U/Pb geochronology of wolframite by LA-ICP-MS; mineralogical constraints, analytical procedures, data interpretation, and comparison with ID-TIMS.

Patrick A. Carr¹, Julien Mercadier¹, Matthieu Harlaux², Rolf L. Romer³, Emeline Moreira¹, H Legros⁴, Michel Cuney¹, Christian Marignac¹, Jean Cauzid¹, Lise Salsi¹, Andre Lecomte¹, Olivier Rouer¹ and Chantal Peiffert¹

¹GeoRessources, CNRS, CREGU, Universit de Lorraine, 54000, Nancy, France

²Nevada Bureau of Mines and Geology, University of Nevada, Reno, NV 89557-0178, United States of America

³GFZ German Research Centre for Geosciences, Telegrafenberg, 14473, Potsdam, Germany

⁴Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada

Keywords

Wolframite; U/Pb geochronology; LA-ICP-MS; ID-TIMS; French Massif Central

Highlights

- The MTM-1 wolframite sample is marked by chemical and isotopic heterogeneities which have biased the calculation of the ID-TIMS age
- LA-ICP-MS ages of wolframite from the French Massif Central are geologically more robust compared to ID-TIMS U/Pb ages
- Guidelines for future U/Pb LA-ICP-MS studies on wolframite are recommended

Abstract

Wolframite has been proposed as a U/Pb geochronometer for direct dating of W mineralisation events, but its isotopic analysis may be hampered by highly variable and low U contents (<200 ppm) and low ²⁰⁶Pb/²⁰⁴Pb ratios (<300), heterogenous common Pb compositions, post-crystallisation alteration, and the presence of non-cogenetic mineral and fluid inclusions. In situ U/Pb dating of wolframite by laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) can avoid these analytical challenges but requires reference materials to

properly correct for matrix and instrumental effects on measured U/Pb ratios. This study presents the U/Pb systematics by LA-ICP-MS of a wolframite sample (MTM-1) from the French Massif Central (FMC) which has been considered for normalisation and validation purposes of U/Pb LA-ICP-MS wolframite data in previous studies. We demonstrate that the MTM-1 wolframite is chemically and isotopically heterogeneous, and more importantly, we show that the previously defined ID-TIMS U/Pb age (334.4 ± 1.7 Ma, 2σ) is invalid due to an inappropriate common Pb correction. We calculate a new U/Pb crystallization age of 316.7 ± 5.8 Ma (2σ). Based on our new calibration, we also present the U-Th-Pb trace element and U/Pb ages of six W deposits from the FMC, also previously studied by ID-TIMS. We show that U/Pb ages determined by LA-ICP-MS are more robust and geological plausible compared to ID-TIMS ages obtained on the same samples. The concentrations of U (*ca* 0.1–150 ppm) and Pb (*ca* 0.01–90 ppm) in FMC wolframite are highly variable and do not ubiquitously correlate to major element composition (such as the Fe/(Fe+Mn) ratio). The chemical variability and isotopic heterogeneity observed in wolframite from the FMC highlights the importance of pre-screening imaging methods (e.g., SEM, EPMA, μ XRF) prior to LA-ICP-MS U/Pb analyses. Based on our results, we propose new guidelines for U/Pb LA-ICP-MS wolframite geochronology to increase accuracy and reproducibility in age determinations, as well as improving interlaboratory comparisons.

1. Introduction

Increasingly, U/Pb geochronology has been applied to constrain the absolute timing and duration of W-forming magmatic-hydrothermal systems (e.g., Frei et al. 1998; Romer and Lüders 2006; Pfaff et al. 2009; Wang et al. 2011; Lecumberri-Sanchez et al. 2014; Zhang et al. 2017; Harlaux et al. 2018a; Luo et al. 2019; Deng et al. 2019; Legros et al. 2020; Tang et al. 2020; Yang et al. 2020). Tungsten mineralisation in magmatic-hydrothermal deposits predominantly occurs as scheelite (CaWO_4) and wolframite ($[\text{Fe},\text{Mn}]\text{WO}_4$), the latter corresponding to a solid solution between hübnerite ($\text{Fe}/[\text{Fe}+\text{Mn}] < 0.2$) and ferberite ($\text{Fe}/[\text{Fe}+\text{Mn}] > 0.8$) endmembers (for this paper, we refer to the whole solid solution as wolframite for simplicity). Scheelite is dominated by non-radiogenic Pb (known as common Pb; Pb_c) content due to its isovalent substitution with Ca^{2+} that strongly limits the precision of U/Pb ages (e.g., Poitrenaud et al. 2019). In contrast, Pb is relatively incompatible in wolframite (Harlaux et al. 2018a,b), but U can occur up to 200 ppm and can provide reliable U/Pb ages (e.g., Romer and Lüders 2006). The first applications of U/Pb dating of wolframite were by isotope dilution - thermal ionisation mass spectrometry (ID-TIMS), following the dissolution of between 0.1 to 3 mg of mineral concentrates (Frei et al. 1998; Romer and

