Accepted Manuscript

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PII: S0883-2927(18)30065-9

DOI: 10.1016/j.apgeochem.2018.03.007

Reference: AG 4055

To appear in: *Applied Geochemistry*

Received Date: 3 April 2017

Revised Date: 5 February 2018

Accepted Date: 7 March 2018

Please cite this article as: Staun, C., Vaughan, J., Lopez-Anton, M.A., Rumayor, M., Martínez-Tarazona, M.R., Geochemical speciation of mercury in bauxite, *Applied Geochemistry* (2018), doi: 10.1016/j.apgeochem.2018.03.007.

Geochemical Speciation of Mercury in Bauxite

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Abstract

The presence of trace concentrations of mercury in bauxite is a potential environmental concern in the Bayer alumina refining process. An understanding of the geochemical speciation of mercury in bauxite provides insight into the behaviour of mercury in the Bayer process. The speciation of mercury was evaluated using a novel continuous thermal desorption methodology, sequential extractions, alkaline digestion, aqua regia digestion and hydrofluoric acid total dissolution assay. Thermal desorption demonstrated two distinct mercury forms. Labile mercury was found to be present as metacinnabar or organic-associated mercury, while refractory mercury was associated with quartz or other refractory silicates.

Keywords: mercury; bauxite; speciation; thermal desorption; sequential extraction

1. Introduction

The refining of alumina is performed using the Bayer process, which involves the alkaline digestion of bauxite ore in order to dissolve amphoteric aluminium hydroxides that leave a predominantly iron oxide residue. Lateritic bauxites are formed in tropical climates through the weathering and dissolution of parent silicates resulting in the precipitation of aluminium hydroxide in the form of gibbsite or boehmite. Mercury is present in bauxite in trace concentrations and due to its electrochemical nobility, hydrophobic character and volatility may deport to condensate waters, presenting problems of an environmental and safety management nature. Mercury is a bio-accumulative neurotoxin with a complex biogeochemical cycle and is subject to increasingly stringent regulation. It is within this framework that technologies have been developed for the remediation of Bayer process stack emissions and condensates (Mullett et al., 2012, Mullett et al., 2007).

The University of Queensland - Rio Tinto Bauxite and Alumina Technology Centre has evaluated the chemical thermodynamics of mercury in the Bayer process and demonstrated the feasibility of techniques for stabilising mercury to a non-volatile phase in Bayer digestion, preventing the deportment of mercury to condensate (Bansal et al., 2014b, Staun et al., 2016). Robust analytical techniques have been developed for the determination of mercury in all Bayer materials (Bansal et al., 2014a). Identification of the geochemical speciation of mercury in bauxite will further contribute to an understanding of the behavior of mercury in the Bayer process, and potentially allow the development of novel process additives.

Determining mercury speciation in bauxite is not an easy task due to the diverse chemical associations of trace metals. Spectroscopic x-ray absorption methods are not useful in this instance, as mercury concentration is in the parts per billion range, below the limits of detection (Jew et al., 2011). However, thermal desorption methodology (HgTPD) for mercury speciation appears to be a new, promising analytical technique for identifying mercury species in solids. This technique

exploits the temperature-dependent sublimation of mercury compounds, an effective procedure for the identification of mercury species at concentrations lower than 10 ppm (Rumayor et al., 2013, Rumayor et al., 2015a). In the present work, HgTPD analysis was performed on different bauxite samples and complimented by a series of sequential extractions, a widely used methodology in soil science to determine geochemical speciation. The total mercury concentration was determined by means of a hydrofluoric acid total dissolution assay, the results of which were in close correlation to those of an alkaline digestion methodology. This work explores the geochemical speciation of mercury in five lateritic bauxites using the above-mentioned methods.

2. Experimental

2.1. Sample preparation

A total of 5 lateritic bauxites were employed for this study. All of the bauxite samples were milled to 100 % passing 150 μm with the exception of bauxite 5 (NIST 600). This is a standard reference material supplied by the National Institute of Standards and Technology, milled to 80 μm.

