Back to Belgium Grants

Final Report

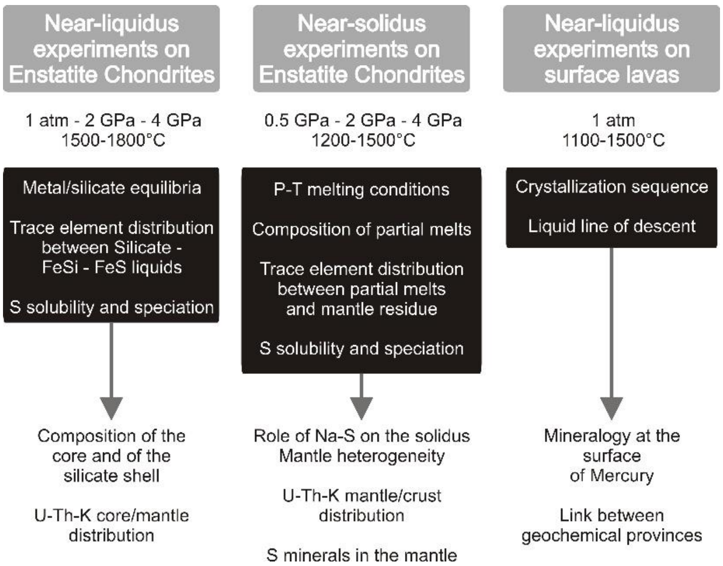
Name of the researcher	Bernard Charlier
Selection Year	2014
Host institution	University of Liege
Supervisor	Pr. Jacqueline Vander Auwera
Period covered by this report	from 01/03/2015 to 29/02/2016
Title of the project	**Early differentiation of terrestrial planets**

1. Objectives of the proposal (1 page)

This project proposes to investigate the early differentiation of terrestrial planets using phase equilibria obtained using experimental petrology and crystallization/melting modeling. I specifically focus on Mercury, Mars and the Moon which have preserved records of the early evolution on their ancient, impact-battered surfaces. The new data provided by spatial missions on the composition of the surfaces and on the geophysical characteristics of the planet surfaces and interiors give unique opportunities to perform innovative experiments on unprecedentedly investigated silicate melt compositions, with conditions of crystallization significantly different to those on Earth. Combining experimental phase equilibria with new constrains on surface compositions will enable us to test existing paradigms and develop new models on the early planetary differentiation.

2. Methodology in a nutshell (1 page)

We perform experiments in a range of pressure and temperature using furnaces and presses, with equipment and methods allowing the control of important parameters such as pressure, temperature, oxygen fugacity (redox conditions) and volatiles content. Experimental data are combined with geochemical modelling using relevant phase equilibria, partitioning of major elements between solid and liquid, and several published and in house algorithms developed to predict crystallization path of silicate liquids and partial melting of mantle rocks.



Schematic illustration of the experimental methodology showing the type of experiments, the pressure-temperature conditions, the data obtained and the output for the implications regarding the early magmatic evolution of Mercury

To reach targeted conditions, two different experimental methods are used in the course of this project: the piston cylinder for high-pressure experiments and a vertical furnace for l-atm experiments.

High-pressure experiments in piston-cylinder - Piston cylinder devices can reach pressures of 0.5 to 4 GPa, and temperature up to 2000°C. Experimental charges are prepared using a double capsule technique with a graphite inner capsule enclosed in a Platinum outer capsule. This capsule is enclosed into a solid Al2O3 sleeve and centred between bottom MgO spacer and top MgO thermocouple insulator in the centre of a sleeve of graphite (the furnace). The graphite furnace is contained in a sleeve of barium carbonate (the pressure medium) closed at the bottom with a graphite disc. Piston cylinder assemblies are pressurized cold to about 80% of the target pressure in 30-60 minutes, heated to the final temperature with ramp of 100°C/min and pressurized to the final pressure (in 10 min) while temperature is maintained constant. Temperature is measured and controlled with a D-type or S-type thermocouple located directly above the capsule upper lid. Experiments are run from a few hours to several days depending on P-T conditions and crystallinity of the experimental charge (see specific methods below), and finally quenched isobarically by turning off the power. Charges are open with a diamond wire saw, mounted in epoxy resin, and polished for analysis.

