**Geophysical insights into reactions and equilibrium in Mars' deep interior with InSight 2018**

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**The physical properties on Mars are functions of the distribution of compositions, temperatures, and pressures in the deep interior. In turn, these distributions are the end result of 4.5 billion years of accretion and dynamic evolution, and as such may provide novel constraints into the history of the planet. NASA's InSight Mission, due to land on Mars at the end of 2018, is expected to provide data related to the areotherm, the distribution of mass, and the seismic wavespeeds in the deep interior. This proposal aims to provide thermodynamic and seismic models of Mars' interior, focusing on the following areas:**

**(1) The composition of sulfide and ferric iron content of Mars' deep mantle.**

**(2) Melting in Mars' deep interior, and the potential effects on present day physical properties.**

**(3) Thermodynamic/thermoelastic models of the deep mantle and core of Mars.**

**(4) Geophysical modelling of Mars and an assessment of parameter trade-offs and uncertainties.**

**(5) Preliminary analysis of data from InSight.**

**Background and Motivation**

The thermochemical state and evolution of Mars' interior has been a topic of great interest for many decades. Currently, observational constraints fall into two categories:

1. **Remote geophysical.** Mars' mass, radius and moment of inertia tell us that Mars has a dense metallic core surrounded by a silicate mantle. Further to this, tidal dissipation (specifically, the k2 Love number) tells us that at least the outer part of the core is likely to be fluid, with a radius of approximately 1500-2000 km. For a core of this size to match the moment of inertia observations, it must have a density significantly less than that of solid iron.
2. **Geochemical.** The compositions of rocks observed by the Mars landers, and the Shergottite-Nakhlite-Chassignite (SNC) meteorites imply that, compared with Earth, Mars is rich in iron (Mg# ~ 75; Wanke and Dreibus, 1994) and sulfur (2000 ppm; Tuff et al., 2013), but has a low oxygen fugacity and low water contents. It has therefore been suggested that the core is rich in sulfur. Nevertheless, the range of proposed sulfur contents is huge: Gaetani and Grove (1997) suggest ∼0.4 wt % S in the core, while Wanke and Dreibus (1994) suggest 14 wt %. On the basis of iron isotope fractionation, Shahar et al. (2015) suggest 0-8 wt % S, while geophysical modelling by Khan and Connolly (2008) suggests >20 wt %. Such variations have major implications for the cooling and solidification of the core and the death of the geodynamo.

New lander-based geophysical data will be provided by the InSight Mission, due to land on Mars (Banerdt et al., 2012). Apparatus on-board includes VBB and SP seismometers (SEIS; Lognonne et al., 2014), which will detect Marsquakes (Phillips and Grimm, 1991) and meteorite impacts (Teanby, 2015). Source locations will be estimated using surface waves, and these estimates of location will be combined with body wave arrivals to constrain the structure of the interior (Panning et al., 2015). Further to this, a heat flow probe (HP3; Spohn et al., 2012) will be used to constrain the thermal gradient in the lithosphere and an X-band RADAR instrument (RISE; Folkner et al., 2012), to measure nutations due to Mars' core. The proposed project is designed to provide results which may be combined with the raw data from the mission (travel times, thermal gradients, core density and radius) to elucidate the current state and evolution of Mars' interior over the history of the solar system.

InSight is expected to yield the following data related to the thermochemical state of the planet:

* The thermal gradient in the uppermost crust
* Seismic travel times through the mantle, including the presence of major discontinuities.
* An estimate of the core radius and average density.

The aims of this project are to provide preliminary data and models for use in conjunction with InSight data to answer the following questions:

1. What are the compositions and temperatures in the deep interior (especially the mantle and core)?
2. How did compositional heterogeneity arise?
3. What is the present dynamical state of Mars' mantle?