2.2. Sequential extraction of mercury

Sequential extractions were completed as per the methodology of Bloom et al. (2003). A sub sample of bauxite was sequentially extracted using solutions of increasing chemical reactivity. The fractions in the order of 1 to 5 were deionised water, 0.1 M acetic acid and 0.01 M hydrochloric acid, 1 M potassium hydroxide, 12 M nitric acid and finally *aqua regia*. The extractions were performed at room temperature for 24 ± 2 hours. The vessels were attached to a barrel rotating horizontally at 20 rpm with the exception of F5 which was left to stand for 24 hours in loosely capped vials to prevent pressure build-up due to the generation of chlorine gas. The size of each sample was 0.4 g, while the extractant volume was 40 mL, with the exception of F5 which was 13

mL. 5 replicates for each bauxite sample were used. The extractant solutions were analysed using a Perkin Elmer flow injection mercury system (FIMS 400) to matrix-matched calibration standards, as per the methodology of Bansal et al. (2014a). Each replicate was analysed 3 times and the mean value was taken as the result. 95 % confidence intervals were generated using a two-tail Student`s distribution (error bars).

2.3. Hydrofluoric acid total dissolution assay

Total mercury bauxite concentrations were determined using hydrofluoric acid-assisted digestion in a Speedwave 4 microwave digestion unit. The bauxite solid loading was 0.4 g. The total extractant volume was 20 mL: 10mL aqua regia, 5 mL hydrofluoric acid, 1.5 mL hydrogen peroxide and 3.5 mL deionised water. 5 replicate digestions were performed for 60 minutes at 230 °C. This ensured the total dissolution of the bauxite matrix, leaving only a fine fluoride precipitate.

2.4. Aqua regia digestion

Aqua regia digestion was performed for the same temperature and duration as hydrofluoric acid, with a solid loading of 1.5 g, and a solution composition of 3.75 mL HCl, 1.25 mL HNO_3, 1 mL H_2O_2 and 9 mL deionised water. The solution was analysed using a FIMS 400 to matrix-matched calibration standards, with confidence intervals generated as per Section 2.2.

2.5. Alkaline digestion

The alkaline digestions were performed in a rotating pressurised digestion vessel, in imitation of a low-temperature Bayer process. 5 replicate digestions were carried out for 1 hour at 140 °C using an alumina refinery sourced digestion stage alkaline with 4 M free sodium hydroxide. 5 g of bauxite was added to 25 mL of extractant, resulting in the complete dissolution of the gibbsite. The post-digestion solution and solid residue was analysed using a Milestone DMA-80 thermal

desorption instrument, and the mercury concentration in the pre-digestion bauxite was determined by means of a mass balance. The temperature was ramped to 750 °C and held at this temperature for three minutes. Flocculation of the solid residue prior to filtration resulted in the formation of insignificant concentrations of mercury in the filtrate. Confidence intervals were generated as per Section 2.2, using a DMA-80. Each replicate was analysed 3 times. Detection limits were determined using 10 replicates of blank solution as the standard deviation multiplied by 3.

2.6. Thermal desorption method for Hg speciation

The HgTPD device consisted of a thermo-desorption furnace coupled to a PYRO 915 furnace and a continuous mercury analyzer (RA-915) (Rumayor et al., 2015c). The novelty of this device is that in the first furnace the desorption of mercury species is carried out using N_2 as an inert gas to avoid interferences, while at the same time O_2 is introduced into the commercial PYRO furnace to ensure the total decomposition of volatile matter derived from the carbonaceous matter. The sample was weighed in a sample boat and its temperature was controlled by a thermocouple. Measurements were carried out at a heating rate of 50 °C min^{-1} under a N_2 flow of 500 mL min^{-1}. The PYRO 915 unit was kept at 800-1000 °C under an O_2 flow of 500 mL min^{-1}.

2.6. Characterisation of bauxites

The elemental composition of the samples was determined through X-ray fluorescence (XRF) using a PANanalytical – MagiX FAST. Surface area was calculated using the Brunauer-Emmett-Teller (BET) adsorption isotherm, and a Micromeritics ASAP 2020 porosimetry instrument using nitrogen gas at -196ºC. Identification of the crystalline mineral matter was performed by X-ray diffraction (XRD) in the range of 2θ=10 °-90°. The diffractograms were obtained using a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA.