Lüders 2006; Pfaff et al. 2009; Lecumberri-Sanchez et al. 2014; Harlaux et al. 2018a; Legros et al. 2020; Yang et al. 2020). Although ID-TIMS is known to produce the most precise U/Pb isotopic analyses, heterogeneous mineralogical and chemical compositions of wolframite can hinder high precision geochronology by this method. Firstly, non-cogenetic mineral inclusions that are relatively enriched in U and Pb (>10 ppm), such as sulphides, xenotime, or monazite, are common in wolframite (Harlaux et al. 2018a; Legros et al. 2020). Such inclusions can be distributed as a complex partially interconnected network within wolframite, and the volume of individual inclusions can be as small as 2–4 μm^3 (Harlaux et al. 2018a). Even if samples are powdered (<30 μm) before washing, micro-inclusions encapsulated in larger wolframite fragments will be shielded from washing acids. Secondly, wolframite potentially has heterogeneous chemical (Harlaux et al. 2018b; Monnier et al. 2019, 2020) and U/Pb isotopic compositions (Deng et al. 2019) that can reflect either primary or secondary (e.g., dissolution-precipitation or alteration) processes with different U/Pb ages and that are difficult to analyse separately by ID-TIMS. Finally, U/Pb isotopic compositions of wolframite by ID-TIMS are commonly discordant in a $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagram and determining crystallization ages require knowledge of the common Pb composition for Discordia anchoring in this diagram or common Pb correction in a $^{207}\text{Pb}/^{235}\text{U}$ vs. $^{206}\text{Pb}/^{238}\text{U}$ diagram (e.g., Harlaux et al. 2018a). Precise common Pb compositions can be obtained from low U/Pb minerals that are assumed to be cogenetic with the wolframite, however, this assumption is not always evidenced.

These mineralogical, chemical, and analytical challenges have recently encouraged the development of U/Pb laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) geochronology applied to wolframite (e.g., Luo et al. 2019; Deng et al. 2019; Tang et al. 2020; Yang et al. 2020). LA-ICP-MS is a versatile method for U/Pb dating of accessory minerals containing at least 1 ppm U (e.g., Chew et al. 2014). Notably, this method requires little sample preparation, can determine internal heterogeneity with a spatial resolution generally between 20 and 150 μm , and data acquisition is relatively fast with a U/Pb isotope analysis taking about 1 minute. The main difficulty in producing reliable U/Pb LA-ICP-MS ages is the necessity of matrix-matched reference materials for correction of instrumental mass fractionation (IMF, e.g., Chew et al. 2014). The traditional method for quantifying and correcting for IMF of U/Pb isotopes is by measuring matrix-matched reference materials throughout the analytical session, however, no well characterised wolframite reference material is currently available to the geoscience community. All LA-ICP-MS U/Pb studies of wolframite have used a sample considered to represent MTM-1 wolframite (dated by ID-TIMS initially in Harlaux et al. 2018a) from the Echassières W district in the French Massif Central (FMC) for normalisation and validation purposes (Luo et al. 2019; Tang et al. 2020; Yang et al. 2020). Yang et al. (2020) proposed the YGX-2113 wolframite (Yaogangxian

W deposit, China) as a potential reference material. Recently, a new method for LA-ICP-MS U/Pb geochronology, in which water vapor is introduced into the sample cell has been applied to wolframite using a zircon matrix reference material (Luo et al. 2019; Deng et al. 2019). However, the physiochemical mechanisms permitting this method are poorly understood. Additionally, this method requires complicated analytical setups and results in enhanced oxide formation in the ablation cell.