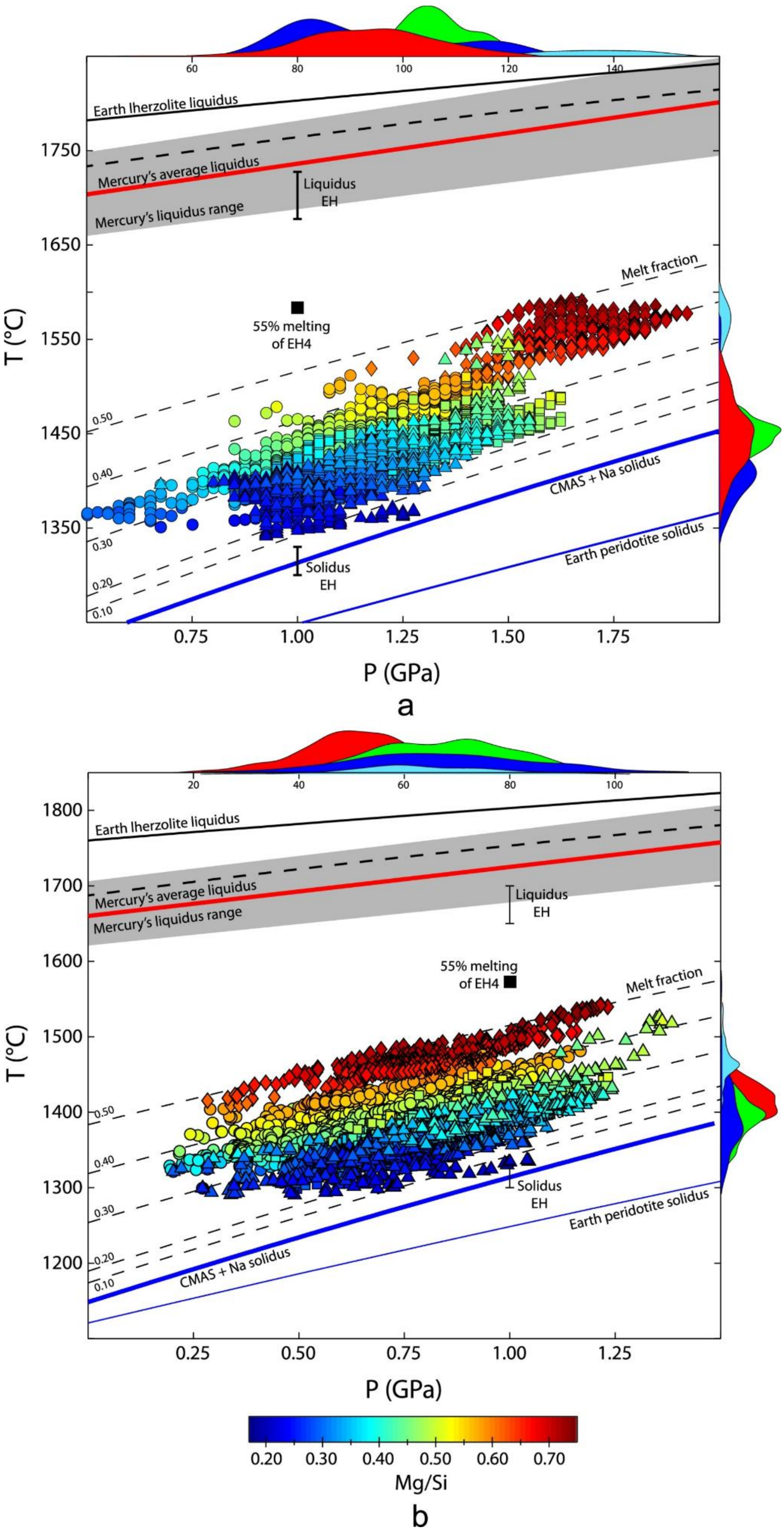
Vertical 1-atm furnace - Low-pressure (1 bar) experiments are performed in a vertical Gero mixing furnace. The ground starting material is packed into graphite capsule with top lid and encapsulated in an outer Pt capsule. Experiments are performed in evacuated and sealed silica tubes. Temperature is controlled using 4 S-type (Pt-Pt90Rh10) thermocouples located along the silica tube (thermal gradient is less than 5°C). Experiments are quenched in water.