**(WP1)** **The composition of sulfide and ferric iron content of Mars' deep mantle**

**Subsolidus phase relationships in simple chemical systems (for example, Na2O–CaO–FeO–MgO–Al2O3–SiO2/NCFMAS) are reasonably well understood over the potential range of Mars pressures, temperatures and compositions. However, models based on these phase relationships ignore the presence of Fe3+, which is predicted to increase markedly at high pressure. Densities, seismic velocities and the compositions of melts in Mars' deep mantle are all sensitive to redox state. This work package will include high pressure laboratory experiments designed to constrain the redox state of Mars' deep interior.**

At high pressures, equilibria between mantle minerals induces so-called autoredox reactions, where ferrous iron disproportionates into ferric and metallic/sulfidic iron (Frost et al., 2004; Rohrbach et al., 2007). One such reaction relevant to minerals in the Earth and Mars is that involving garnet and one of the olivine polymorphs (fayalite, Fe-wadsleyite or Fe-ringwoodite):

3Fe2SiO4 (e.g. ringwoodite) = Fe3Fe2Si3O12 (garnet) + Fe (metallic/sulfidic)

As pressure increases, the negative volume change of the reaction pushes such equilibria to the right, such that in Earth-like mantle (Mg# ~ 90) garnet can accommodate over 25% iron as Fe3+ at 14 GPa (Rohrbach et al., 2007; 2011). On Mars, iron contents are much higher than on Earth (Mg# ~ 75; Wanke and Dreibus, 1994), and the mantle is believed to contain markedly more sulphur (2000 wt ppm; Tuff et al., 2013). As a result, autoredox is likely to be at least as important on Mars as on Earth. Such reactions have two implications for the InSight Mission:

* Changes in phase compositions and proportions will affect bulk density and seismic velocity.
* The Fe0 created by the reaction will enter the sulfide phase. Depending on the estimates of core composition derived from InSight, this sulfide could prove to be more, less or equally rich in sulfur, which would allow us to differentiate between different models for its origin. If more rich in sulphur, for example the sulfides probably represent a late stage exsolution product from a magma ocean and their abundances contain information about temperatures and pressures of formation. If equally rich, they may represent a stranded core fraction, providing new information about core-mantle segregation processes.
* Solid redox state governs the composition of fluids/melts in Mars' mantle, which could have an observable effect on seismic velocities in the interior.

In this study, I will conduct multi anvil experiments at high pressure with Mars-like mantle compositions in equilibrium with metal or sulfide melts. Experiments will be run under conditions similar to those expected of Mars' deep mantle (14-20 GPa). Recovered phases will be analysed for ferric iron content using techniques such as Mossbauer spectroscopy.

Products from project:

* Experiments to inform a solution model for ferric iron-bearing majoritic garnets (see WP3).
* An estimate of oxygen fugacity in the deep mantle. This estimate will inform models of deep melting, similar to those used for Earth (e.g. Rohrbach and Schmidt, 2011; Stagno et al., 2013). It has been suggested that CO2-CO-C equilibria control oxygen fugacity in Mars' mantle (Righter et al., 2008); the data from this project could be used to test this hypothesis.
* A prediction of changes in sulfide state with depth in Mars mantle, and (with WP2 and WP5) an estimate of core-mantle disequilibrium.

*Figure XXXX: Back-scattered electron image of a recovered charge from a multi-anvil run, showing precipitation of metallic iron and the presence of ferric-iron bearing silicates.*

**(WP2) Melts in Mars' deep interior: Effects on present day chemistry and seismic properties**

**The formation of Mars is believed to have been accompanied by large scale melting of the mantle which was induced by dissipation of gravitational energy from impacts and/or energy from short-lived radionuclides. This would have facilitated core-mantle segregation and promoted mantle stratification. The InSight Mission is expected to constrain the proportion of light elements in the core and presence of mantle stratification; the interpretation of which will require an understanding of the reactions that took place in Mars' magma oceans. This work package will involve high pressure experiments investigating equilibria between majoritic garnet, silicate and sulfide melts in order to investigate links between the early history of Mars and present day compositions.**

During magma ocean formation, it is commonly believed that earlier cores emulsified, mixing and equilibrating with the molten silicate mantle (e.g. Deguen et al., 2014), then segregating without further reequilibration (see Rubie et al., 2015). Magma ocean crystallisation occurs over a longer (and unknown) period of time, creating thick piles of cumulates that may become gravitationally unstable and overturn (Elkins-Tanton et al., 2003). Much is still unknown about the changes in chemistry during solidification.