Based on these previous works and the growing interest in U/Pb geochronology of wolframite by LA-ICP-MS, we have conducted a detailed study coupling micron-scale mineralogical and chemical characterisations of wolframite by imaging techniques and in situ LA-ICP-MS U/Pb isotopic analyses on a sample set from the FMC. The FMC was the subject of a large-scale U/Pb ID-TIMS study of Harlaux et al. (2018a) that allows for a direct comparison between ID-TIMS and LA-ICP-MS U/Pb wolframite ages. Initially, we redefine the U-Pb age of the MTM-1 wolframite after normalisation to three different wolframites. We then present major and trace element concentration and U-Pb ages (after normalisation to MTM-1) of six wolframites from six W deposits in the FMC and we propose a new timeline for W mineralisation in this region. Finally, we suggest new guidelines for data acquisition by LA-ICP-MS and data treatment to enhance reproducibility of U-Pb wolframite ages.

2. Materials

2.1 Wolframite reference materials

The U-Pb age of the MTM-1 wolframite is initially determined by LA-ICP-MS after normalisation of $^{238}\text{U}/^{206}\text{Pb}$ to the Sweet Home hübnerite, and the YGX-2113 and Xihuashan wolframites separately (described in detail in the following section). These materials were selected as they have relatively precise U/Pb ages determined by ID-TIMS (Sweet Home hübnerite; 1.2% 2SD, and YGX-2113; 0.12% 2SD), or the wolframite crystallisation age is well constrained by independent geochronometers (Xihuashan) and these precise absolute ages reduce the systematic uncertainty propagated to all other wolframite ages.

Hübnerite from the Sweet Home Mine (Colorado, USA) was previously described and characterized for its U/Pb and Pb/Pb isotopic composition by ID-TIMS (Romer and Lüders 2006). This sample shows low Pb_c and Th and does not exhibit evidence of open system behaviour (e.g., alteration features) following its initial crystallisation. Romer and Lüders (2006) define a $^{206}\text{Pb}/^{238}\text{U}$ ID-TIMS age of 25.7 ± 0.3 Ma (2σ) for this hübnerite using the most radiogenic analyses. This crystallisation age is slightly older than the $^{206}\text{Pb}/^{238}\text{U}$ age of 24.8 ± 0.5 Ma (2σ ; Romer

and Lüders 2006) calculated for late-magmatic apatite and falls between $^{40}\text{Ar}/^{39}\text{Ar}$ age determinations of sericite from the same deposit ranging from 26.1 ± 0.1 to 25.5 ± 0.1 Ma (2σ ; Barbá et al. 2005).

The YGX-2113 wolframite originates from the Yaogangxian W deposit located in the Nanling Range, southeast China. The U-Pb age of the YGX-2113 wolframite has been determined by ID-TIMS as 160.9 ± 0.2 Ma (2SD; Yang et al. 2020). Numerous Re-Os isochron ages of molybdenite occurring within these veins range from 170 ± 5 Ma to 153 ± 7 Ma (Peng et al. 2006; Mao et al. 2007; Wang et al. 2009; Li et al. 2011) and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of vein-hosted phlogopite and muscovite yield plateau ages of 153.0 ± 1.1 Ma and 155.1 ± 1.1 Ma, respectively (Peng et al. 2006). The wolframite sample used here was provided by M. Yang.

The Xihuashan W deposit consists of quartz-wolframite veins that are genetically associated with the Xihuashan granite in the Nanling Range, southeast China (Wang et al. 2011). The crystallisation age of wolframite from the Xihuashan W deposit is constrained by other geochronometers described here. The Xihuashan granite has three textural phases that yielded U/Pb ages on magmatic monazite of 158.7 ± 0.7 , 158.0 ± 0.7 , and 156.9 ± 0.7 Ma (2σ), respectively (Li et al. 2013). The first textural phase of the Xihuashan granite has magmatic xenotime with U/Pb ages of 159.5 ± 4.4 and 159.4 ± 0.9 Ma (2σ ; Li et al. 2013). Molybdenite that occurs with wolframite in quartz veins yields a Re-Os isochron age of 157.0 ± 2.5 Ma (2σ ; Wang et al. 2011). Two studies have reported a U/Pb LA-ICP-MS wolframite age of 160.9 ± 1.9 Ma (2σ ; Tang et al. 2020; after normalisation to the MTM-1 wolframite) and 160.7 ± 3.3 Ma (2σ ; Yang et al. 2020) from the Xihuashan deposit. A single wolframite grain of approximately 5 mm in diameter was mounted in an epoxy mount and polished prior to analysis. The analysed wolframite was collected from a quartz vein in Xihuashan Mine by co-authors of this study in 2013.

