Identification of mercury species in minerals with different matrices and impurities by thermal desorption technique

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Abstract

Because of its low concentration, its unique physico-chemical properties and the analytical difficulties associated with its measurement, the determination of mercury species in solids is not an easy task. Thermal desorption (HgTPD) is an attractive option for the identification of mercury species in solids due to its simplicity and accessibility. However, there are still issues that need to be solved for it to reach its full potential. One such issue is the availability of reference materials that will reproduce real mercury associations. The novelty of this study is the use of six uncommon mercury minerals, taken from around the world, and a sphalerite sample to expand the data base of reference materials for mercury speciation by thermal desorption at programmed temperature. In addition, by using such materials, a number of matrix effects can be ascertained. Different mercury associations were identified depending on the temperature of desorption, thereby validating the thermal desorption as a reliable technique for mercury speciation in solid samples and as a consequence improving the knowledge of the geochemistry of mercury in the environment.

Keywords: mercury; minerals; thermal desorption; speciation; geochemistry

1. Introduction

Mercury is a metal that is well-known for its high toxicity and detrimental effects on health and the environment (WHO 2017). This unquestionable concern makes the identification of mercury species in solids critical for understanding and monitoring mercury-contaminated materials and soils. The Global Mercury Cycle is one of the most interesting and scientifically challenging biogeochemical cycles at the Earth`s surface. A particular mercury speciation determines its bioavailability, environmental mobility and toxicity. Moreover the mode of occurrence of mercury also determines the choice of a suitable remediation method for its control (Rallo et al. 2012).

A variety of techniques have already been studied to identify mercury species in solids. The most consistent are: (i) sequential selective extractions (SSEs) (Biester and Scholz 1996; Bloom et al. 2003; Han et al. 2003; Issaro et al. 2009), (ii) extended X-ray absorption fine structure spectroscopy (EXAFS) (Huggins et al. 2003; Kim et al. 2003; 2004[6-8] and (iii) thermal programmed desorption (HgTPD) (Biester et al. 2002; Raposo et al. 2003, Reis et al. 2012; Rumayor et al. 2013; 2016). Each one of these techniques has inherent methodological limitations. SSEs is lacking in selectivity, EXAFS has high limits of detection (1 mg kg^{-1}), and in HgTPD matrix effects may be missed due to the common use of pure mercury compounds as reference materials. HgTPD is an easily accessible technique that can be implemented with simple instrumentation and requires less time for sample pre-treatment than EXAFS and SSE. However, the validity of the HgTPD method must remain open to doubt until the influence of several parameters upon the results can be clearly established. Among these parameters, matrix effects are a clear priority.

Although the dilemma about the best method for mercury speciation has not been solved, in the present study the method of HgTPD has been chosen and refined. Up until now the identification of mercury species in solids by HgTPD relied on the comparison of a sample desorption profile with the desorption profiles of commercial pure compounds (Lopez-Anton et al. 2010; Rumayor et al. 2013). However, the selection and preparation of other mercury reference materials is a key issue that needs to be addressed to account for potential matrix effects and to confirm the reliability of the technique. There is a need to determine whether the thermograms obtained with mercury pure compounds correspond with those obtained from real samples where the mercury species are associated to complex matrices. In addition, it is necessary to identify mercury species in common and rare mineral phases, such as sphalerite, edgarbaileyite, myrickite, and others, that are present in nature. Once each mercury species is matched to a characteristic desorption temperature, the HgTPD method will allow the identification of mercury species in contaminated and natural associations, which is the final goal pursued with this study.

Although mercury is mostly found in nature in the form of cinnabar (red HgS), and this is the primary mercury species to be used as a mercury reference, mercury can also be found in a wide range of complex minerals and complementary polymetallic ores such as livingstonite ($HgSb_4S_8$), corderoite ($Hg_3S_2(Cl,Br)_2$, edgarbaileyite ($Hg_6Si_2O_7$), etc. (Kozin et al. 2015). Some of these minerals can be found in areas close to mercury mining and processing activities which are sources of pollution regarded as of primary environmental concern (Jiménez-Moreno et al. 2016; Kobal et al. 2017; Matanzas et al. 2017; Yin et al. 2017). The analysis of the minerals containing mercury by HgTPD may be a useful tool for identifying sources of pollution related to mercury-mining or

metallurgy and for distinguishing them from other sources such as coal combustion or chlor-alkali industry.

These minerals are difficult replicate from the pure species that constitute the mercury reference materials. For example, edgarbaileyite is the first reported structure to contain both Hg and Si (Angel et al. 1990). It is also difficult to prepare standards that simulate other mercury sources in nature such as sphalerite, where mercury is often present as an impurity usually related to Zn smelters. Intrusive magmatic rocks and subaerial and submarine volcanic regions may contain high mercury concentrations. In these rocks values may be as high as several percent in ore-grade minerals (e.g., 35% mercury in sphalerite) (Ozerova 1996). Mercury desorption in these types of minerals and rocks has barely been studied although potentially they represent significant natural standards required for applying the HgTPD technique on the basis of their characteristic mercury desorption temperatures. To fill this gap, in this study a series of mercury minerals and rocks are evaluated by thermal desorption, improving the current database on the basis of which mercury species can be identified from their desorption temperature.

