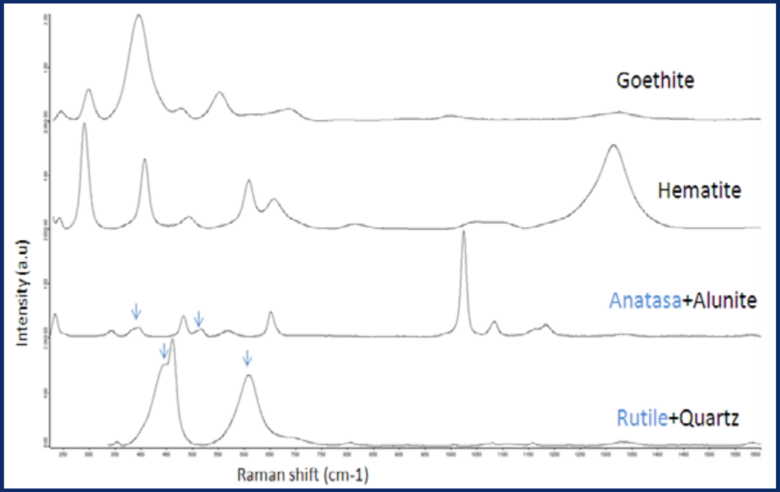
Sulfates



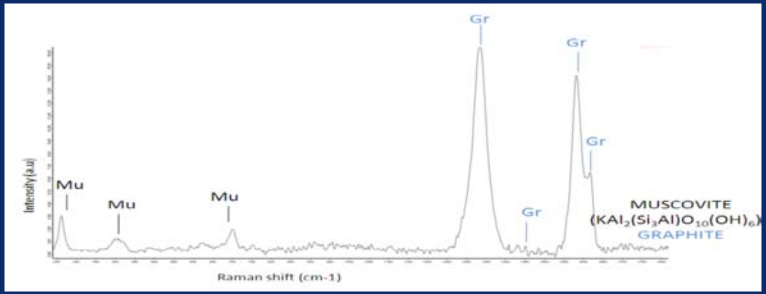
Carbonates

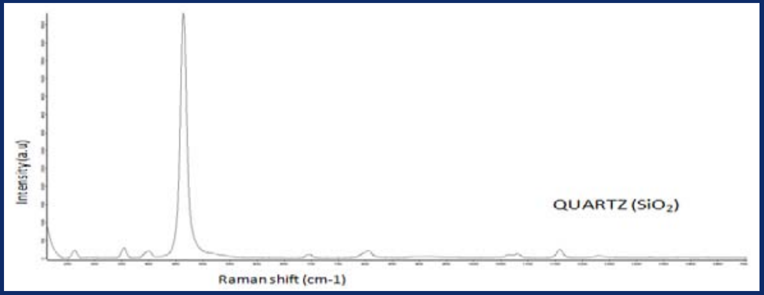


Oxides / Hydroxides

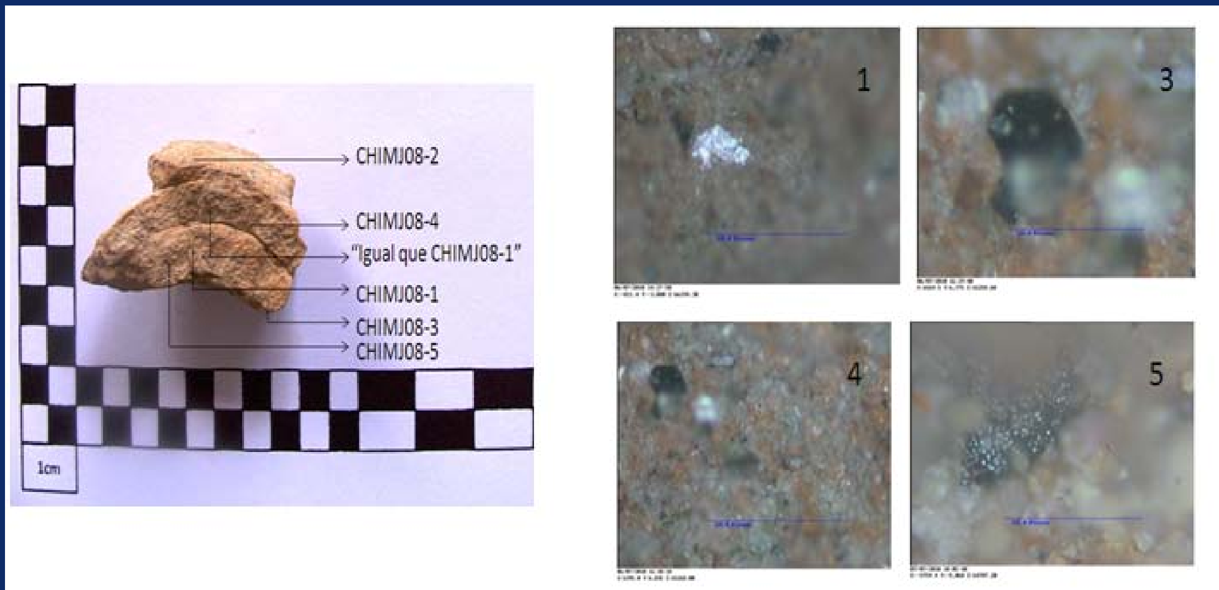


Silicates

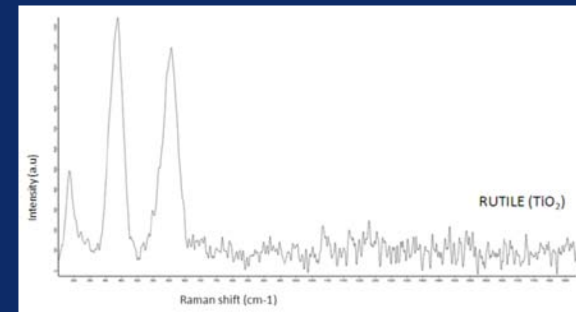




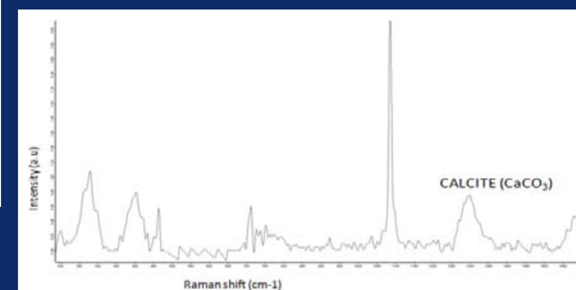
Raman results from a hydrothermal vent



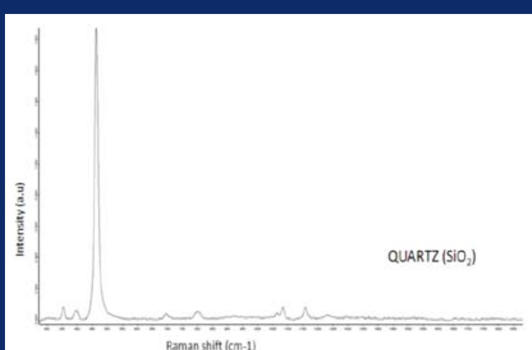
(5)



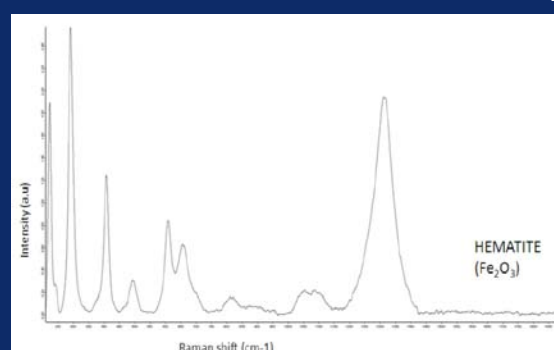
(4)

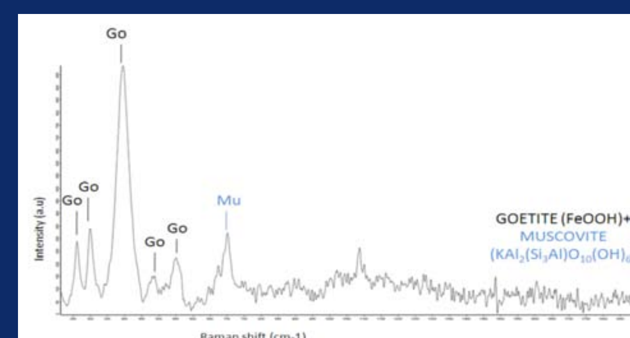


(1)



(2,3)





The performances of the combined science and the potential inside the framework of future missions (Exomars and MSR):

At Rio Tinto:

2 Days field deployment (+ around 40 samples analysed from the same area): near all the main reported minerals in the literature identified

At Jaroso Hydrothermal Complex:

1 day field deployment (+ around 30 samples analysed) : many of the most important minerals reported in literature identified

CONCLUSIONS

Mössbauer spectroscopy has a wide heritage on Mars (MER)

Raman is a new technique in planetary exploration under development for Exomars.

The combination of the two has proved to be very valuable for unique mineral identification in-situ at the field and on collected samples at the laboratory.

While Raman spectroscopy is sensitive to a large number of minerals and organic phases, Mössbauer spectroscopy provides detailed, depth-selective information about Fe-bearing mineral phases, Fe-oxidation states and the distribution of Fe among them.

The determination of organic phases and Fe oxidation states (Redox cycling of Fe) contributes to the search for traces of past or present life on Mars - the main goal of the ExoMars mission


Thanks for your attention