3. Results and discussion

3.1. Sequential extractions

The results of the sequential extractions are shown in Figure 1. The sequential extraction results without confidence intervals were below the detection limit of the method. The percent fraction of sequentially extracted mercury is listed in Table 1, with the data below detection limits excluded. The total mercury concentrations determined using hydrofluoric acid total dissolution assay are incorporated into Table 2. No significant amount of mercury was extracted in fraction 1 or 2, suggesting the absence of exchangeable cations and outer sphere adsorbed species. All the bauxites released mercury in fraction 3 (1 M KOH) suggesting that there is an association with organic species. Bauxite 5 is noticeable for releasing the bulk of its sequentially extracted total in fraction 3, and releasing 59 % of its total mercury content in the sequential extraction process, indicating that the mercury in this bauxite is relatively labile (Table 2). However, this lability may be a result of the extremely fine particle size of bauxite 5.

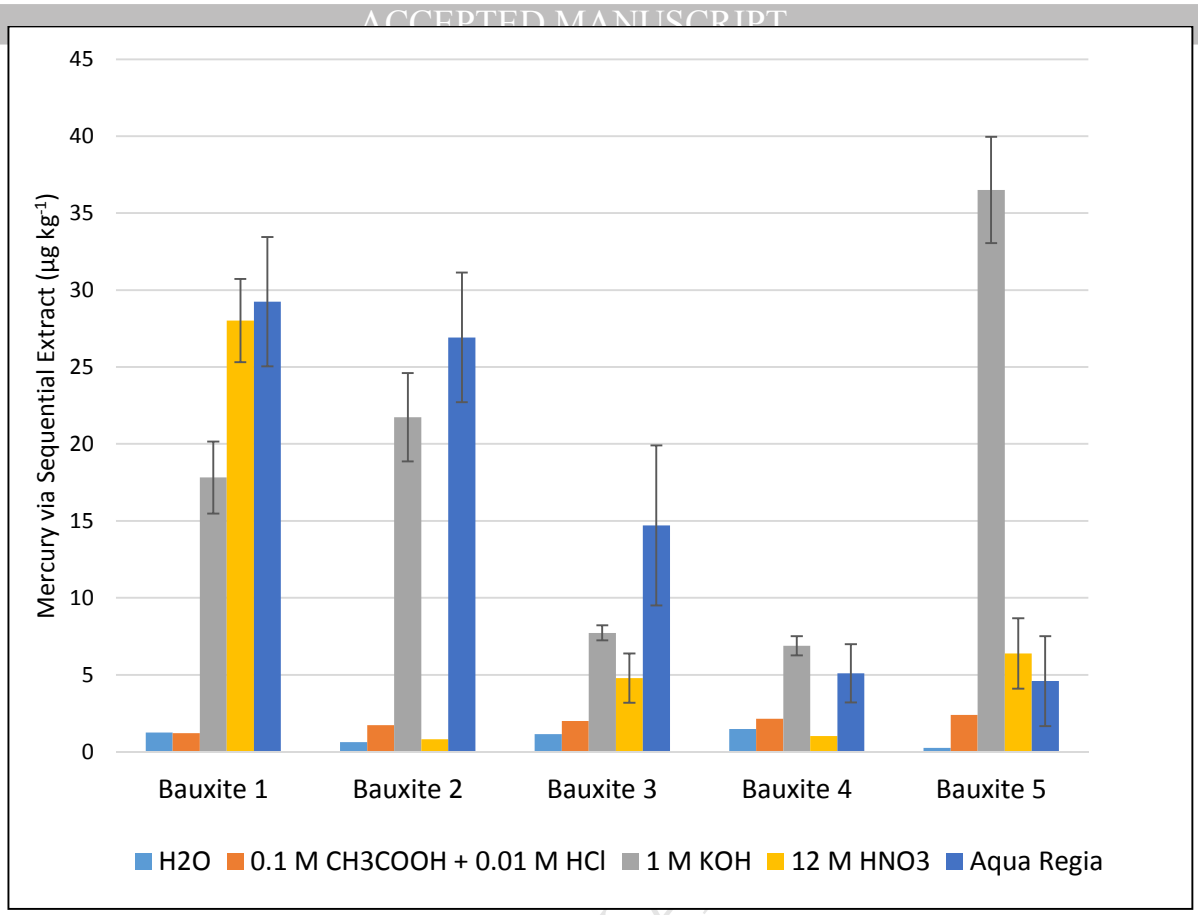


Figure 1. Sequential extraction of bauxite (5 replicates).

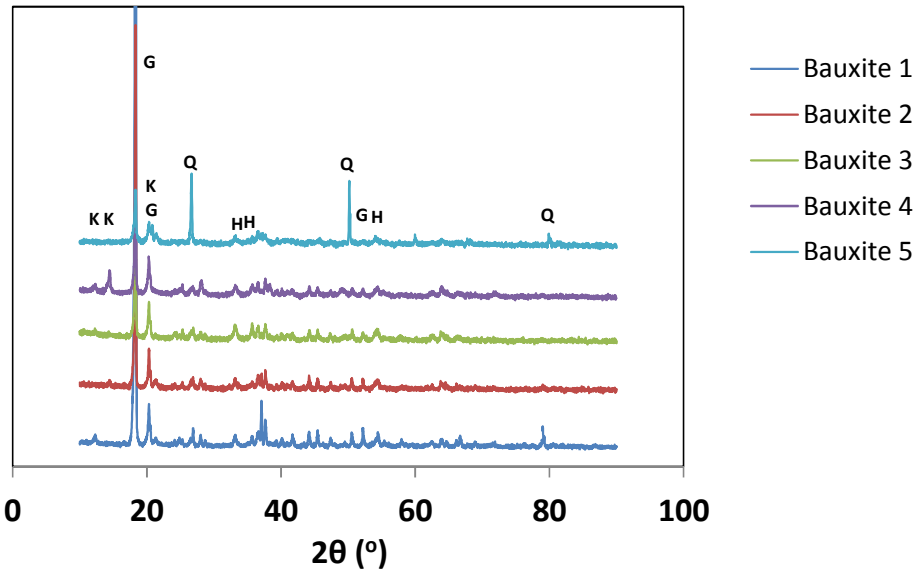
Table 1. Percent fraction of sequentially extracted mercury *(data below limits of detection omitted).*

	H_2O	**0.1 M CH_3COOH \ 0.01 M HCl**	**1 M KOH**	**12 M HNO_3**	**Aqua Regia**
Bauxite 1	-	-	23.7	37.3	39.0
Bauxite 2	-	-	44.7	-	55.3
Bauxite 3	-	-	28.4	17.6	54.0
Bauxite 4	-	-	57.5	-	42.5
Bauxite 5	-	-	76.9	13.4	9.7