2.2 MTM-1 wolframite - The Echassières W district

The MTM-1 wolframite comes from the Echassières district, located in the north-eastern FMC, which contains several W±Sn vein deposits spatially associated with the Carboniferous peraluminous Colettes and Beauvoir granites (Cuney et al. 1992; Raimbault et al. 1995; Harlaux et al. 2017; Monnier et al. 2018; Monnier et al. 2019; Monnier et al. 2021). Mineralisation occurs as a series of NNE-SSW-trending wolframite-bearing quartz veins and stockworks hosted in mica schists. Three generations of wolframite have been described at Echassières (named wlf a, b, and c; Monnier et al. 2019, 2020). The volumetrically most important generation (wlf b) occurs in a stockwork vein system that is assumed to originate from the concealed and inferred La Bosse granite (referred as “La Bosse stockwork”). Wolframite from the La Bosse stockwork has been dated by ID-TIMS at 333.4 ± 2.4

Ma (Harlaux et al. 2018a) and the vein system was successively overprinted by both the Colettes and the Beauvoir granites, which therefore postdate the formation of wolframite wlf b. The emplacement age of the Colettes granite is estimated at 317 ± 8 Ma (Rb–Sr isochron age recalculated from Pin 1991, using the ^{87}Rb decay constant of Villa et al. 2015). The emplacement of the Beauvoir granite is constrained at 308 ± 2 Ma (^{40}Ar – ^{39}Ar lepidolite age; Cheilletz et al. 1992) and 317 ± 6 Ma (columbite-tantalite U/Pb age; Melleton et al. 2015). These granites are crosscut by a series of NNE–SSW orientated hübnerite-bearing quartz veins (including the Mazet veins) and these veins are thought to be related to the Beauvoir granite (Monnier et al. 2019, 2020).

The MTM-1 sample was originally mislabelled as coming from the Les Montmins locality at Echassières, however, it is now considered to come from the La Bosse stockwork, as discussed by Monnier et al. (2019). Of the eight ID-TIMS analyses performed, Harlaux et al. (2018a) used 5 aliquots to calculate a Concordia age of 334.4 ± 1.7 Ma (2σ) from Pb_c corrected $^{207}\text{Pb}^*/^{235}\text{U}$ and $^{206}\text{Pb}^*/^{238}\text{U}$ ratios. Those authors performed the Pb_c correction using $^{206}\text{Pb}/^{204}\text{Pb}_{(i)} = 17.86$ and $^{207}\text{Pb}/^{204}\text{Pb}_{(i)} = 15.57$ ($^{207}\text{Pb}/^{206}\text{Pb}_{(i)} = 0.87$) that was determined from quartz separates taken from the same sample and in physical contact with wolframite.

Since this initial publication, samples labelled as ‘MTM-1’ have been used by several studies as reference or validation material for U/Pb LA-ICP-MS dating of wolframite (Luo et al. 2019; Deng et al. 2019; Tang et al. 2020; Yang et al. 2020). However, it is noteworthy that the MTM-1 sample used in these studies was obtained from a mineral collector (Luo *pers. comm.*) and the precise geological location of this sample is not reported.

We use the MTM-1 wolframite analysed by Harlaux et al. (2018a) that originates from the historical collection of the Ecole Nationale Supérieure de Géologie (Nancy, France). In addition, we analysed wolframite from four other localities in the Echassières district, including three samples from the La Bosse stockwork (named ECH20-1, ECH20-3, and ECH20-4). Samples ECH20-3 and ECH20-4 come from the GPF1 drill core that cut through the Beauvoir granite (Cuney et al. 1992; Raimbault et al. 1995) while sample ECH20-1 was collected from the former La Bosse open pit, now inaccessible. Sample ECH20-5 was collected from the Mazet veins, in the northern part of the Echassières district, and was provided by L. Monnier.

2.3 French Massif Central wolframite

We analysed six wolframite samples from granite-related W vein-type deposits located in the FMC that were previously petrographically and chemically characterized and dated by ID-TIMS (Harlaux et al. 2018a,b). All samples come from quartz-wolframite vein deposits spatially associated with Carboniferous peraluminous granites (see Harlaux et al. 2018a for detailed information). These deposits include (sample name and ID-TIMS

wolframite age in parentheses): Vaulry (CFM; 298 ± 1.2 Ma), St-Goussaud (BOS; 332.6 ± 6.1 Ma), Leucamp (LCP; 276.5 ± 2.9 Ma), Engualès (ENG; 273.7 ± 6.5 Ma), St-Mélany (SM; 315 ± 15 Ma), and Montredon-Labessonnié (ML; 315.9 ± 2.3 Ma). Note that wolframite from the Puy-les-Vignes deposit (PLV; 317.7 ± 0.7 Ma) from Harlaux et al. (2018a) was found to have an insufficient signal for ^{207}Pb (<50 cps) for meaningful ages by LA-ICP-MS and, therefore, was not selected for this study. All wolframite grains were mounted in polished epoxy mounts. This sample set from the FMC currently represents the most complete dataset of ID-TIMS U/Pb isotope data of wolframite from a single W province.