2. Experimental part

2.1 Mineral samples

Six mercury-containing mineral samples (coloradoite (Mine Bessie G, La Plata, Colorado, USA), edgarbaileyite (Clear Creek, S. Benito, California, USA), myrickite (Myrick Spring, Napa, California, USA), livingstonite (Guadalcazar, Potosí, Mexico), terlinguaite (Emerald Lake District, San Mateo Country, California, USA) and corderoite (Mine Usagre, Badajoz, Spain) and a sphalerite mineral (Mine Troya, Mutiloa, Guipuzkoa, Spain) were chosen for assessing the potential of HgTPD analysis

(Figure 1). The samples constitute a broad spectrum, including a natural mercury silicate (1 sample), natural mercury sulphides (4 samples), a natural mercury telluride (1 sample), and a natural mercury oxychloride (1 sample).

The grinding and homogenization of mineral samples for their analysis was carried out by crushing the sample in a mortar to a particle size < 0.1 mm. The composition of the mineral and its impurities was identified by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Analytical Systems (EDAS). The analysis was performed in the samples before and after grinding.

2.2 Hg-thermo-desorption device

The HgTPD device consists of a temperature-programed furnace coupled to a PYRO 915 furnace from LUMEX and a continuous mercury analyzer (RA-915) (Rumayor et al 2015a). The peculiarity of this device, developed by the authors (Rumayor et al 2015b), is that the mercury species are desorbed in the first furnace using N_2 as an inert gas, while at the same time O_2 is introduced into the PYRO furnace to ensure the total decomposition of volatile matter. The solid is weighed in a sample boat where temperature is controlled by a thermocouple. Desorption profiles are obtained by heating the sample at a rate of 50 °C min^{-1} under a N_2 flow of 500 mL min^{-1}. The PYRO 915 unit is kept approximately at 800ºC under an O_2 flow of 500 mL min^{-1}. In this unit all mercury species, vaporized from the sample in the inert atmosphere, are transformed into elemental gaseous mercury (Hg^0).

As Hg^0 reaches de detector in the continuous analyzer, the software registers temperature or time versus mercury and records the desorption profiles that correspond to evaporation of the mercury species present in the sample. As already described, each desorption peak is assigned to each species of mercury by using the reference data base

of different pure mercury compounds. The pure compounds used in this work as reference were Hg^0 and HgS, as they are the most likely species to be present in mercury minerals, and HgO and $HgCl_2$, which are also possible. All samples were analyzed sequentially with the reference pure compound.

Overlapping peaks were deconvoluted using Origin 6.0 software.

3. Results and discussion

The thermograms of the mercury pure compounds and mineral samples containing mercury are shown in Fig. 2. Table 1 shows the maximum temperature of decomposition (high peak temperature) of each pure mercury compound registered in Fig. 2A. The precision of the analysis has been established from the results of the standard deviation obtained after analyzing each sample in triplicate.

Fig. 2B shows the thermal desorption profile of sphalerite. Sphalerite ((Zn, Fe) S) is not a mercury mineral, it is a zinc sulfide mineral in crystalline form with variable amounts of iron (0.3-2.5 wt%) (Grammatikopoulos et al. 2006), usually found in association with dolomite ($CaMg(CO_3)_2$) and siderite ($FeCO_3$) (Fig. 1A, Fig. 3). However, this mineral may also contain variable amounts of mercury (0.1-16% wt%) (Grammatikopoulos et al. 2006). Sphalerite is usually associated with cinnabar and several sulfides, sulphosalts and non-opaque minerals. The thermogram of mercury species from the sphalerite sample analyzed showed a broad peak between 400-1000ºC (Fig. 2B). This wide band does not correspond to the signal of any of the pure mercury compounds studied so far, suggesting that mercury with Zn and Fe sulfide may form stronger associations that result in these high desorption temperatures. Mercury in sphalerite could be also found as HgS impurity. In fact, the thermogram of this mineral showed a small peak around 200ºC that can be assigned to HgS (Fig. 2B).

Coloradoite is the name of the mercury telluride (HgTe) mineral (Fig. 1C). It is a telluride ore associated with metallic deposits (especially gold and silver) (Fadda et al. 2005). It is a mineral that belongs to group 16 of the chalcogen family of elements, which includes HgS. Even though the type of thermal desorption could be expect to be slightly different than that of HgS, by similarity to was observed to occur with the halide family (Lopez-Anton et al. 2010; Rumayor et al. 2013), the analysis by HgTPD showed that the maximum desorption peak of coloradoite overlaps with that obtained for HgS (Fig. 2C). It should be noticed that the analysis by SEM/EDAS (Fig. 4) of the mineral individual particles before and after grinding confirms that the only mercury species in the sample studied was HgTe.

Myrickite is the name for both agatized and opalized cinnabar (HgS SiO_2) (Fig. 1B) It is only found overlying gold deposits. Analysis by SEM/EDAS of the sample corroborated the HgS/SiO_2 association (Fig. 5a). The presence of SiO_2 in the mineral's structure has a considerable impact on the temperature of mercury release. As it can be seen in Fig. 2D, the peak of mercury desorption from this mineral moved to higher temperatures than the characteristic peak of HgS (Fig. 2D). This result suggests that the SiO_2 in myrickite makes the binding of mercury stronger than in pure HgS. This behavior was not observed when HgS and SiO_2 were mixed from individual species (Lopez-Anton et al. 2010; Rumayor et al. 2013). Therefore, myrickite becomes an essential natural standard to be considered in HgTPD analysis.