Fraction 4 (12 M HNO_3) is the first fraction which is strongly acidic and oxidising. It is remarkable that a high proportion of mercury in bauxite 1 was extracted in this fraction, while a minimal amount of mercury was extracted from bauxite 2. Notionally this implies an absence of

elemental mercury in bauxite 2, due to the poor kinetics of cinnabar dissolution in nitric acid, which lacks a strong mercury complexing ligand (Mikac et al., 2003). The redox potential required to preferentially enrich gibbsite and leach iron during bauxitisation is sufficiently reducing to render elemental mercury thermodynamically stable (Petersen, 1971). However, outside of certain hydrothermal deposits and as a minor phase in cinnabar-rich ores, elemental mercury is exceptionally rare (Rytuba, 2003). Hematite, goethite and gibbsite demonstrate substantially increased dissolution kinetics in highly acidic conditions, all of which demonstrates an association with mercury in tropical oxisols (Guedron et al., 2009). In synthetic systems mercury (II) has been found to specifically adsorb to goethite and the gibbsite polymorph bayerite (Collins et al., 1999, Kim et al., 2004), potentially allowing encapsulation to take place during the bauxitisation process, mediated through crystallographic defects. The mercury extracted in fraction 4 may also be indicative of an incomplete extraction of humic acids. It should be noted that sequential extractions at the mercury concentrations analysed here have a poor specificity (Bloom et al., 2003).

