No FeS layer in Mercury? Evidence from Ti/Al measured by MESSENGER C. Cartier[1*], O. Namur[2], B. Charlier[1], *c.cartier@ulg.ac.be, [1]Department of Geology, Université de Liège, B-4000 Sart Tilman - Belgium, [2]Leibniz University Hannover, Institute of Mineralogy, Germany.

Introduction: Geophysical and geochemical measurements by MESSENGER have refined our understanding of the internal structure and geological history of Mercury. In particular, measurements of low iron and exceptionally high sulfur contents in lavas support the idea of a highly reduced planet [1-3]. Based on these data and experiments in reduced conditions, the intrinsic oxygen fugacity (fO_2) of the mantle has recently been estimated to IW-5.4 ± 0.4, with IW being the iron-wüstite redox equilibrium [1]. Nevertheless, some important questions remain unresolved, particularly regarding the structure of Mercury's core, which may contain a ≤ 200 km-thick external FeS layer [2,4-6]. In this work we compare MESSENGER chemical data and experimentally constrained geochemical models to evaluate the presence of such a layer and estimate its likely thickness.

Ti/Al in Mercury silicate portion: Ti and Al, two highly refractory elements, display a constant and solar ratio in bulk chondritic meteorites, and are assumed to be in chondritic proportions in bulk planets [7]. Moreover these elements do not significantly fractionate from each other during early igneous differentiation processes. The Ti/Al ratio of the Earth's crust is, for example, similar to the CI ratio [8]. Ti/Al ratios measured in Mercurian lavas (data from [9]) are rather constant and not correlated to Mg/Al (Fig.1), which is a good proxy of silicate differentiation [10].

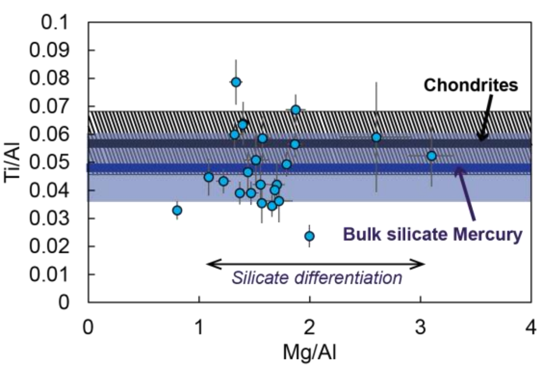

Figure 1: *Ti/Al versus Mg/Al ratios measured in Mercury lavas (data from [9]). The bulk silicate Mercury (BSM) is very slightly subchondritic.*

Accordingly we argue that the silicate fraction of Mercury has a Ti/Al ratio identical to the average composition of Mercury lavas (Ti/Al = 0.048 ± 0.013). Mercury's silicate fraction is therfore very slightly subchondritic (Fig.1). Unlike Al, Ti changes its behavior from lithophile to chalcophile under extremely reducing conditions [2,10], meaning it could have been extracted from the silicate portion into a sulfide reservoir during core formation. We therefore use Ti/Al as a tracer for the potential formation of a FeS layer.

Ti partitioning under extremely reducing conditions: We conducted equilibrium experiments in a multi-anvil apparatus at 5 GPa, 1640–1850°C, and under a range of highly reducing conditions, consistent with Mercury's core-mantle equilibration. Experimental products consist of 3 equilibrated melts: silicate, sulfide (~FeS), and Fe-rich metal alloy. Intrinsic oxygen fugacity of each sample has been estimated using Si-SiO_2 equilibrium [12], and ranges from IW-1 to IW-7 (Fig.2). At IW-5.4 ± 0.4 Ti is chalcophile (D ≈ 7), but not siderophile. However its metal/silicate partitioning is not negligible (D ≈ 0.1).

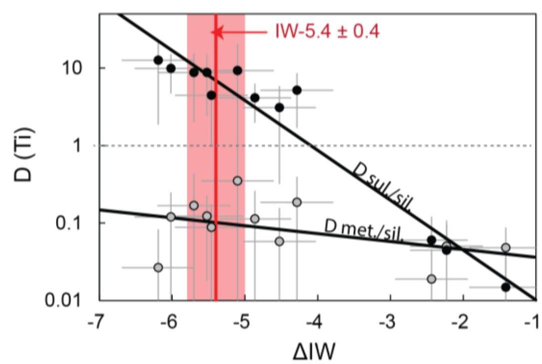

Figure 2: *Partitioning of Ti bewteen FeS/silicate (black points) and metal/silicate (grey points) at 5 GPa versus fO_2. Under Mercury's mantle redox conditions (IW-5.4 ± 0.4 [1]), Ti is chalcophile.*