Preparation of starting materials - Starting compositions are prepared from high purity reagent grade oxides, silicates, carbonates and metals. Sulfur is added as a mixture of iron sulphide, elemental sulfur or CaS. The synthetic mixture is milled with ethanol in an agate mortar to homogenize the powder. To add the trace elements, the powder is doped with premixed solutions of trace elements. We can change the intrinsic oxygen fugacity of the starting material by using contrasting ratios of Si/SiO2. With this method, we are able to reach moderately to highly reducing conditions. Due to potential oxidation of Si during experiments, the ratio of Si/SiO2 cannot be used to accurately estimate oxygen fugacity conditions. However, accurate fO2 can be calculated a posteriori using both the Fe-FeO and Si-SiO2 equilibria between the silicate and metal melts.

3. Results (8-10 pages)

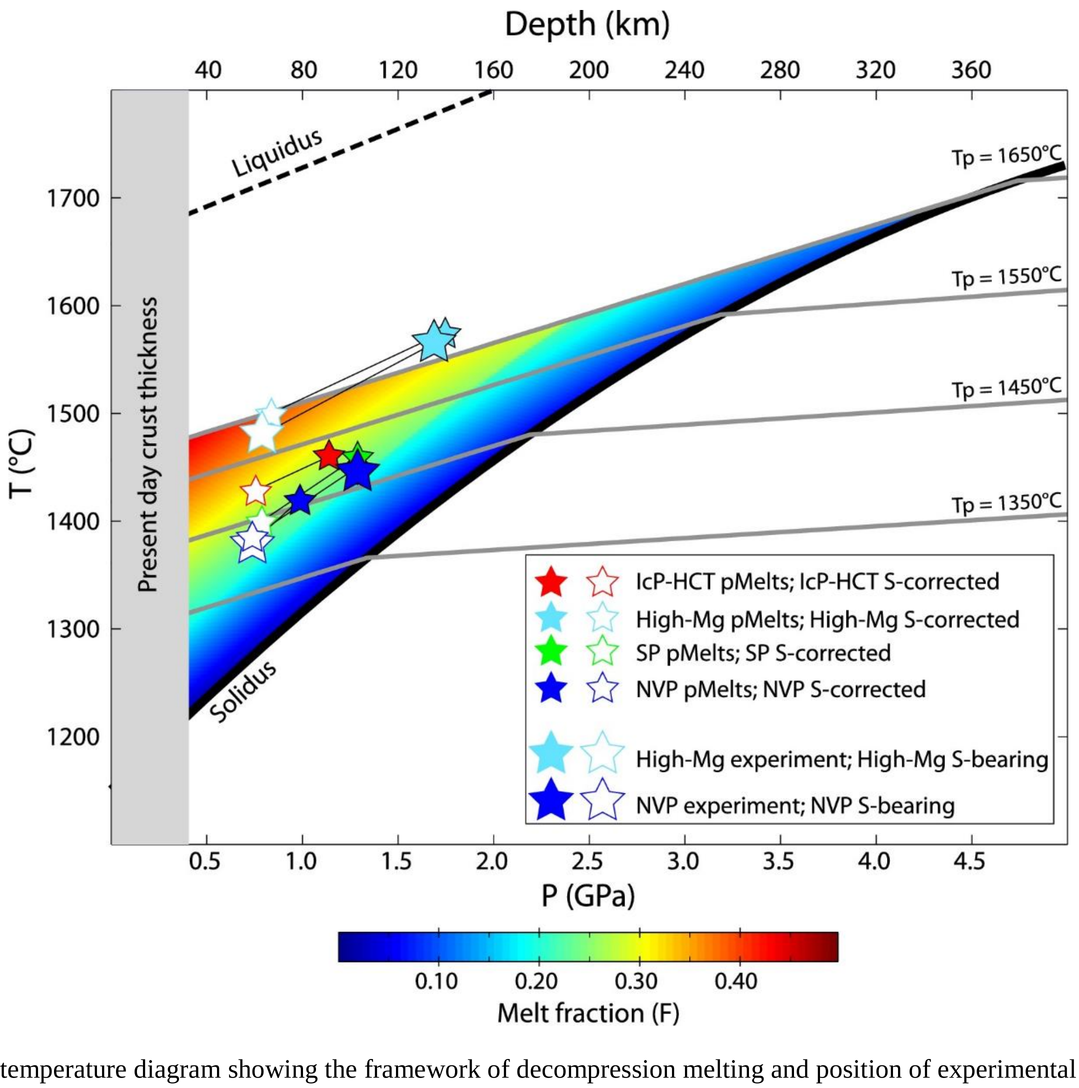
Here I present the results of two major studies we perform during the second reporting year of the project.