Pyrite is susceptible to acidic oxidative dissolution (Bryson and Crundwell, 2014). Although the presence of pyrite cannot be ruled out (Figure 2), the fate of mercury-bound pyrite in fraction 4 is questionable. If the mercury-sulfur bond remains unbroken, mercury is expected to precipitate as metacinnabar, as sulfide is required to solubilise metacinnabar as a polysulfide aqueous neutral (Clever et al., 1985). Sulfide in nitric acid solutions is rapidly oxidised to elemental sulfur and oxyanionic species (Flatt and Woods, 1995).



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194 **Figure 2.** XRD analysis of bauxite samples G: Gibbsite; H: Hematite; Q: Quartz; K: Kaolinite

195

196 All the bauxites released significant quantities of mercury in Fraction 5 (aqua regia), indicating
197 the presence of cinnabar. Bauxites 1, 2 and 3 released most mercury in the strongly acidic and
198 oxidising fractions, reflecting the relatively refractory nature of the mercury bound in these
199 bauxites. Bauxites 4 and 5 were comparatively labile. Table 2 lists the sequential extraction sum
200 total as a percentage of total mercury as determined through total dissolution assay, as well as the
201 specific surface area determined using the Brunauer–Emmett–Teller (BET) theory. Clearly
202 sequential extraction dissolves only a small fraction of total mercury. It is worth noting that there is
203 a loose correlation between lability and surface area, with the exception of bauxite 3. This implies
204 that a physical process such as solution penetration is governing lability, as the solution must
205 diffuse through the mineral matrix, which dissolves incompletely at 25°C. As bauxite 3 is a
206 substantial outlier, it is implied that bauxite 3 contains a significant amount of mercury of a
207 different chemical speciation, refractory to leaching.

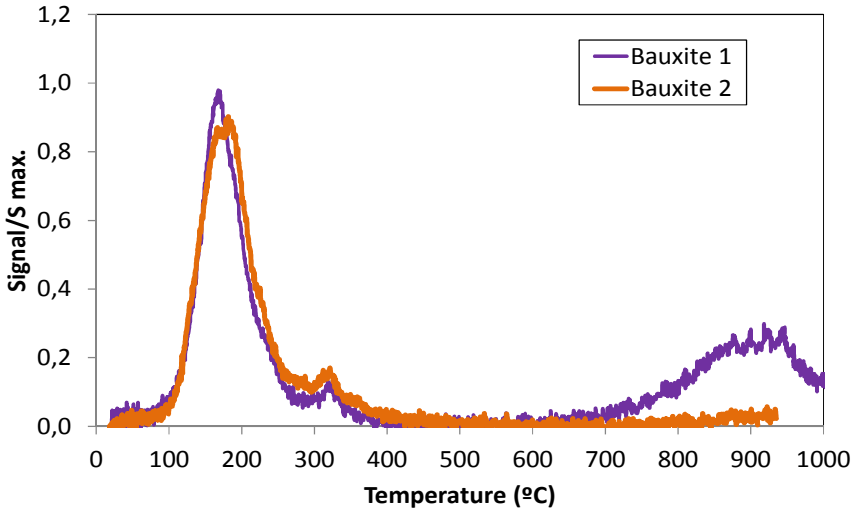
208 **Table 2.** Sum total of sequentially extracted mercury as a percentage of total mercury concentration
209 and BET surface area (5 replicates).

	Bauxite 1	Bauxite 2	Bauxite 3	Bauxite 4	Bauxite 5
Seq. Extr. Total (ng g^{-1})	75 ± 9	49 ± 7	27 ± 7	12 ± 3	48 ± 23
HF Total Dissolution (ng g^{-1})	350 ± 2	218 ± 5	280 ± 3	27 ± 1	82 ± 7
Extraction Efficiency (%)	21	22	10	44	59
BET (m^2 g^{-1})	23	44	73	111	126

210

211 3.2. Continuous thermal desorption

212 The relevant peaks obtained for reference materials are listed in Table 3, including the result of
213 an unknown iron (III) oxide analysis performed by Reis et al. (2015). HgTPD analysis of all the
214 bauxites (Figures 3 and 4) show the main band of desorption as being between 125-325 °C.