Terlinguaite is a naturally occurring mineral with the formula Hg_2ClO that is formed by weathering of other mercury minerals (Hillebrand and Schaller 1907). Its color is greenish yellow (Fig. 1D). The association of mercury with chlorine and oxygen in the terlinguaite sample studied was demonstrated by SEM/EDAS (Fig. 5b). Terlinguaite showed a wide band between 300-1000ºC (Fig. 2E). A narrow peak at

approximately 40ºC due to the impurity of elemental mercury is observed. The wand band, which could be characteristic of this mineral, does not correspond to the signal of any of the pure mercury compounds studied so far. The high temperature that it is necessary to decompose this mineral (close to 1000ºC) would explain why some researchers (Bloom et al. 2002; Staun et al. 2018) have observed that a variety of samples require temperatures above 900 °C to achieve complete liberation of mercury, and suggest that is due to an association with refractory silicates. According to SEM/EDAS (Fig. 5b), a remarkable concentration of Si is present in this mineral sample, with what the Hg_2ClO-Si association cannot be ruled out.

Corderoite is a mercury sulfide chloride mineral ($Hg_3S_2Cl_2$) (Fig. 1E) that occurs as isolated grains or together with cinnabar. Corderoite occurs as a low temperature supergene mineral (Foord et al. 1974). The analysis of its particles by SEM/EDAS showed that the sample studied did not contain other mercury species in significant concentrations (Fig. 6b). However, the thermogram of this mineral made it possible to identify three mercury species: Hg^0, $HgCl_2$ and HgS (Fig. 2F). The presence of three possible peaks when the desorption profile was deconvoluted suggests that the thermal decomposition of $Hg_3S_2Cl_2$ could take place during desorption, and this could happen via reactions 1 and 2 (Lopez-Anton et al. 2010; Rumayor et al. 2013; Cotte et al. 2006).

$$Hg_3S_2Cl_2 \rightarrow Hg_2Cl_2 + S + HgS \quad (1)$$

$$Hg_2Cl_2 \rightarrow HgCl_2 + Hg^0 \quad (2)$$

At this point it should be mentioned that analysis by HgTPD would also allow to follow the effect of temperature on the decomposition of the mercury species.

Livingstonite ($HgSb_4S_8$) is a mercury mineral of a gray steel color (Fig. 1F). It occurs in low-temperature hydrothermal veins mainly associated with cinnabar, stibnite,

sulfur and gypsum. Particles containing Hg/Sb/S were identified by SEM/EDAS analysis (Fig. 7a). Its thermal behavior was similar to that observed for pure HgS, with a maximum decomposition temperature of approximately 155ºC (Table 1, Fig. 2G). The presence of Sb did not modify the thermal behavior of pure HgS.

The identification of mercury species was completed with the inclusion of the thermal profile of edgarbaileyite, ($Hg_6Si_2O_7$) (Fig. 1G), the first structure reported to contain both Hg and Si (Fig. 8). It occurs as a secondary mineral and is probably the result of the reaction of mercury with quartz in conditions that so far have not been completely understood (Angel et al. 1990). The results of HgTPD (Fig. 2H) showed the following signals: (i) a narrow peak corresponding to Hg^0. As occurred in terlinguaite and corderoite, it is an impurity that is often found in these types of mercury minerals, (ii) a short peak at approximately 150ºC corresponding to HgS, the most abundant mercury mineral in nature and probably present as an impurity and (iii) a broad band between 200-850ºC with two main peaks corresponding to HgO (Table 1). As it can also be observed (Fig. 2A and 2H), the height of each of the HgO peaks depends on the sample matrix.

It must be emphasized that sulfurized mercury minerals like myrickite (HgS SiO_2) or corderoite ($Hg_3S_2Cl_2$) showed different thermograms than those obtained for pure HgS. Thus, HgTPD may be a useful tool to help understand the possible degradation or change of color of cinnabar (HgS) in different materials.

4. Conclusions

Thermal desorption profiles of mercury rare minerals and mercury species in mineral matrices are presented for the first time. Different profiles were obtained

depending on the mineral and the type of mercury association in the mineral. The results confirm that certain species of mercury are desorbed at the same temperature regardless of their matrix (livingstonite, coloradoite). However, certain matrices can affect the desorption temperature of mercury species (HgS SiO_2 (myrickite)). This is very important when comparing mercury desorption temperatures of real samples with those obtained with mercury standards prepared in the laboratory.

The data obtained in the analysis of minerals containing mercury performed in this work allow the HgTPD technique to be applied to the identification of possible uncommon sources of mercury pollution in areas such as mining where some of the minerals studied in this work might be found. Moreover, unlike most commercial analyzers, the HgTPD device employed in this work may reach temperatures of 950ºC, making it possible to identify unknown refractory mercury bearing phases.

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References

Angel RJ, Gressey G, Criddle A (1990) Edgarbileyite, $Hg_6Si_2O_7$: The crystal structure of the first mercury silicate. Am Mineral 75:1192-1196.