The MESSENGER spacecraft provided geochemical data for surface rocks on Mercury. In this study, we use the major element composition of these lavas to constrain melting conditions and residual mantle sources on Mercury. We combine modelling and high-temperature (1320–1580 °C), low- to high-pressure (0.1 to 3 GPa) experiments on average compositions for the Northern Volcanic Plains (NVP) and the high-Mg region of the Intercrater Plains and Heavily Cratered Terrains (High-Mg IcP-HCT). Near-liquidus phase relations show that the S-free NVP and High-Mg IcP-HCT compositions are multiply saturated with forsterite and enstatite at 1450 °C – 1.3 GPa and 1570 °C – 1.7 GPa, respectively. For S-saturated melts (1.5–3 wt.% S), the multiple saturation point (MSP) is shifted to 1380 °C – 0.75 GPa for NVP and 1480 °C – 0.8 GPa for High-Mg IcP-HCT. To expand our experimental results to the range of surface compositions, we used and calibrated the pMELTS thermodynamic calculator and estimated phase equilibria of ∼5800 compositions from the Mercurian surface and determined the *P–T* conditions of liquid–forsterite–enstatite MSP (1300–1600 °C; 0.25–1.25 GPa). Surface basalts were produced by 10 to 50% partial melting of variably enriched lherzolitic mantle sources. The relatively low pressure of the olivine–enstatite–liquid MSP seems most consistent with decompression batch melting and melts being segregated from their residues near the base of Mercury's ancient lithosphere. The average melting degree is lower for the young NVP (0.27±0.04) than for the older IcP-HCT (0.46±0.02), indicating that melt productivity decreased with time. The mantle potential temperature required to form Mercurian lavas and the initial depth of melting also decreased from the older High-Mg IcP-HCT terrane (1650 °C and 360 km) to the younger lavas covering the NVP regions (1410 °C and 160 km). This evolution supports strong secular cooling of Mercury's mantle between 4.2 and 3.7 Ga and explains why very little magmatic activity occurred after 3.7 Ga.



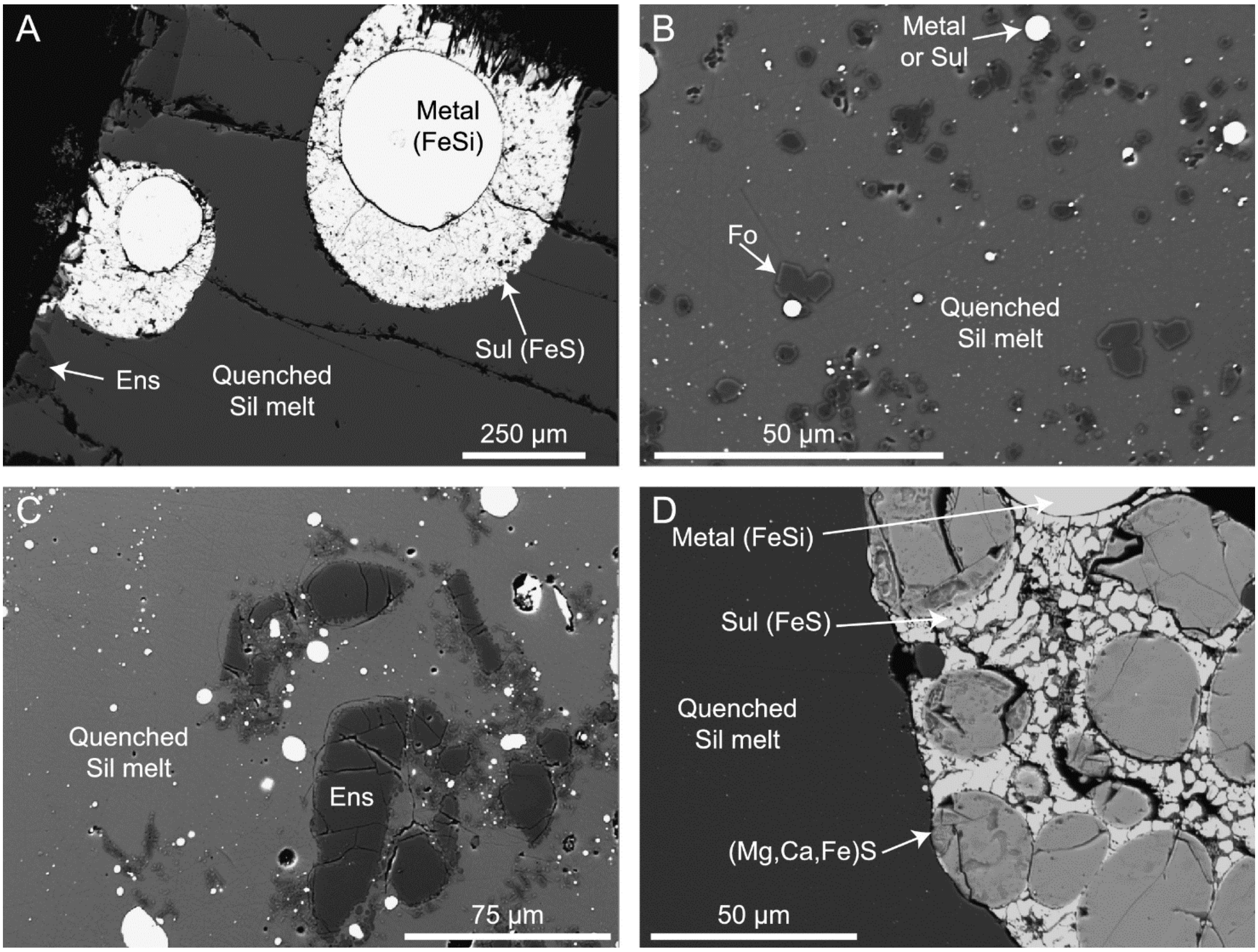
Temperature (°C) versus pressure (GPa) diagrams showing the position of the liquid–forsterite–enstatite multiple saturation points (MSP) of Mercurian lavas as calculated with the pMELTS algorithm (Ghiorso et al., 2002). (a)