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217 **Figure 3.** Thermal profiles of bauxite 1 and 2 obtained by means of HgTPD

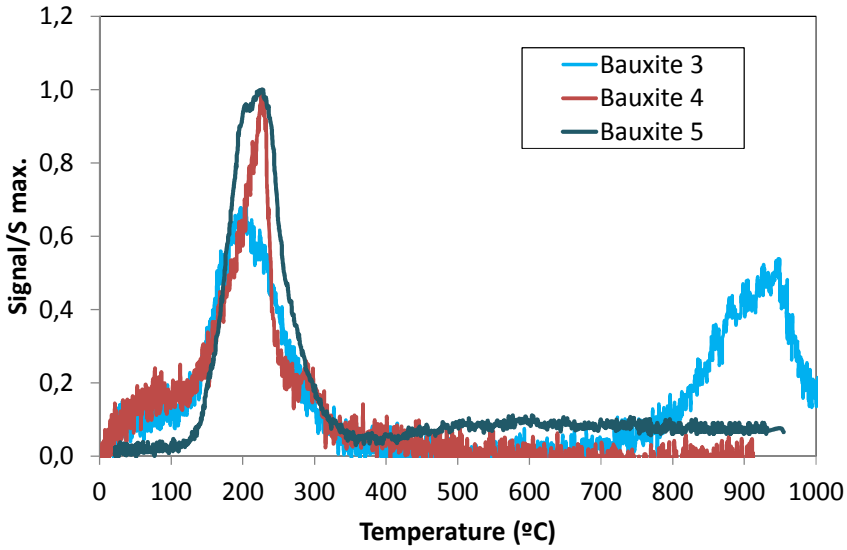

Figure 4. Thermal profile of bauxite 3, 4 and 5 obtained by means of HgTPD

Table 3. HgTPD desorption peaks, as determined by (a) Rumayor et al. (2015c), (b) Reis et al. (2015), (c) Rumayor et al. (2015b) in different species containing mercury

Pyrite (a)	169 °C ± 5
Unknown Iron (III) Oxide (b)	180 °C
Metacinnabar (c)	190 °C ± 11
Humic Acids (c)	220 °C ± 5
Cinnabar (c)	305 °C ± 12
Mercuric Sulfate (c)	583 °C ± 8

Identification of the species in the low temperature desorption band is difficult. The sequential extraction for bauxite 5 indicate a strong association with organics. However, it has a lower temperature peak which is closer to metacinnabar. The humic acid standard referenced here is acid-soluble by definition and centrifuged to achieve phase separation. Organics in bauxite are a complex assemblage of macromolecular humic substances, and slight changes in temperature peaks are to be expected with varying composition. The varying porosity of the bauxites may also reasonably be expected to affect the desorption kinetics.

Cinnabar is the thermodynamically stable mercuric sulfide phase at ambient temperatures, and the desorption data recorded would seemingly eliminate cinnabar as a major mercury sink. However, in soils exposed to mercury contamination in the 1960's, metacinnabar was found to be the predominant phase (Barnett et al., 1997). The organic content in lateritic bauxite is the result of a dynamic process, the leaching and mechanical weathering of soil matter in the surface horizon (Power et al., 2011). The mercury present in surface organics is a product of biogeochemical cycling and is predominantly metacinnabar in the anoxic layer. Moreover, the high binding potential of mercury with sulfur ligands in humic substances favours the mercury-organics association, and organics are known to stabilise metacinnabar in solution (Deonarine and Hsu-Kim, 2009, Ravichandran, 2004). Therefore, organics are a source of both mercury and sulfur, and may mobilise metacinnabar to the bauxite horizon. In this case, the low temperature desorption band for all the bauxites may be taken to be indicative of organics and-or metacinnabar.