Biester H, Müller G, Schöler HF (2002) Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. Sci Total Environ 284:191-203. https://doi.org/10.1016/S0048-9697(01)00885-3.

Biester H, Scholz C (1996) Determination of Mercury Binding Forms in Contaminated Soils: Mercury Pyrolysis versus Sequential Extractions. Environ Sci Technol 31:233-239. https://doi.org/10.1021/es960369h.

Bloom NS, Preus E, Katon J, Hiltner M (2003) Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. Anal Chim Acta 479:233-248. https://doi.org/10.1016/10.1016/S0003-2670(02)01550-7

Bloom NS, Vondergeest V, Preus E (2002) Intercomparison of four methods for the determination of total mercury in recalcitrant solids. Annual Meeting of SETAC Europe, 347-348, Vienna.

Cotte M, Susini J, Metrich N, Moscato A, Gratziu C, Bertagnini A, Pagon M (2006) Blackening of Pompeian cinnabar paintings: X-ray microspectroscopy analysis. Anal Chem 78:7484-7492. https://doi.org/10.1021/ac0612224.

Fadda S, Fiori M, Grillo SM. (2005) Chemical variations in tetrahedrite - tennantite minerals from the Furtei epithermal Au deposit, Sardinia, Italy: Mineral zoning and ore fluids evolution. Geochemistry, Mineralogy and Petrology. Bulgarian Academy of Sciences. 43:79–84.

Foord EE, Berendsen P, Storey LO (1974) Corderoite, first natural occurrence of $Hg_3S_2Cl_2$, from the Cordero mercury deposit, Humboldt County, Nevada. Am Mineral 59:652–655.

Grammatikopoulos TA, Valeyev O, Roth T (2006) Compositional variation in Hg-bearing sphalerite from the polymetallic Eskay Creek deposit, British Columbia, Canada. Chemie der Erde – Geochemistry 66:307-314. http://doi:10.1016/j.chemer.2005.11.003.

Han Y, Kingston HM, Boylan HM, Rahman GMM, Shah S, Richter RC, Link DD, Bhandari S (2003) Speciation of mercury in soil and sediment by selective solvent and acid extraction. Anal Bioanal Chem 375:428-436. https://doi.org/10.1007/s00216-002-1701-4.

Hillebrand WF, Schaller WT (1907) The Mercury Minerals from Terlingua, Texas: Kleinite, Terlinguaite, Eglestonite, Montroydite, Calomel, Mercury. J Am Chem Soc 29:1180-1194

Huggins FE, Yap N, Huffman GP, Senior CL (2003) XAFS characterization of mercury captured from combustion gases on sorbents at low temperatures. Fuel Process Technol 82:167-196. https://doi.org/10.1016/S0378-3820(03)00068-7.

Issaro N, Abi-Ghanem C, Bermond A (2009) Frationation studies of mercury in soils and sediments: A review of the chemical reagents used for mercury extraction. Anal Chim Acta 631:1-12. https://doi.org/10.1016/j.aca.2008.10.020.

Jiménez-Moreno M, Barre JPG, Perrot V, Bérail S, Rodríguez Martín-Doimeadios RC, Amouroux D (2016) Sources and fate of mercury pollution in almadén mining district (Spain): Evidences from mercury isotopic compositions in sediments and lichens. Chemosphere 147:430-438. https://doi:10.1016/j.chemosphere.2015.12.094

Kim CS, Bloom NS, Rytuba JJ, Brown GE (2003) Mercury Speciation by X-ray Absorption Fine Structure Spectroscopy and Sequential Chemical Extractions: A Comparison of Speciation Methods. Environ Sci Technol 37:5102-5108. https://doi.org/10.1021/es0341485.

Kim CS, Rytuba JJ, Brown GE (2004) EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides II. Effects of chloride and sulfate. J Colloid Interf Sci 270:9-20. https://doi.org/10.1016/j.jcis.2003.07.029.

Kobal AB, Snoj Tratnik J, Mazej D, Fajon V, Gibičar D, Miklavčič A, Kocman D, Kotnik J, Sešek Briški A, Osredkar J, Krsnik M, Prezelj M, Knap Č, Križaj B, Liang L, Horvat M (2017) Exposure to mercury in susceptible population groups living in the former mercury mining town of idrija, slovenia. Environ Res 152:434-445. https://doi:10.1016/j.envres.2016.06.037.

Kozin LF, Hansen SC, Zakharchenko NF, Gray J (2013) CHAPTER 12 Environmental Aspects of the Industrial Application of Mercury, in: Mercury Handbook: Chemistry, Applications and Environmental Impact. The Royal Society of Chemistry, pp. 209–227. https://doi.org/10.1039/9781849735155-00209.

Lopez-Anton MA, Yuan Y, Perry R, Maroto-Valer MM (2010) Analysis of mercury species present during coal combustion by thermal desorption. Fuel 89:629-634. https://doi.org/10.1016/j.fuel.2009.08.034.

Matanzas N, Sierra MJ, Afif E, Díaz TE, Gallego JR, Millán R (2017) Geochemical study of a mining-metallurgy site polluted with as and hg and the transfer of these contaminants to equisetum sp. J Geochem Explor 182:1-9. http://doi:10.1016/j.gexplo.2017.08.008.