In this project, the aim is to study the parts of the magma ocean phase of Mars' growth which may affect InSight observables; namely, the moment of inertia, state of the core and effects on seismic wave propagation. We split this work package into two segments:

* **Reduced phases in Mars' early history.** It has been shown that the crystallisation of small magma chambers on Earth at the present day can reduce or oxidise the residual melt (Carmichael et al., 1991). The fundamental requirement is that the segregating phase must have an cation-oxygen ratio which is different to the bulk. It has recently been shown that even under highly reducing conditions, high pressure crystallising phases can have significant ferric iron contents, resulting in coprecipitation of metallic/sulfidic phases (Boujibar et al., 2016). If some of the metallic/sulfidic phases remain in suspension, as is likely during highly turbulent convection, then magma oceans will become reduced by bottom-up crystallisation. Using multi-anvil experiments, I will investigate the composition of core-forming melts, and the expected changes in sulfide speciation in the magma ocean.
* **Mantle reservoirs in Mars' deep interior.** As Mars crystallised, it would have produced a sequence of cumulates, starting with majorite (e.g. Elkins-Tanton et al., 2003) and ending with volatile-rich pegmatites. Unlike Earth, which was thoroughly homogenised after magma ocean crystallisation, Mars may preserve the crystallisation of these late stage bodies, which could produce major seismic discontinuities. In this part of the project, I will assess the relative volumes and initial thickness of cumulate sequences, and their potential effect on seismic velocities in Mars' interior.  
  … XXXX THIS IS VERY FLUFFY AT THE MOMENT.

*Figure XXXX: Schematic for Mars magma ocean evolution.*

**(WP3) Thermodynamic/thermoelastic models of the deep mantle and core of Mars.**

**Existing thermodynamic models for high pressure minerals and liquid solutions (metallic or sulfidic melts) can be improved by considering the full range of solutions expected, and non-ideality in excess terms such as bulk modulus. This work package seeks to make such improvements for garnets and core liquids, in order to use them during interrogation of seismic data from InSight.**

A key improvement to be made in models of major mantle mineralogy is a consideration of ferric iron in majorite. At present, two sets of solution models exist: low pressure models, with ferric iron, and high pressure models, with a majoritic component. The experimental results from WP1, coupled with previous results at lower FeO contents (Rohrbach et al., 2007; 2011) should provide the required information to create a single, self-consistent model of high pressure garnets.

Thermodynamic models of core liquids are still at a very preliminary stage. It has been noted that excess bulk moduli are likely to play a significant role in determining the properties of metallic solutions (Komabayashi, 2014), but so far there has been little attempt to create such a model. Working with Dan Frost and Dave Rubie, I have built a thermodynamic model for Si and O in metallic melts (Myhill et al., in prep), using modifications to existing solution models that enable excess bulk moduli to change in a physically reasonable manner as a function of pressure and temperature. This work package seeks to extend that model by adding sulfur, using existing experimental data (e.g. Buono and Walker, 2011; Tsuno et al., 2011).

*Figure XXXX: Modelled silicon and oxygen partitioning in metallic iron at 25 and 130 GPa, in comparison with independent (non-fitted) experimental data. One of the aims of this work package is to add sulfur to the model.*

Products from project:

* Improved garnet thermodynamic model enabling the calculation of chemical properties in Mars' deep mantle
* A preliminary Fe-Si-O-S metallic/sulfidic melt model, created using 1 bar, high pressure static, and shock data.
* Seismic velocities corresponding to the deep mantle and core of Mars, as a function of pressure, temperature and composition.