Bauxites 1 and 2 show a small, but definitive, cinnabar peak. It is unlikely that cinnabar exists in the absence of metacinnabar, and the major low temperature peak may be assumed to contain a metacinnabar contribution.

Bauxites 1 and 3 show a broad high temperature peak, above 900 °C (Figures 3 and 4). This peak matches no known reference material. The highest desorption temperature recorded is 583 °C for mercuric sulfate (Table 3). Bauxite 3 contains a substantial concentration of this unknown mineral phase, and this chemical difference is the source of its refractory response to sequential extraction. Bloom et al. (2002) demonstrated that a variety of bauxites require temperatures in excess of 900 °C to achieve complete liberation of mercury. To obtain a similar result using an aqueous digestion hydrofluoric acid (HF) was required, reflecting an association with refractory silicates. The inadequacy of aqua regia digestions and the requirement of HF to release all mercury was similarly encountered by Bloom et al. (2002). Gibbsite is highly soluble in strong acids (Dietzel et al., 2005), and kaolinite rapidly decomposes to release metal cations (Carrol & Walther, 1990),

leaving quartz and other refractory silicates the mineral phases insoluble in strong acid digestion without HF.

Table 4 compares the total mercury concentrations using hydrofluoric acid total dissolution, aqua regia digestion and the alkaline digestion method at 140 °C using Bayer liquor. The mercury content for alkaline digestion was determined by thermal desorption analysis of the residue at 750 °C and a subsequent mass balance. Once extracted to solution, mercury is easily desorbed from the residue as the elemental species, since digestion conditions are highly reducing (Bansal et al., 2014b).

Table 4. Bauxite total mercury concentration as determined by total dissolution, aqua regia digestion and alkaline digestion methods (5 replicates).

	Bauxite 1	**Bauxite 2**	**Bauxite 3**	**Bauxite 4**
HF Total Dissolution (ng g^{-1})	350 ± 2	218 ± 5	280 ± 3	27 ± 1
Aqua Regia Digestion (ng g^{-1})	272 ± 13	226 ± 10	136 ± 9	36 ± 4
Alkaline Digestion (ng g^{-1})	363 ± 6	224 ± 6	280 ± 3	25 ± 2

The close correlation of alkaline digestion with the total dissolution results (Table 4) indicates complete extraction of mercury. This would seemingly indicate that mercury is not associated with quartz, as alkaline quartz dissolution at 140 °C is insignificant (Oku & Yamada, 1971). Bauxite 3 shows minor quartz peaks in the XRD analysis (Figure 2) and a silica content of 3 % (Table 5). Furthermore, Figures 3 and 4 clearly demonstrate that high temperature desorption of mercury is isolated to bauxites 1 and 3. Table 4 demonstrates aqua regia digestion extracted all mercury, except in the case of bauxites 1 and 3. This refractory mercury was extracted with the addition of HF to the aqua regia digestion. This is contradictory of the alkaline digestion data, as it strongly implies that refractory mercury is associated with quartz and other refractory silicates.

Table 5. Elemental composition as determined by XRF, presented as percentages of oxide

	LOI	Al_2O_3	Fe_2O_3	SO_3	SiO_2	TiO_2
Bauxite 1	28.7	53.9	10.3	0.08	5.3	1.5
Bauxite 2	26.3	48.6	19.9	0.08	2.0	2.7
Bauxite 3	25.5	47.2	21.0	0.06	3.0	2.8
Bauxite 4	24.1	53.2	13.2	0.06	6.5	2.6
Bauxite 5	21.0	39.8	17.0	0.14	20.1	1.3

The results obtained by HgTPD suggest that the high-temperature release of mercury could be sulfate-associated (Table 3). This association may develop as sulfide associated mercury is oxidised. Alunite is a basic potassium aluminium sulfate that is known to be present in bauxite and undergoes substantial thermal decomposition in excess of 800 °C as the sulfate sublimates (Foldvari, 2011). However, basic sulfate minerals of similar composition, such as jarosite, are dissolved easily in aqua regia digestion (Basciano & Peterson, 2008). Table 4 demonstrates that this does not occur for the refractory mercury in bauxites 1 and 2. Taking into account also that alunite is a rare mineral in bauxite, alunite is an unlikely candidate.

