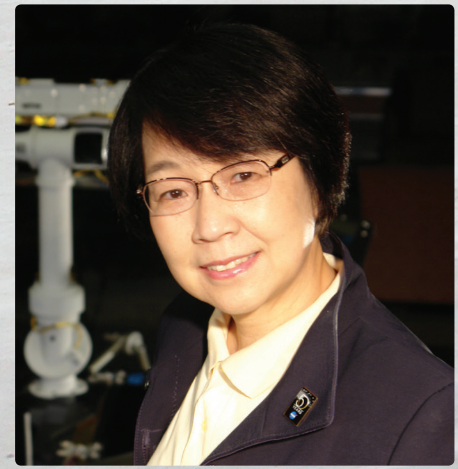
Understanding **Martian sulfates**

In the quest to discover more about our neighbouring planet, **Dr Alian Wang** and her team are carrying out experimental investigations on the fundamental properties of hydrous sulfates found on Mars, using laser Raman spectroscopy



Could you begin by outlining the main objectives of your research?

Hydrous sulfates are one of the two major types of secondary minerals (the other type is phyllosilicates) that have been found in large quantities and widely spread on the surface of Mars. The hydration degree of these sulfates on the martian surface is influenced by environmental conditions, which are determined by the diurnal and seasonal cycles, and in the long term, by the cycles of Mars' obliquity.

The current degrees of hydration of Mg, Fe, Ca and Al-sulfates at the surface and subsurface of Mars can shed light on the hydrologic evolution of the planet, and provide information about its current water reservoirs. Both aspects relate to the potential formation and preservation of Martian life (if that ever happened). Laboratory experimental studies on the stability fields and reaction rates of hydrous sulfates under Mars-relevant conditions can be used to explain phenomena observed during past and current exploration missions on the planet.

In what ways can laser Raman spectroscopy help to deepen our understanding of Mars?

Laser Raman spectroscopy (LRS) has been proposed as a powerful new technique for definitive identification and characterisation of inorganic (mineral) and organic (biomarker) species during robotic surface explorations on Mars. Compared with other spectroscopic techniques, LRS provides information on molecules, for example chemical bonding and crystal structure. Moreover, LRS peaks are much sharper and almost free of overtones and combination modes, thus giving more distinct fingerprint spectra with a very low degree of peak-overlaps for mixtures (such as soils and rocks on the surface of Mars). LRS is extremely sensitive to carbon, and can distinguish the structural variations in carbonaceous materials, thus it can be useful in the search for traces of life.

LRS is the major phase identification tool that my team used in the experimental study of fundamental properties of hydrous sulfates. Our studies demonstrated that LRS can provide conclusive characterisation of sulfates with various hydration degrees and solid-solution sulfates with different cations.

What are the difficulties associated with LRS? Are there specific problems relating to its use in space? How do you overcome these issues?

Raman scattering is intrinsically a weak process. We need to collect as many Raman photons as possible from a sample, while, at the same time, reduce the photon loss in the optical train and prevent the interference from other light sources. Having good optical design is the key, as well as first-class mechanical, thermal and electronic subsystems to ensure a robust flight system. Our engineering team at NASA's Jet Propulsion Laboratory (JPL) has been working on these issues and have found good solutions.

How important are collaboration and embracing an interdisciplinary approach to the Mars Rover project?

I benefited greatly from interdisciplinary collaborations during the Mars Exploration Rover Mission. Over the past nine years, I have worked mainly in a mineralogy and geochemistry 'theme group'; while for my investigations on subsurface sulfate-rich regolith and phyllosilicate-bearing rocks, I have used data from all scientific instrument payloads, as well as support from mechanical engineers and atmospheric scientists. Furthermore, in order to understand our Mars observations on sulfate dehydration, I run laboratory experiments on hydrous sulfates, liaise with theoretical modelling experts, and travel to terrestrial field sites like the Tibetan Plateau and the Atacama Desert to see analogous subsurface salty layers.

Do you have any current or future research plans?