Ozerova NA (1996) Mercury in geological systems, in: Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. Edited by Willy Baeyens, Ralf Ebinghaus and Oleg Vasiliev. Published by Kluwer Academic Publishers, The Netherlands, pp. 463-474. ISBN-13: 978-94-010-7295-3; D0I: 10.1007/978-94-009-1780-4; e-ISBN-13: 978-94-009-1780-4

Rallo M, López-Antón MA, Contreras ML, Maroto-Valer MM (2012) Mercury policy and regulations for coal-fired power plants. Environ Sci Pollut R 19:1084-1096. https://doi.org/10.1007/s11356-011-0658-2

Raposo C, Windmöller CC, Junior WAD (2003) Mercury speciation in fluorescent lamps by thermal release analysis. Waste Manage 23:879-886. https://doi.org/10.1016/S0956-053X(03)00089-8.

Reis AT, Coelho JP, Rodrigues SM, Rocha R, Davidson CM, Duarte AC, Pereira E (2012) Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments. Talanta 99:363-638. https://doi.org/10.1016/j.talanta.2012.05.065.

Rumayor M, Díaz-Somoano M, López-Antón MA, Martínez-Tarazona MR (2013) Mercury compounds characterization by thermal desorption. Talanta 114:318-322. https://doi.org/10.1016/j.talanta.2013.05.059.

Rumayor M, Lopez-Anton MA, Díaz-Somoano M, Martínez-Tarazona MR (2015a) A new approach to mercury speciation in solids using a thermal desorption technique. Fuel 160:525-530. https://doi.org/10.1016/j.fuel.2015.08.028.

Rumayor M, López-Antón MA, Díaz-Somoano M, Martínez-Tarazona MR (2015b) Device for identification of mercury species in solids. Consejo Superior de Investigaciones Científicas (CSIC). Patent ES1641.1031 Application number: P201530310.

Rumayor M, López-Antón MA, Díaz-Somoano M, Maroto-Valer MM, Richard J-H, Biester H, Martínez-Tarazona MR (2016) A comparison of devices using thermal desorption for mercury speciation in solids. Talanta 150:272-277. https://doi.org/10.1016/j.talanta.2015.12.058.

Staun C, Vaughan J, Lopez-Anton MA, Rumayor M, Martínez-Tarazona M.R (2018) Geochemical speciation of mercury in bauxite. Appl Geochem 93:30-35. https://doi.org/10.1016/j.apgeochem.2018.03.007.

WHO (2017) World Health Organization. http://www.who.int/news-room/fact-sheets/detail/mercury-and-health

Yin R, Zhang W, Sun G, Feng Z, Hurley JP, Yang L, Shang L, Feng X (2017) Mercury risk in poultry in the wanshan mercury mine, china. Environ Pollut 230:810-816. http://doi:10.1016/j.envpol.2017.07.027.

Table 1 Characteristic maximum temperature of desorption corresponding to pure mercury compounds.

Mercury compound	**High peak T (ºC)**
Hg^0	46±10
$HgCl_2$	116±9
HgS black	160±12
HgO	280±10; 480±10

Figure captions

Fig. 1 Photographs of mineral samples containing mercury.

Fig. 2 Thermal profiles of A) mercury pure compounds (Hg^0, $HgCl_2$, HgS, HgO), B) sphalerite, C) coloradoite, D) myrickite, E) terlinguaite, F) corderoite, G) livingstonite and H) edgarbaileyite).

Fig. 3 EDX analysis and SEM images of spahlerite.

Fig. 4 EDX analysis and SEM images of coloradoite.

Fig. 5 EDX analysis and SEM images of myrickite and terlinguaite.

Fig. 6 EDX analysis and SEM images of corderoite.

Fig. 7 EDX analysis and SEM images of livingstonite.

Fig. 8 EDX analysis and SEM images of edgarbaileyite.