Calculations performed on S-free compositions. Triangles = lavas from NVP, squares = lavas from SP, circles = lavas from IcP-HCT, diamonds = lavas from HMg. (b) Corrected MSP taking into account the effect of S on phase equilibria (see text for details). Dashed black lines represent melt fraction isopleths calculated after Katz et al. (2003) and Shorttle et al. (2014). We broke the melting interval between a clinopyroxene present melting interval and a clinopyroxene free interval and assumed an initial clinopyroxene mass fraction of 0.15. We considered the solidus surface of a lherzolite in the CMAS system (Presnall et al., 1979) that we corrected for the Na_2O content (∼1.5 wt.%) of an EH chondrite (Walter and Presnall, 1994 and Kiefer et al., 2015). The solidus was calculated using the following equation: T_s(°C)=1148 + 177 × P (GPa) − 12.2 × P^2. We considered the liquidus surface of an EH chondrite calculated with pMELTS. Solidus and liquidus curves for terrestrial peridotites and lherzolites are shown for comparison (Herzberg, 1983, Hirschmann, 2000 and Katz et al., 2003). Vertical black lines represent liquidus and solidus temperatures of an enstatite chondrite (EH4) at 1 GPa and reducing conditions (Berthet et al., 2009). Black symbol represents the pressure–temperature conditions at which 55% melt is produced from EH4 (Boujibar et al., 2015). Numbers on the upper *x*-axis represent depth in km assuming that the Mercury's mantle is 400 km thick (Smith et al., 2012) and has an average density of 3350 kg/m^3 (Padovan et al., 2015). Histograms of the *X* and *Y* axes are as in Fig. 2.