3. Methods

3.1 Wolframite imaging by μXRF and SEM

The texture and chemical heterogeneity of wolframite and other coexisting minerals was investigated by element X-ray distribution maps obtained by using a Bruker M4 Tornado μXRF benchtop spectrometer and a TESCAN VEGA3LM scanning electron microscope (SEM) with an energy dispersive X-ray spectrometry (EDS) detector, both located at SCMEM, GeoRessources laboratory (Université de Lorraine, Nancy, France). The M4 Tornado is equipped with a 30 W Rh-anode X-ray source operating at 50 kV and 200 μA . The primary X-ray beam was focussed to a 20 μm spot on the sample surface. This instrument has two XFlash® silicon drift energy dispersive X-ray detectors with an energy resolution of <145 eV. Each analysis is represented by pixel and includes 10 ms of counting time. All maps (henceforth referred to as μXRF maps) have a 30 μm spacing between each analysis. The TESCAN VEGA3LM SEM uses a tungsten filament operating at a voltage of 15 kV and beam current of 10 nA and working distance of 15 mm. This SEM has a Bruker XFlash6® 30mm² EDS detector. Element intensity maps were created with a dwell time of 1,024 μs per pixel.

3.2 Chemical analysis of wolframite by EPMA

Major and minor element concentrations of wolframite were determined by spot analysis on a CAMECA SX100 electron probe microanalyzer (EPMA) at SCMEM, GeoRessources laboratory. This system is equipped with a tungsten filament source and 5 wavelength dispersive X-ray spectrometers (WDS). Analytical conditions are shown in Table 1. Each analysis includes two analytical settings. The first analytical setting is for quantification of Fe, Mn, and W, and has an operating voltage of 20 kV and a beam current of 20 nA. The second analytical setting is for F, Sc, Ti, Nb, Sn, Ta, and U, and has an operating voltage of 25 kV and a beam current of 100 nA.

Table 1: Analytical settings used for EPMA analysis of wolframite.

3.3 U/Pb geochronology by LA-SF-ICP-MS

U/Pb isotopes were measured in wolframite, NIST 614 glass, and 91500 zircon using a Nu Instruments AttoMTM ES sector field - inductively coupled plasma - mass spectrometer (SF-ICP-MS) at the GeoRessources laboratory. This instrument is coupled to an ESI 193 nm, ArF excimer laser ablation system with a two-volume ‘TwoVol2’ ablation chamber. A small cylinder with a volume of less than 1 cm³ is centred above the ablation spot in the main chamber (100 mm x 100 mm). Ablation occurs in a helium environment (flow rate between 615- and 700-mL min⁻¹) within the sample cell and is then mixed with N₂ with a Y-connector and at a flow rate of 3 mL min⁻¹. An Ar makeup gas with a flow rate of between 330 to 400 mL min⁻¹ is added with a Y-connector following the N₂ and before entering a gas mixing bulb and then the ICP torch. Gas flow rates and ion lenses parameters were optimised on the NIST 612 glass in raster mode to provide the highest sensitivity, to maintain a low oxide levels and to minimize the fractionation of Th/U. The ThO/Th ratio was below 0.05% and a Th/U ratio was typically from 0.95 to 1.0 (accepted value = 1.01; Jochum et al. 2011).

We conducted 14 analytical sessions on wolframite with different laser spot sizes between 85 and 130 µm, repetition rates of 5, 8 and 10 Hz, and laser energy density between 5.0 and 7.0 J/cm². Prior to each analysis the targeted region was ablated with 5 pulses of a larger laser spot and with a lower fluence (2 J/cm²) to remove any surficial Pb or other contaminants.