As the complete extraction of mercury using alkaline digestion at 140 °C renders hematite, goethite, boehmite and quartz as unlikely sources, and sulfidic mercury is proven to desorb at low temperature, it could be proposed that the mercury is strongly bound to either gibbsite or kaolinite, both of which are soluble or decompose in alkaline digestion. This implies incorporation into the mineral lattice as opposed to specific adsorption. Isomorphous and interstitial substitutions are unlikely. However, in trace concentrations and in the presence of nanoparticulate mesocrystals, unorthodox reactions can occur, as demonstrated by data suggesting the structural incorporation of oxidised mercury into growing nanoparticulate goethite (Kim et al., 2007). This proposition of mercury associated with amphoteric species is contradicted by Table 4, as gibbsite and kaolinite will dissolve or decompose respectively in aqua regia digestion.

Alternatively, it is possible that the bauxitic quartz in this instance is nanocrystalline, has high surface energy and therefore is susceptible to alkaline digestion at low temperature. A similar suggestion may be made for feldspars, and both are tectosilicate parent minerals in bauxite.

Tremblay et al. (2014) reported that noble gases can be incorporated into quartz and feldspars through their presence in the melt, and elemental mercury shares their neutral, volatile character, and lack of silicate chemical reactivity. Dissanayake and Vincent (1975) proposed the incorporation of mercury into a distortion of the hole in the 12 membered ring of the feldspar framework. Therefore, it is possible that trace mercury concentrations are released in solution through the dissolution of nanocrystalline quartz particles.

Laskou et al. (2006) performed an emanation thermal analysis (ETA) of bauxite, whereby recoil energy produced by the spontaneous alpha decay of the radium isotope solution results in the penetration of radon gas. Radon is subsequently released through thermal desorption, with an order of magnitude increase in the radon emanation rate post 900 °C, due to increased structural disorder in the mineral phase. Subsequently the emanation rate declines, due to sintering of the bauxite macrostructure. The effect is very similar to that observed for thermal desorption of bauxitic mercury. ETA analysis of quartz demonstrates a similar increase in kinetics, but without a subsequent decrease in rate due to sintering (Balek et al., 1995). If mercury is transformed by a redox reaction at high temperature, and thermally desorbs as the elemental species and not a charged ionic gas, the kinetics of solid state diffusion then desorption of the elemental gas are likely similar to neutral gases of similar atomic radius such as radon.

4. Conclusions

The geochemical speciation of mercury in bauxites was evaluated using sequential extractions, continuous thermal desorption and alkaline digestion methodologies. Sequential extractions indicated the relative lability of bauxitic mercury, and some correlation between lability and specific surface area. All the bauxites showed a main low-temperature band during thermal desorption, indicative of mercury associated with organics or metacinnabar. Bauxites 1 and 2 showed a definite cinnabar peak, probably coexistent with metacinnabar. Bauxites 1 and 3 exhibited

a very high-temperature desorption peak, associated with refractory bauxitic mercury. The use of thermal desorption and wet chemical methods isolates the unidentified mineral phase to mercury associated with quartz and other refractory silicates.

Acknowledgments

Financial support for this research was provided Rio Tinto and by the project GRUPIN14-031.

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423 **Figure captions**

424 **Figure 1.** Sequential extraction of bauxite (5 replicates).

425 **Figure 2.** XRD analysis of bauxite samples G: Gibbsite; H: Hematite; Q: Quartz; K: Kaolinite

426 **Figure 3.** Thermal profiles of bauxite 1 and 2 obtained by means of HgTPD

427 **Figure 4.** Thermal profile of bauxite 3, 4 and 5 obtained by means of HgTPD

- Mercury is present in bauxite at trace concentrations
- Thermal desorption is utilised as a novel technique for mercury geochemical speciation
- Mercury species in bauxite are distinctly refractory or labile to thermal desorption
- Hydrofluoric acid dissolution assay is required to determine total mercury concentration