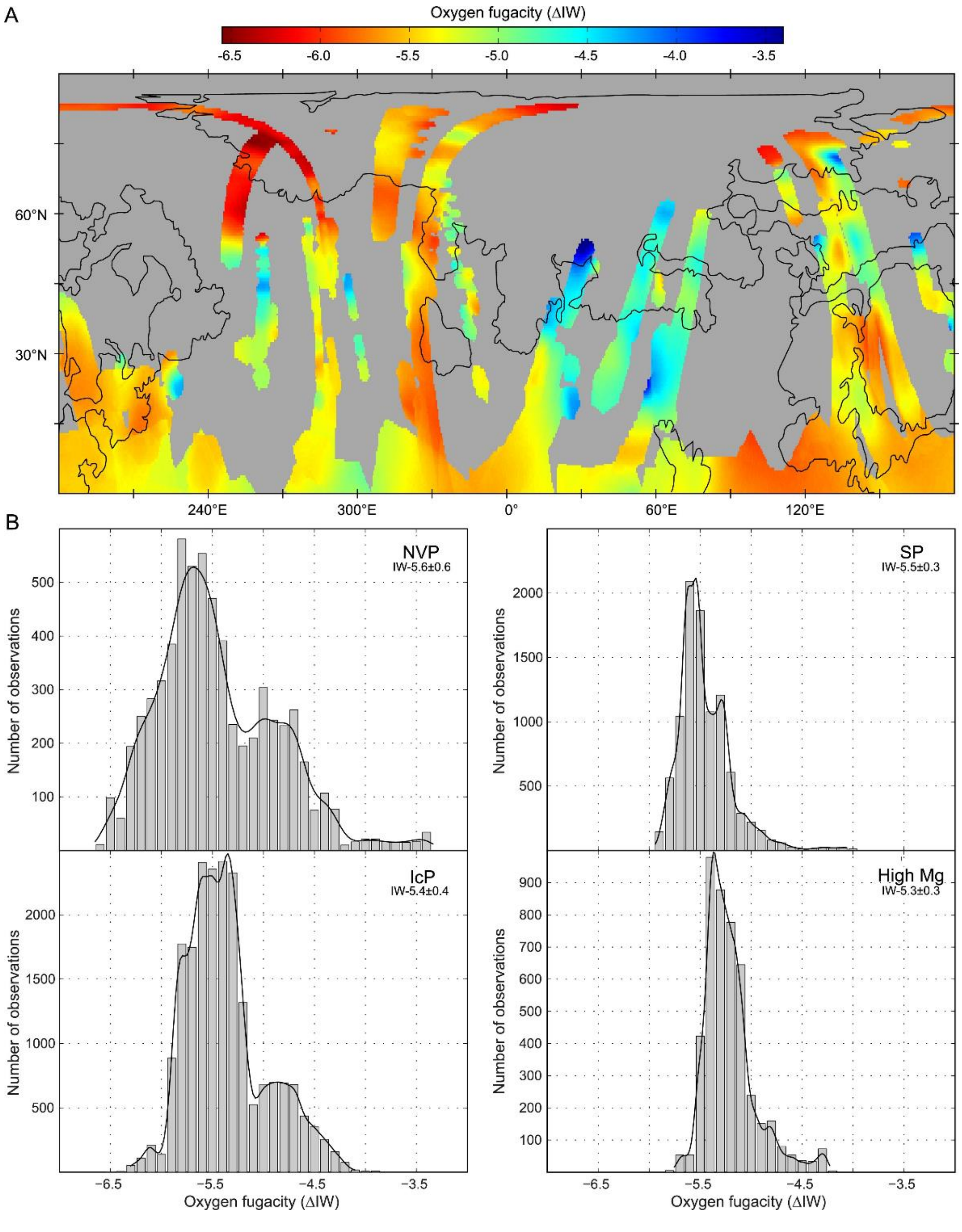


Pressure–temperature diagram showing the framework of decompression melting and position of experimental liquid–forsterite–enstatite multiple saturation points (MSP) and median values of MSP calculated with pMELTS for NVP, SP and IcP-HCT (low-Mg and high-Mg) (see stars in Fig. 4). Solidus and liquidus curves are as in Fig. 6. Adiabatic paths for mantle potential temperatures (T_p) from 1350 to 1650 °C were calculated following Shorttle et al. (2014). Melt fractions are calculated assuming adiabatic decompression of a lherzolitic mantle. The grey vertical box represents the average present day crustal thickness of Mercury (Padovan et al., 2015).