**(WP4) Geophysical modelling of Mars and an assessment of parameter trade-offs and uncertainties.**

**Using the results from WP1–3, it will be possible to create self-consistent models of Mars' interior, including temperature and composition, but also allowing more detailed forward-modelling informed by geochemical data. This work package seeks to build a large set of potential models, and analyse the trade-offs and uncertainties in parameters of interest in terms of InSight observables (e.g. P-S differential times, receiver functions).**

The strategy of the work package will be to simplify models of Mars into a few key parameters(e.g. lithospheric thickness, mantle potential temperature, Rayleigh number), create synthetic data (using TauP, SpecFem), and compare the seismograms generated to identify diagnostic waveform properties and parameter trade-offs. This study will enable rapid interrogation of data when it arrives from InSight. It will also reveal sources of uncertainty that might otherwise be missed.

*Figure XXXX: Example 1D seismic model of Mars, fitting the mass and moment of inertia of the planet and geochemical estimates of heat-producing elements (U, Th and K). Model includes thermal boundary layers at the top and bottom of the convecting mantle, and a mechanical boundary layer with experimentally-constrained temperature-dependent conductivity. Such models can be used to create synthetic seismograms of the Martian interior.*

*Figure XXXX: Core properties for a simplified set of Martian models*

In addition to three layer chemical models (crust, mantle, core), I shall also investigate the effects of a heterogeneous mantle. Heterogeneity is clearly seen in samples from Mars (Mezger et al., 2013), and indicates that mixing has been far less efficient than on Earth. Two classes of 3D mantle heterogeneity (stratified/marble-cake) will be studied, where heterogeneity has been created through fractional crystallisation of a magma ocean.

**(WP5) Preliminary analysis of data from InSight.**

**InSight will start returning seismic data in Early 2019. Of particular interest for early scientific return will be the properties of the lithosphere. This may include crustal thickness, lithospheric thickness, and the presence of a mid-lithospheric seismic discontinuity (Selway et al., 2015). The preliminary models created in WP4 will provide the ideal starting point to analyse data from the mission and contribute to the primary mission aims (core size and composition, structure of the mantle and crust).**

*Figure XXXX: Some sort of trade-off figure? Example waveforms?*

b) Management plan – Management of the project and resources, training and development opportunities

Work flow

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | 01-04 /2018 | 05-08 /2018 | 09-12 /2018 | 01-04 /2019 | 05-08 /2019 | 09-12 /2019 | 01-04 /2020 | 05-08 /2020 | 09-12 /2020 |
| Redox experiments (solid) | E | A | W1 |  |  |  |  |  |  |
| Redox experiments (liquid) |  |  | E | E | A | W2 |  |  |  |
| Metal-sulfide melt model (Fe-Si-O-S) |  |  | M | M | M | W3 |  |  |  |
| Silicate modelling |  | M | W4 |  |  |  |  |  |  |
| Seismic modelling |  | M | A | W5 |  |  |  |  |  |
| Planetary simulation |  |  |  |  |  | M | M | A | W6 |
| InSight data analysis |  |  |  | A | A | A/W? | A/W? | A/W? | A/W? |
|  |  |  |  |  |  |  |  |  |  |

E = Experiments

M = Model creation

A = Analysis of results

WX = Write up of paper X

? = Dependent on results of mission

c) Relationship to earlier or current work of the applicant/collaborating organisations, relevant work elsewhere

Light element modelling

Solution model scheme

Mars modelling – investigating the effect of lithospheric thickness and thermal boundary layers on seismic wave propagation.