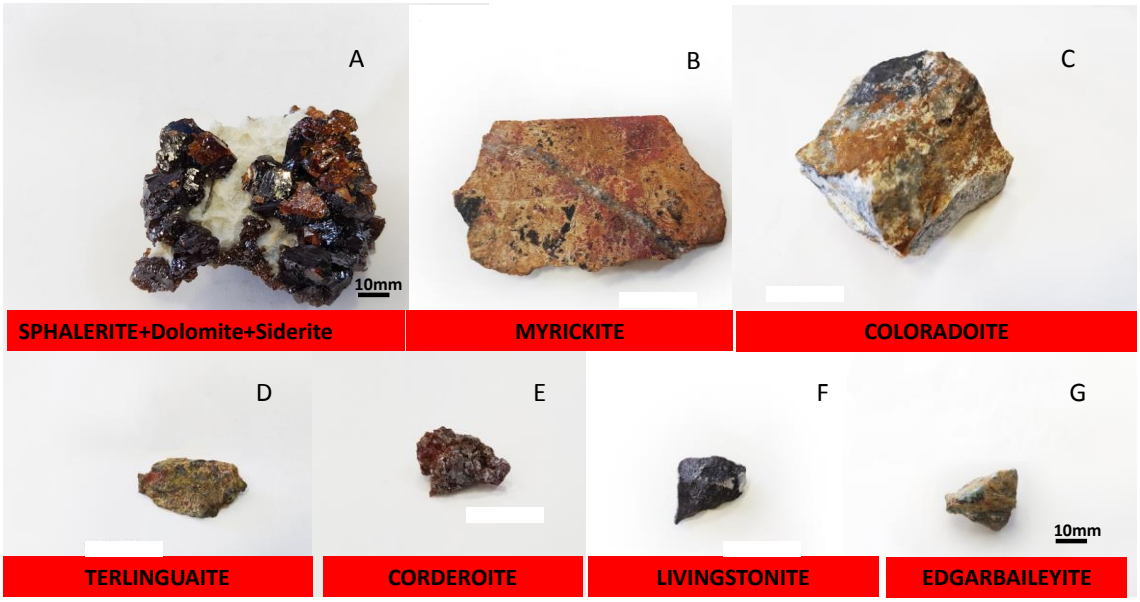

A
10mm
SPHALERITE+Dolomite+Siderite
B
MYRICKITE
C
COLORADOITE
D
TERLINGUAITE
E
CORDEROITE
F
LIVINGSTONITE
G
10mm
EDGARBAILEYITE

Fig. 1

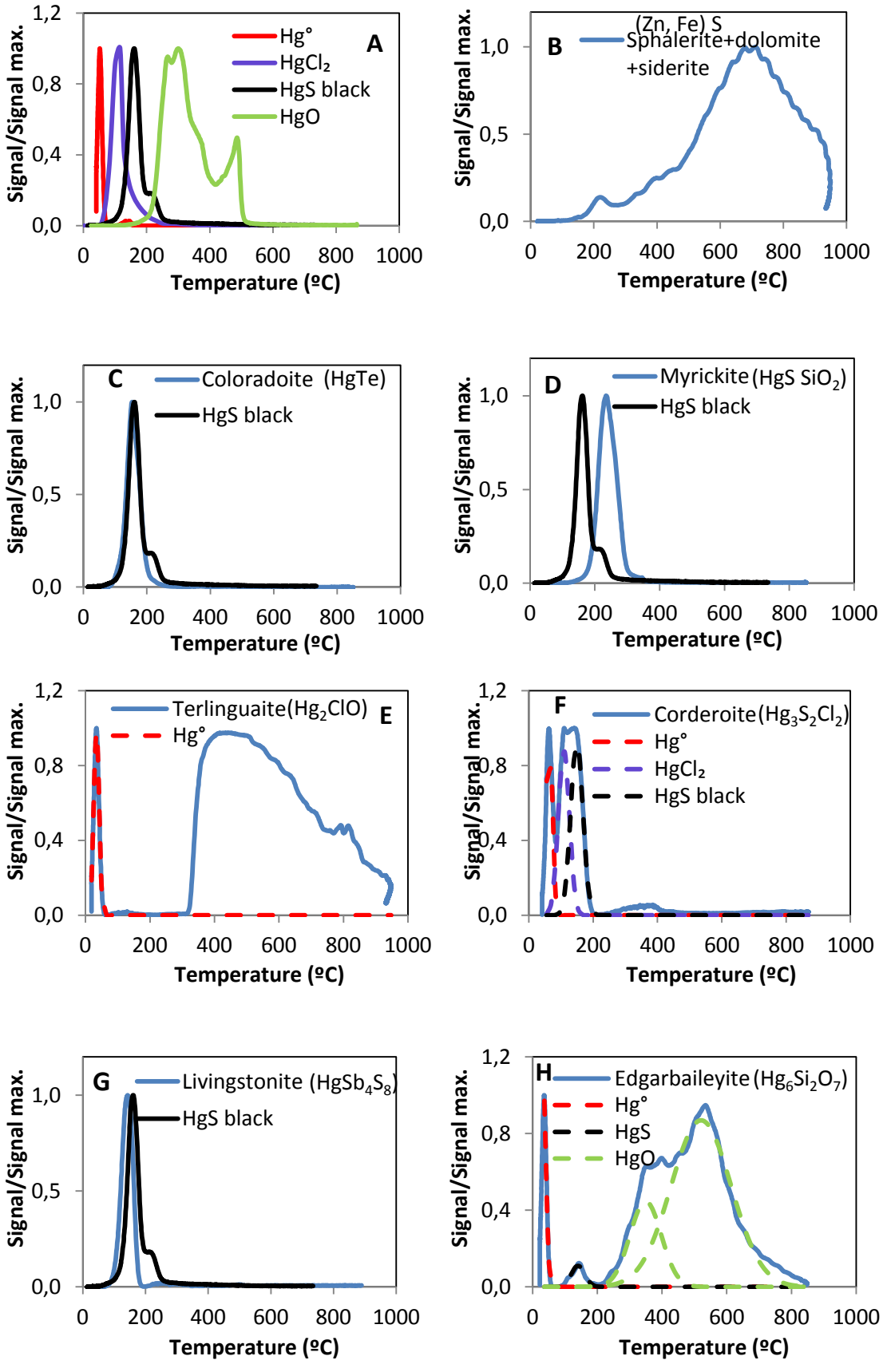

A
Hg°
HgCl₂
HgS black
HgO
B
(Zn, Fe) S
Sphalerite+dolomite
+siderite
C
Coloradoite (HgTe)
HgS black
D
Myrickite (HgS SiO₂)
HgS black
E
Terlinguaite(Hg₂ClO)
Hg°
F
Corderoite(Hg₃S₂Cl₂)
Hg°
HgCl₂
HgS black
G
Livingstonite (HgSb₄S₈)
HgS black
H
Edgarbaileyite (Hg₆Si₂O₇)
Hg°
HgS
HgO
Signal/Signal max.
Temperature (ºC)