Mercury core formation models: We construct a single-step model for Mercury's core formation using Ti partitioning data at IW-5.4 ± 0.4. The main structure of the planet is imposed by geophysical constraints [4]: the metallic core is ~2020 km in diameter for a mean density of 6.98 g/cm^3, while the outer solid shell is 420 km thick with a mean density of ~3.38 g/cm^3 and consists of the crust, mantle, and a potential FeS layer at the core-mantle boundary with a thickness between 0 and 200 km (Model 1). We also consider the possibility of a liquid FeS layer, localized in the outer part of the core (Model 2). These data impose a mass for each of the 3 main reservoirs (silicate portion, FeS layer, and metallic core), in which the concentration of Ti is calculated using the experimental partition coefficients (Al entirely remains in the silicate portion). For the bulk Mercury composition we took the mean chondritic Ti/Al with the error bar. Results are displayed in Fig. 3. In both scenarios the best match between Mercury data and our models corresponds to no (0 km) FeS layer. Considering all uncertainties, a FeS layer would probably be less than 20 km thick and certainly not thicker than 70 km. Considering no FeS extraction, the model reproduces the slightly subchondritic Ti/Al of the bulk silicate Mercury. This subchondritic ratio can thus be explained by the selective extraction of Ti by the metallic core.

Implications: The potential existence of such a FeS layer in Mercury is of particular importance because it could have trapped heat producing elements U and Th, which are known to change from lithophile to chalcophile under highly reducing condition [13]. Mercury has a significant global magnetic field that can be explained by the dynamo theory, requiring that part of the core remains liquid. Futhermore, Mercury lavas give evidence of strong secular cooling of Mercury's mantle and termination of magmatic activity at 3.5 Ga [14,15]. Models for the thermal history of the planet should take into account a negligible FeS layer. Our results should also be taken into account when looking at K/U and K/Th surface ratio to infer information about the volatile inventory of the innermost planet [16,17].

References: [1] Namur et al. (2016b) *EPSL*, *448*, 102–114. [2] Malavergne et al. (2010) *Icarus*, *206*, 199–209. [3] Zolotov et al. (2013) *JGR*, *118*, 138–146. [4] Hauck et al. (2013) *JGR*, *118*, 1204–1220. [5] Smith et al. (2012) *Science*, *336*, 214–7. [6] Chabot et al. (2014) *EPSL*, *390*, 199–208. [7] McDonough and Sun (1995) *Chem. Geol.*, *120*, 223–253. [8] Klerner and Palme (2000) *MPS*, *35*. [9] Weider et al. (2014) *Icarus*, *235*, 170–186 [10] Vander Kaaden et al. (2016) *GCA*, *173*, 246–263. [11] Palme and O'Neill (2014) *Treat. Cosm.* [12] Cartier et al. (2014) *GCA*, *130*, 167–187. [13] Wohlers and Wood (2015) *Nature*, *520*, 337–340. [14] Namur et al. (2016a) *EPSL*, *439*, 117–128. [15] Byrne et al. (2016) *GRL*, *43*, 7408–7416. [16] Peplowski et al. (2011) *Science*, *446*, 1850–1852. [17] McCubbin et al. (2012) *GRL*, *39*, 1–5.

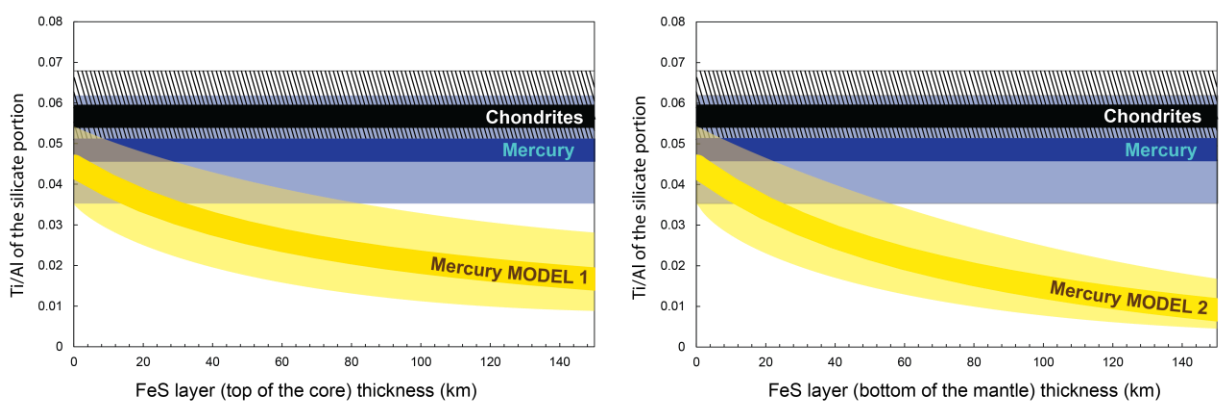

Figure 3: *Ti/Al of the silicate portion versus thickness of a potential FeS layer calculated with the two models (see text). The error bar takes into account the uncertainties on fO_2 and on the bulk Mercury Ti/Al. For both models, best match is with no FeS layer. The slightly subchondritic Ti/Al of the BSM is due to metal core formation.*