BurnMan

Collaborators:

Nick Teanby (University of Bristol, UK)

James Wookey (University of Bristol, UK)

Tim Elliott (University of Bristol, UK)

Mike Walter (University of Bristol, UK)

Dan Frost (Bayerisches Geoinstitut, Germany)

Dave Rubie (Bayerisches Geoinstitut, Germany)

Stefanie Hempel (ISAE Toulouse, France)

Sanne Cottaar (University of Cambridge, UK)

d) Justification of Resources Requested

Majorite-ringwoodite-metal → 10 experiments (P-T as variables)

Majorite-melt-metal → 20 experiments (P-T-XS as variables)

2) Impact and outreach plan: one side, 11pt text (A4 paper, with minimum 2cm

margins)

3) CV

4) Publications list

5) Statement from the HoD

6) Two references (one from host institution, including advantages gained from hosting the fellowship)

7) Letter of support from UK instrument team member

**Objectives**

This proposal is to prepare for and analyse data from the SEIS experiment onboard NASA's InSight Lander, due to reach Mars in November 2018. The main objectives are:

1. To determine the expected past and present day equilibrium redox and metal/sulfide state within the deep mantle of Mars through high pressure experimental petrology. These data will be used to assess the state of equilibrium within Mars' deep interior.

2. To develop thermodynamic/thermoelastic models of light elements in metallic iron (sulfur, hydrogen, silicon, oxygen) in order to interpret densities and compressional wave velocities in Mars' core in terms of composition (and pressure and temperature).

3. To use the thermoelastic models derived in Objectives 1–2, coupled with pre-existing data on Mars composition, mass, radius, moment of inertia and Love number, in order to develop synthetic seismograms corresponding to Marsquakes.

4. Analyse Marsquake and impact data from the SEIS experiment in light of Objectives 1–3, as the data is transmitted from InSight.

**Summary**

**Academic beneficiaries**

**Impact Summary**

Public Outreach:

Space travel and planetary formation are both extremely popular topics, and the work in this project provides an ideal opportunity to engage the public.

The work contained within this proposal will be used during Outreach events, such as those regularly conducted by @-Bristol. The PI has already conducted successful seismological outreach with @-Bristol.

The School of Earth Sciences works regularly with this museum. Bristol is also part of a recently funded UKSA public engagement project 'Marsquake Monitor: measuring the pulse of the planet', led by Paul Denton (British Geological Survey), which aims to provide school-age children with the opportunity to perform seismic experiments and analyse real mission data. The work from this project would provide excellent material to provide children with easily understandable and testable hypotheses.

Education:

The PI has recently been involved with the Global Summer School, hosted by Imperial College London, which aims to provide engineering-track A-level students with insights into real world applications. The school includes two focused days on Mars missions, and is already starting to incorporate InSight into the teaching schedule. The proposed work would provide a perfect scientific “big-picture” for teaching purposes.

The development of thermodynamic and thermoelastic models will be conducted with BurnMan, an easy-to-use, modular thermoelastic toolkit (Cottaar et al., 2013), which much of the thermodynamics functionality developed by the PI in collaboration with an international group of Earth and planetary scientists. The development of the code has been supported by NSF and the Computational Institute for Geodynamics, and is already used as an educational and research tool.

One of the planned additions for BurnMan is a comprehensive planet builder with associated graphical user interface, where a user can input a bulk composition and structure and visualise the effects of structure and planetary evolution on observables such as mass, moment of inertia and seismic profiles. Three months of project time are devoted to implementing this functionality and an associated GUI, for use as an educational web-tool. One of the other developers of BurnMan (I. Rose) has developed a web tool linking seismology and mantle convection (http://ian-r-rose.github.io/interactive\_earth/thermal\_hires.html), and the two projects could easily be combined to demonstrate the propagation of seismic waves on Mars (or other terrestrial planets).