Fig. 2

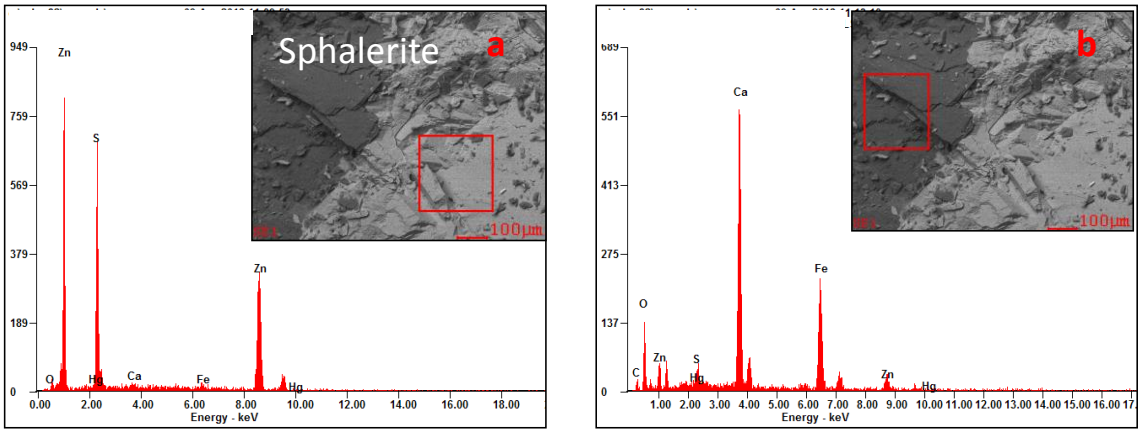
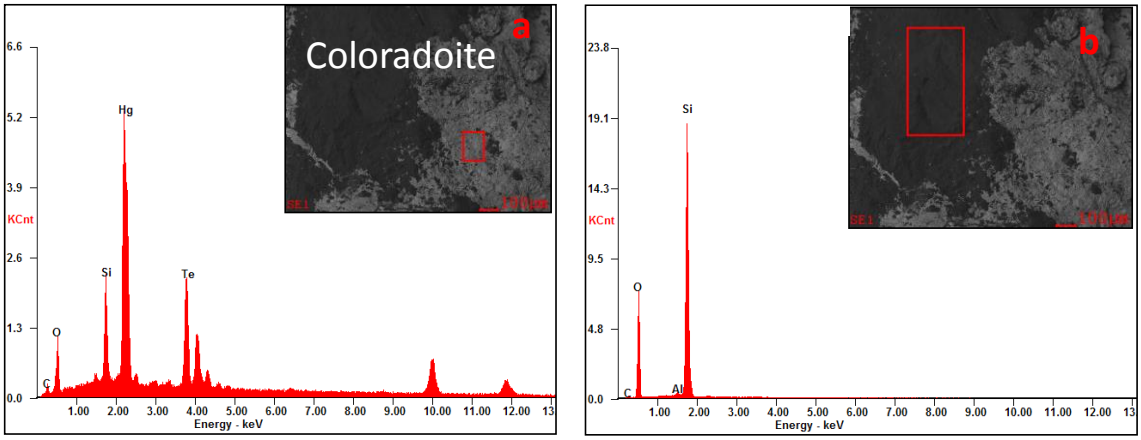


Fig. 3



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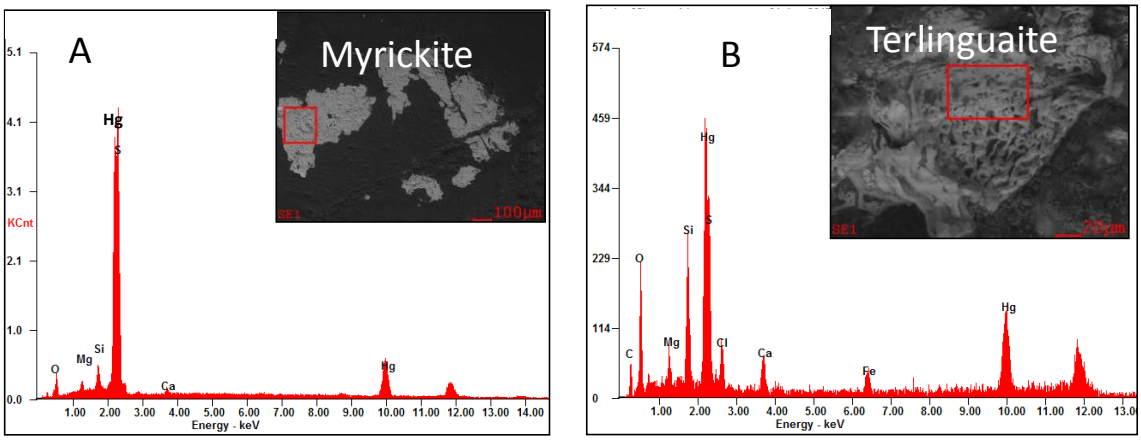