My team is starting systematic experimental studies on the stability fields and reaction rates of hydrous Al-sulfates and chloride hydrates. Al-sulfates should be formed from extensive weathering processes, thus they are less likely to exist in large quantities and be widespread on Mars. However, Al-sulfates were actually observed by orbital remote sensing in localised areas, so are worth more detailed study. More importantly, we need to compare the reaction rates among the common Mg, Fe, Ca, and Al-sulfates through experiments.

In addition, we propose that a subsurface layer of chloride hydrates could be the potential source for recurring slope lineae (RSL) which have been observed on many equator-facing slopes during warm seasons on Mars. The assesment of their stability fields under Mars' subsurface conditions and the rate of deliquescence as a function of temperature will help improve understanding of RSL phenomena, and can further address questions about Mars' hydrologic history and current water reservoirs.

Another even more important plan is to propose the laser Raman system that we (Washington University in St Louis and JPL) have been developing as a science payload for the NASA Mars 2020 Mission. Having this Raman system as a fine-scale mineralogy tool will allow us to characterise – directly and *in situ* – the hydrous sulfates on Mars' surface and within the subsurface.

Mission to **Mars**

Researchers at **Washington University in St Louis** are investigating the fundamental properties of subsurface materials found on Mars to shed light on its evolution and their significance to other planetary bodies

AS ON EARTH, SULFATES and hydrated sulfate minerals have been found in abundant quantities on the surface of Mars; identified as a result of spectroscopic observations from orbital remote sensing as well as landed exploration missions by rovers. This discovery implies that there is substantial sulfur cycling taking place among gases, liquids and solids on the planet, and that Martian sulfates may have played a critical role in the weathering of surface and subsurface materials, circulation of metals, circulation and storage of water and hydroxyl, and the hydrologic processes that took place over the course of Mars' long history. As many of these sulfates have been found in layers that have thicknesses rarely seen in terrestrial deposits, scientists are keen to understand the environmental conditions that have enabled such large amounts of layered sulfate deposition to take place.

However, the findings from past and current missions to Mars revealed very little information about the degree of hydration of martian minerals; information that is essential to enable scientists to interpret the hydrologic history of the planet. Consequently, laboratory experiments carried out on Mars-relevant sulfates under Mars-relevant conditions can enhance understanding about the degree of hydration of different ubiquitous sulfates at various seasons and locations and during the change of Mars' obliquity periods.

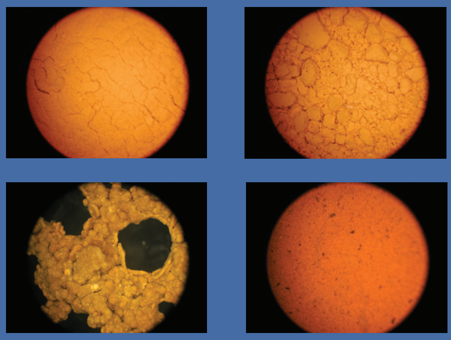
LASER RAMAN SPECTROSCOPY

One research group studying the fundamental properties of hydrous sulfates relevant to Mars is based at Washington University in St Louis, USA. Led by Dr Alian Wang, the group is investigating stability fields, phase transition pathways and reaction rates of hydrous sulfates likely to be found on the planet. The researchers current project is one of two that has been funded by the NASA Mars Fundamental Research Program. Over eight years, Wang's team has conducted two sets of systematic experimental investigations in Earth atmospheric pressure and under Mars relevant atmospheric pressure into Mg and ferric sulfates, and it is currently embarking on a study of Al-sulfates.

The group is working with information from three rovers (Spirit, Opportunity and Curiosity) and three orbiters (Mars Express, ODY and MRO) on Mars. In the laboratory, they are using laser Raman spectroscopy (LRS) as a major tool to monitor the phase transitions. LRS is a spectroscopic technique used to observe vibrational, rotational and other low-frequency modes in a molecular system. Modern Raman spectroscopy uses a laser to stimulate Raman scattering from a sample, collect the Raman photons and analyse their wavelengths. The energy difference between the excitation laser and the photons is called the 'Raman shift' which is dependent entirely upon the structure and composition of the molecule that is emitting the photons. Compared with other spectroscopic tools, LRS gives very dinstinct fingerprint spectra, which permit detection of minor changes in hydration degree and the co-existence of multiple sulfates.