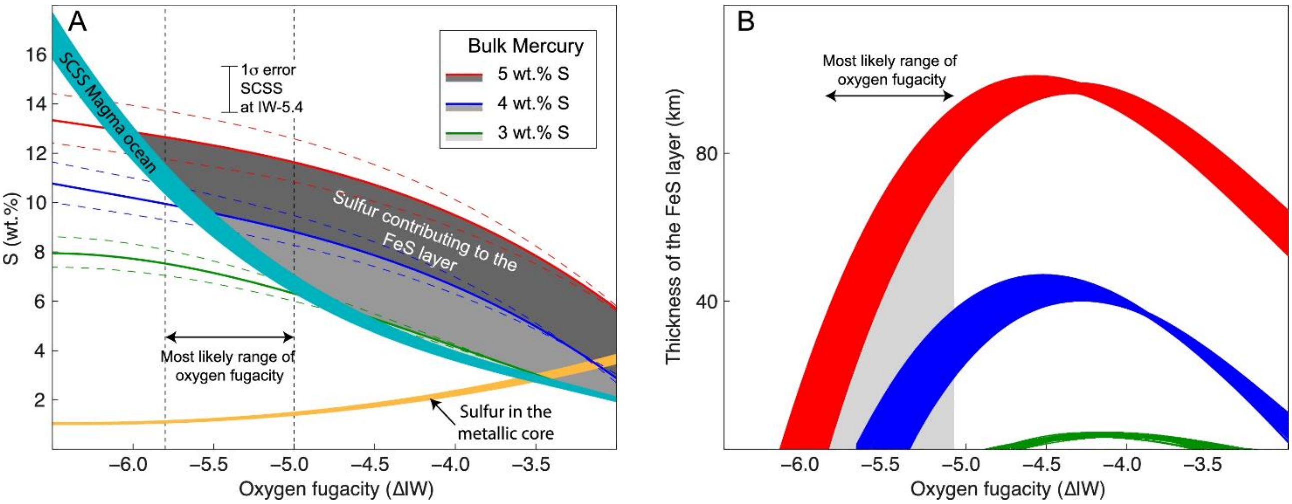
Chemical data from the MESSENGER spacecraft revealed that surface rocks on Mercury are unusually enriched in sulfur compared to samples from other terrestrial planets. In order to understand the speciation and distribution of sulfur on Mercury, we performed high temperature (1200–1750 °C), low- to high-pressure (1 bar to 4 GPa) experiments on compositions representative of Mercurian lavas and on the silicate composition of an enstatite chondrite. We equilibrated silicate melts with sulfide and metallic melts under highly reducing conditions (IW-1.5 to IW-9.4; IW = iron-wüstite oxygen fugacity buffer). Under these oxygen fugacity conditions, sulfur dissolves in the silicate melt as S^{2-}S2− and forms complexes with Fe^{2+}Fe2+, Mg^{2+}Mg2+ and Ca^{2+}Ca2+. The sulfur concentration in silicate melts at sulfide saturation (SCSS) increases with increasing reducing conditions (from <1 wt.% S at IW-2 to >10 wt.% S at IW-8) and with increasing temperature. Metallic melts have a low sulfur content which decreases from 3 wt.% at IW-2 to 0 wt.% at IW-9. We developed an empirical parameterization to predict SCSS in Mercurian magmas as a function of oxygen fugacity (fO_2fO2), temperature, pressure and silicate melt composition. SCSS being not strictly a redox reaction, our expression is fully valid for magmatic systems containing a metal phase. Using physical constraints of the Mercurian mantle and magmas as well as our experimental results, we suggest that basalts on Mercury were free of sulfide globules when they erupted. The high sulfur contents revealed by MESSENGER result from the high sulfur solubility in silicate melt at reducing conditions. We make the realistic assumption that the oxygen fugacity of mantle rocks was set during equilibration of the magma ocean with the core and/or that the mantle contains a minor metal phase and combine our parameterization of SCSS with chemical data from MESSENGER to constrain the oxygen fugacity of Mercury's interior to IW-$5.4\pm0.4$5.4±0.4. We also calculate that the mantle of Mercury contains 7–11 wt.% S and that the metallic core of the planet has little sulfur (<1.5 wt.% S). The external part of the Mercurian core is likely to be made up of a thin (<90 km) FeS layer.



Back-scattered electron images of experimental products. A. Run A707; 1560 °C; 2 GPa. Sulfide melt is observed around droplets of metallic melt. Note the presence of quench crystals in the sulfide melts. Enstatite forms large crystals on the edges of the experimental charge. B. RY-14-1; 1250 °C; 0.3 GPa. Forsterite forms small crystals disseminated in the quenched silicate melt. Note the presence of micro globules (nuggets) of metal (FeSi alloy) in this experiment performed in IHPV. C. RY-10; 1250 °C; 0.3 GPa. Enstatite forms small and large crystals disseminated in the silicate melt. Note the presence of micro globules (nuggets) of metal (IHPV experiment). D. Y030-1; 1420 °C; 0.1 GPa. Note the presence of (Mg,Ca,Fe)S globules in a matrix of FeS melt. Sil = silicate; Sul = sulfide; Ens = enstatite; Fo = forsterite



A. Map of the northern hemisphere of Mercury showing calculated conditions of fO_2 during mantle melting and eruption of Mercurian basalts. Calculations are based on the bulk compositions of the lavas (Weider et al., 2015), an estimate of their liquidus temperatures (Supplementary Fig. S4) and the assumption that Mercurian lavas were sulfide saturated when they erupted (see text for details). The thin black lines represent the limits of the smooth plains as mapped by Denevi et al. (2013). B. Histograms showing the distribution of fO_2 conditions calculated for each geochemical province.