Fig. 5

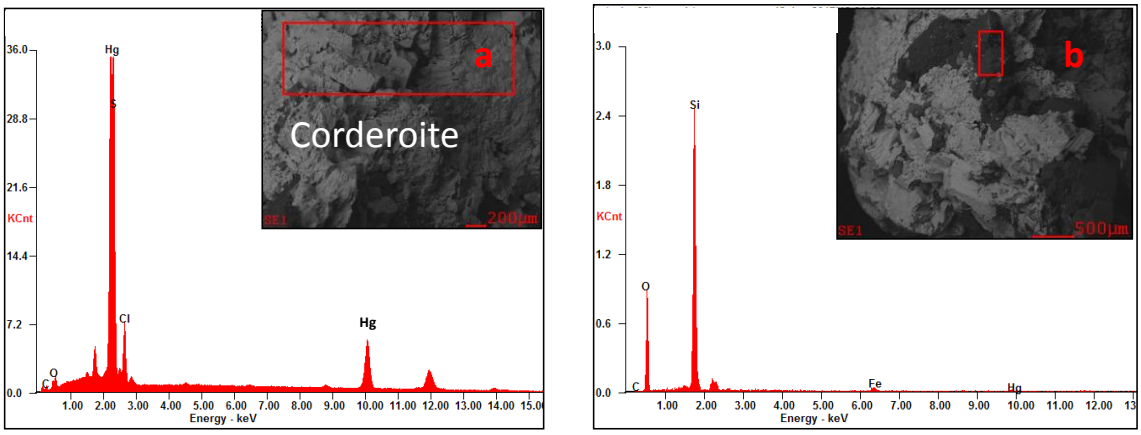

Fig. 6

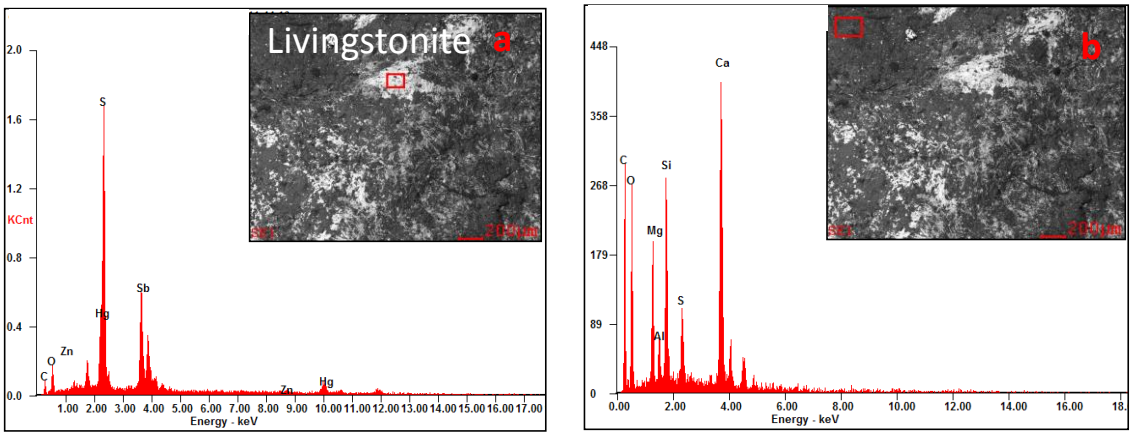

Fig. 7

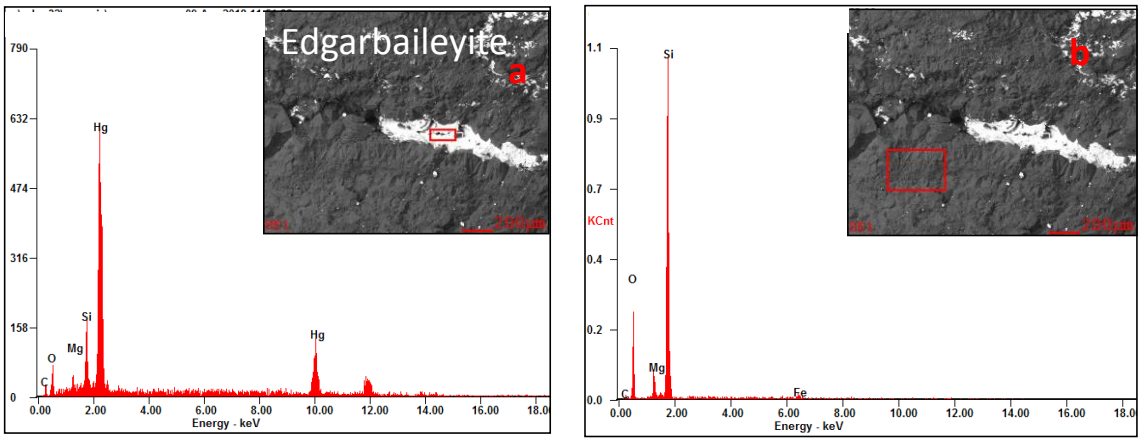

Fig. 8