Wang's team joined a field expedition to saline lakes and playas at Atacama desert, to test instruments developed for future planetary missions.

Wang led a team of US scientists on a field expedition to the saline lakes and playas of the Tibetan plateau to study hydrous sulfates at the surface and subsurface.

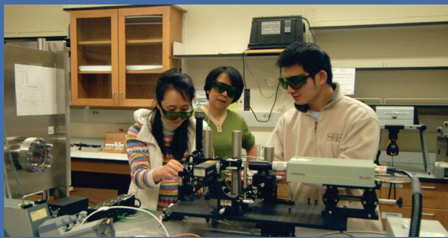


Wang's team synthesised a set of OH-bearing ferric sulfates to study their thermodynamic and kinetic properties.

SUBSURFACE MINERAL WATER RESERVOIR

By exploring their general hypothesis – that there is likely to be a subsurface mineral water reservoir on Mars – the group has successfully revealed stability fields and rates of dehydration and rehydration for a range of hydrous sulfates. Specifically, it conducted experiments at three different temperature scenarios with Mars-relevant atmospheric pressure and partial water pressure to extract the activation energy and extrapolate the half-life of dehydration of sulfates on the subsurface of Mars. "At low temperature, the sulfates with a high degree of hydration have enlarged stability fields toward low relative humidity," Wang elucidates. "They are capable of maintaining high relative humidity in a closed environment and an aqueous film at their grain surfaces. More importantly, their dehydration processes are much slower than water-ice sublimation."

Using the experimentally extracted activation energy and half-life, they found that subsurface hydrous Mg-sulfates which formed during past high obliquity periods have a high probability of maintaining mid- to high-degrees of hydration, possibly until the present epoch. Among the Mg, Fe, Ca and Al-sulfates explored, they found that Mg varieties have the lowest thermal stability, suggesting that the



Wang's team is making measurements using laser induced breakdown spectroscopy (LIBS) and laser Raman spectroscopy (LRS) of the samples in a Mars environmental chamber.

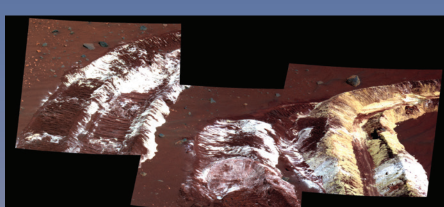
Wang's team uses a new facility, laser Raman Spectroscopic imaging, to study extraterrestrial materials.

remaining sulfates on Mars must dehydrate even slower.

These results are consistent with an excavation made by the Spirit rover at Gusev Crater on Mars, where evidence of dehydration of subsurface Fe sulfates was found after their exposure at the surface. Furthermore, they are consistent with the findings of highly hydrated sulfate (epsomite) and chloride (carnallite) in the subsurface of a hyper-arid Mars analogue site, the Da Lang Tan saline playa on the Tibetan Plateau. "Our study supports our hypothesis that subsurface hydrated sulfates hosting large amounts of water are major contributors to high water-equivalent-hydrogen (WEH) values observed at two equatorial regions on Mars," Wang adds. On Earth, this type of subsurface environment is life-friendly, as demonstrated by the discovery of halophiles in salt-rich subsurfaces in the Atacama Desert and Tibetan Plateau.

RECURRING SLOPE LINEAE

A related hypothesis proposed by the group is that chloride hydrates may exist in some areas within the subsurface of the southern hemisphere on Mars and that the deliquescence of these chloride hydrates at elevated temperatures may produce large quantities of brine that cause an event known as recurring slope lineae (RSL). Repeatedly observed on Mars, this phenomenon occurs on steep slopes and appears to grow incrementally during warm seasons and reduce during cold seasons, possibly pointing to evidence of past liquid water flow.