A. Theoretical model showing the evolution of SCSS as a function of fO_2 (ΔIW) in the Mercurian magma ocean (1900 ± 25 °C at 5 GPa; cyan curve) and the sulfur content of the equilibrium metallic core (orange curve). Vertical dashed lines show the most likely fO_2 conditions for Mercury's accretion and differentiation (IW-5.4 ± 0.4). We considered three potential bulk sulfur contents for Mercury (3, 4 and 5 wt.%), a bulk Fe content of 65 ± 5 wt.% (Hauck et al., 2013) and that the thickness of the mantle is 420 ± 30 km. Grey fields below the red, blue and green curves show the result of iterative calculations of the amount of sulfur that does not dissolve in the metallic core and contributes to the formation of a FeS external core. Dashed red, blue and green curves show the effect of the uncertainty on the bulk Fe content (65 ± 5 wt.%) of the planet and the mantle thickness. B. Results of a Monte Carlo simulation showing the calculated thickness of the FeS layer as a function of fO_2. We used metal and sulfide densities from Hauck et al. (2013). Red, blue and green curves correspond to a Mercurian bulk S content of 5, 4 and 3 wt.%, respectively

4. Valorisation/Diffusion (including Publications, Conferences, Seminars, Missions abroad...)

In addition to the papers published during the first year, here are the 2016 papers:

International publications related to the project

Namur O, Charlier B, Holtz F, Cartier C, McCammon C (2016) Sulfur solubility in reduced mafic silicate melts: Implications for the speciation and distribution of sulfur on Mercury. Earth and Planetary Science Letters 448: 102-114. (IF_{2015}: 4.326)

Namur O, Collinet M, Charlier B, Grove TL, Holtz F, McCammon C (2016) Melting processes and mantle sources of lavas on Mercury. Earth and Planetary Science Letters 439: 117-128. (IF_{2015}: 4.326)

Abstracts related to the project

Cartier C, Namur O, **Charlier B**, Hammouda T (2016) Elements partitioning during Mercury's two shells core formation. *Goldschmidt Conference, Yokohama, Japan*, 373.

Honour VC, Holness M, **Charlier B** (2016) The physical behaviour of emulsions in a crystal mush: insights from synthetic experiments and natural samples. *Geological Society of America Penrose Conference, Montana, USA.*

Linsler SA, Namur O, Albrecht M, **Charlier B**, Holtz F, McCammon C (2016) Metal-silicate trace element partitioning at reducing conditions: Implications for Mercury's differentiation. *EMPG XV, ETH Zurich, Switzerland.*

Namur O, **Charlier B**, Holtz F, Cartier C, McCammon C (2016) Sulfur solubility in reduced mafic silicate melts: Implications for the speciation and distribution of sulfur on Mercury. *Geophysical Research Abstracts Vol. 18, EGU2016-6068.*

During this project, I have been invited in meetings and by universities to present my research:

03/2016: China University of Geosciences, Beijing, China

01/2016: Geologica Belgica Meeting, Mons, Belgium
12/2015: RWTH Aachen University, Germany
06/2015: MESSENGER – BepiColombo Joint Science Meeting, DLR Berlin, Germany
04/2015: AGU-GAC-MAC-CGU Joint Assembly, Montreal, Canada
04/2015: Ghent University, Belgium
03/2015: DLR Berlin, Germany
03/2015: Lunar and Planetary Science Conference, Houston, USA

5. Future prospects for a permanent position in Belgium

In January 2016, I have applied for a position of Chercheur Qualifié FNRS. I have been classified first of the commission SEN-4 and have been selected by my University. I will thus start a new permanent position of Chercheur Qualifié FNRS at ULg in October 2016.

6. Miscellaneous

In February 2016, I have submitted the project *"Early Magmatic Evolution of Planet Mercury*" to the European Research Council (ERC) Consolidator Grant. I have been evaluated positively in step 1 and will have the step 2 interview in September 2016. The budget requested is 2.71 Million euros.