NOTES:

On Earth, the state of disequilibrium between the core and the mantle are further constrained by a large number of high pressure experiments on Earth-like compositions, and a vast quantity of seismic and other geophysical data. To link the experimental and seismological data, detailed thermodynamic/thermoelastic models are required. Such models are currently in their infancy (Komabayashi, 2014). The PI is currently extending and improving such models with flexible equations of state that can be used to match multi-anvil, diamond-anvil, shock and ab-initio experiments, both for silicate melts (de Koker et al.) and metallic melts (Anderson and Ahrens, 1994). These models are further informed by melting curves, 1 bar data and equilibria experiments (Myhill et al., in prep.). The author has also developed modifications to existing solution models to allow excess bulk moduli (Myhill, in review), thermal expansion and heat capacity data to be modelled; additions which are vital for high pressure phase equilibria and seismic velocities (e.g. Williams et al., 2015).

Gaetani and Grove (1996) Important constraints on core formation in Mars are provided by our experimental determination of the partitioning of Cu between silicate and sulfide melts. When combined with existing estimates for siderophile element abundances in the Martian mantle and a mass balance constraint from Fe, the experiments allow a determination of the mass of the Martian core (∼17 to 22 wt% of the planet) and its S content (∼0.4 wt%). These modeling results indicate that Mars is depleted in S, and that its core is solid.

MSE abundances on Earth suggest moderate pressure equilibrium (25-60 GPa, 2200-4000 K, mostly based on Ni,Co), see summary in Rubie et al

HSE abundances on Earth and Mars are similar (Warren et al., 1999) and in chondritic abundances, but pressures and temperatures of core formation were presumably quite different; support for late veneer (e.g. Righter, 2005).

Wade and Wood (2005) suggested continuous core accretion based on MSE, require low fO2 early in Earth history. Problem is that tantalum is highly siderophile under reducing conditions, but is present in chondritic abundance in the Earth (Mann et al., 2006).

Jones and Drake (1986) – inefficient core segregation (trapped metal fraction).

Rubie et al. suggest Mars more reduced because no Fe3+-rich pv layer.

Hustoft and Kohlstedt (2006) – deformation enhanced percolation

Wood et al., 2006 suggest from chondritic model, using elements of similar volatilities to adjust for loss to space:

85% Fe,

5% Ni,

0.9% Cr,

0.25% Co,

~1.9 wt% S (1.5-2.0 from McDonough, 2003),

0.2 P

0.2 C

0.1 H

6–7 Si, O (proportions controversial)

Rudge et al., 2010 suggest >=36% of Earth's core formed in eqm with mantle

Tuff et al., 2013 – early oxidation of a sulphur rich mantle.

Boujibar et al., 2016 – perovskite-melt more complex in Fe3+ than previously thought.

Wood, 2008 – Earth requires oxidation during growth

Georg and Shahar, 2015 – Earth requires reduction during growth

Jana and Walker (1997) – Fe ↔ FeS effect on MSEs, HSEs, lithophiles, chalcophiles.

Boujibar et al (2014) – FeS on quench … reflects magma ocean solubility?

Elkins-Tanton et al., 2003 – Mantle overturn – alumina segregation into the deep Mars mantle.

Tait and Jaupart (1992) – Mush thin when reacts

Dynamo driven by early S-rich core followed by late, more Fe-rich core material?

From WP2

It has been suggested that the reduced, iron rich mantle of Mars is a consequence of low magma ocean temperatures in Mars (Rubie et al., 2004).

Righter and Chabot, 2011

Q. How to design sulfide melt system?

add nickel and cobalt? “free” partitioning experiments

Bonus – dihedral angle study. (Terasaki et al.)

The concentrations of the moderately and highly siderophile elements in the SNC meteorites have been used to imply the rapid formation of a core by segregation from a deep magma ocean. Published estimates of pressures and temperatures vary widely, even for Earth (Rubie et al., 2007). Part of the problem may arise from modelling core formation as a single-stage process, despite accretion occuring via oligarchic growth.

Finally, isotopic heterogeneity in Nd, Hf, Os recorded by different groups of the SNC meteorites indicates that Mars' mantle preserves distinct primordial reservoirs generated by early silicate differentiation processes (Lee and Halliday, 1997; Foley et al., 2005; Borg and Draper, 2003; Brandon et al., 2012; Mezger et al., 2013).