Subsurface salty soils excavated by the Spirit Rover at 'Tyrone' site near Home Plate at Gusev Crater. The yellowish salty soil enriched with ferric sulfates was dug out from a deeper depth by the non-function right-front wheel of the Spirit rover. A colour change was observed after ~ 200 sols.

This premise is supported by the widespread existence of chlorine on Mars, putative chloride deposits in the southern hemisphere of the planet and especially by the properties of chloride hydrates revealed in previous studies of saline fluid inclusions within terrestrial rocks. Wang's group is just beginning a systematic experimental study on chloride hydrates but their preliminary results show that the temperature dependence of their stability fields and the extremely fast rates of deliquence processes when required conditions are met support the hypothesis.

BROAD AND DEEP SIGNIFICANCE

The rovers and orbiters currently working at Mars' surface and in orbits are generating exciting new information every day and will – in the near future – study thick sulfate deposits found at depth. Two further orbiter missions to the planet (Maven 2013, Trace Gas Orbiter 2016) and three more landed missions (InSight Mars 2016 Lander, ExoMars 2018 and Mars 2020 Mission) are currently under development. As a result, more information from the planet will be obtained, enabling a deeper understanding of Mars as a dynamic system; from atmosphere, to surface and subsurface material to interior structure.

The outcomes of Wang's research have broad and deep scientific significance as sulfates and hydrated sulfate minerals are anticipated to exist not only on Mars but also on many other planetary bodies, for example Europa, an icy-satellite of Jupiter. "Getting unaltered records from other planets like Mars will help us to understand the processes that our own Earth has experienced during its early age. Understanding the current status of other planets will help us to see the potential future of our own home," Wang enthuses.

INTELLIGENCE

EXPERIMENTAL INVESTIGATION OF SULFATES RELEVANT TO MARS: STABILITY FIELDS, PHASE TRANSITION PATHWAYS AND REACTION RATES

OBJECTIVES

To understand the past and current status of Subsurface Mineralogical Water Reservoirs on Mars through studying the changes of hydration degrees of sulfates affected by atmospheric and subsurface environmental conditions. Shedding light on their evolution as influenced by the martian obliquity cycle, this will improve understanding of Mars' hydrologic history.

KEY COLLABORATORS

Scott Rudolph Professor of Earth and Planetary Sciences **Bradley L Jolliff**; James S McDonnell Distinguished University **Professor Raymond E Arvidson**, Washington University in St Louis, USA • **Research Geologist I-Ming Chou**, U.S. Geological Survey • **Dr William C Feldman**, Planetary Science Institute, New Mexico, USA • **Staff Scientist Michael T Mellon**, Southwest Research Institute, Texas, USA • **Academician MianPing Zheng**, PhD, Chinese Academy of Geological Sciences, China

PARTNER

NASA Jet Propulsion Laboratory

FUNDING

NASA, Mars Fundamental Research Program – grant nos. NNX07AQ34G, NNX10AM89G • NASA, Science Team support for MER mission and MoO support for Wang as Co-PI in ESA ExoMars rover mission • NASA's Planetary Instrument Definition and Development Program (PIDDP), Mars Instrument Development Project (MIDP), Astrobiology Science and Technology for Exploring Planets (ASTEP) and Maturation of Instruments for Solar System Exploration (MatISSE) programmes • McDonnell Center for the Space Sciences at Washington University in St Louis

CONTACT

Dr Alian Wang
Research Professor and Principal Investigator

Earth and Planetary Sciences
McDonnell Center for Space Sciences
Washington University in St Louis
Office – Rudolph Hall, Room 338
Campus Box 1169, 1 Brookings Drive
Saint Louis, Missouri 63130-4899, USA

T +1 314 935 5671
E alianw@levee.wustl.edu

ALIAN WANG is a Research Professor at Washington University in St Louis and a renowned laser Raman spectroscopist, specialising in its applications for planetary surface exploration and planetary fundamental science investigations. She is the Principal Investigator of Mars Microbeam Raman Spectrometer (MMRS) supported by NASA PIDDP, MIDP, ASTEP and MatISSE programmes.

Washington University in St.Louis