The LA-SF-ICP-MS system operated in deflector jump mode, whereby the magnet remains static at the midpoint of all measured masses (mass 215 in this study) and the ion beam is deflected over an electron multiplier ion counting detector by a sequence of deflectors before and after the magnet. The following isotopes were measured (integration time in parentheses): ²⁰²Hg (500 µs), ²⁰⁴Pb (500 µs), ²⁰⁶Pb (500 µs), ²⁰⁷Pb (1.5 ms), ²⁰⁸Pb (500 µs), ²³²Th (500 µs), ²³⁵U (500 µs), and ²³⁸U (500 µs). A sweep of all isotopes took about 5 ms. Each measurement consists of 30 s analysis and 20 s of pre- and post-ablation background washout time, respectively. The sensitivity on this LA-SF-ICP-MS on ²³⁸U was quantified with the NIST 614 glass and was between 82,000 and 115,000 cps/ppm depending on the laser spot size and repetition rate used. The detection limits for this system on U, Th and Pb were *ca* 0.001 ppm.

3.3.1 Pb/Pb and U/Pb normalisation and common Pb corrections

The subtraction of background signals was done in IoLite (version 3.7.1) and produced cps intensities for each isotope and $^{238}\text{U}/^{206}\text{Pb}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios that are uncorrected for IMF. The laser spot size and repetition rate used in this study produced ablation pits with low aspect ratios (<0.3) that reduce the effect of downhole element fractionation (DHF). We do not apply a downhole element fractionation correction to U/Pb ratios and instead use the mean $^{238}\text{U}/^{206}\text{Pb}$ for each analysis, and we justify this in Section 4.2. The uranium concentration of wolframite can be highly variable and generates a large dynamic range in the signal arriving at the ICP-MS detector. To avoid issues of non-linearity in ion detection of large signals, we use the measured ^{235}U when ^{238}U has over 2×10^6 counts per second to generate $^{238}\text{U}/^{206}\text{Pb}$ and assume a $^{235}\text{U}/^{238}\text{U}$ of 137.818 (Heiss et al. 2012).

Pb/Pb isotopes for all samples are normalised to the NIST 614 glass using $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values of 0.8710 ± 0.0008 and 2.101 ± 0.002 , respectively (Woodhead and Hergt 2001). This correction is minor with the measured values between 1–3% higher than the accepted values in the NIST 614. There is no isotopically characterised and homogenous wolframite reference material available for normalisation of $^{238}\text{U}/^{206}\text{Pb}$. Initially, we determined the U/Pb age of the MTM-1 wolframite by LA-ICP-MS on a $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagram after normalisation of $^{238}\text{U}/^{206}\text{Pb}$ to the Sweet Home hübnerite (Romer and Lüdres, 2006), and the Xihuashan and YGX-2113 wolframites (Yang et al. 2020). However, these materials are not available in large quantities at our laboratory and therefore could not be used for normalisation of wolframite from the FMC. Normalisation of $^{238}\text{U}/^{206}\text{Pb}$ for wolframite of the FMC is achieved by dividing the X-intercept of the measured Discordia of MTM-1 for each analytical session on a traditional $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagram (i.e., Tera-Wasserburg diagram), by the X-intercept value of the accepted Discordia defined for MTM-1 (21.40) (as described in Li et al. 2014). This quotient provides a session correction factor that is applied to all wolframite samples. Measured $^{238}\text{U}/^{206}\text{Pb}$ are generally between 20 and 30% higher than the accepted values depending on the laser ablation parameters used.

During each analytical session, the 91500 zircon (Wiedenbeck et al. 1995) was analysed between approximately 15 analyses of wolframite. Due to the relatively low U concentration in wolframite and potential for U-Pb heterogeneity, the 91500 zircon was used to identify and correct for instrument drift, (this was only noted in a single session) and determine the session repeatability of the $^{238}\text{U}/^{206}\text{Pb}$ (*ca* 1.8%) and $^{207}\text{Pb}/^{206}\text{Pb}$ (*ca* 0.8%) ratios that is added in quadrature to the uncertainty of wolframite isotope ratios.

Th and U concentrations of wolframite were determined by normalising the cps of each isotope to the NIST 614 glass (Jochum et al. 2011). Although the NIST 614 glass has a very different matrix to wolframite, Harlaux et al. (2018b) indicate very minor matrix effects for the determination of elemental concentrations in their study using a NIST 610 glass and wolframite. Total Pb concentrations were determined by addition of each isotope and normalisation to the NIST 614 glass (Jochum et al. 2011). We quantify the mass interference of $^{186}\text{W}^{18}\text{O}$ on ^{204}Pb by monitoring $^{186}\text{W}^{16}\text{O}$ (AMU 202) and assuming a $^{18}\text{O}/^{16}\text{O}$ of 0.002 (discussed further in section 5.3).

3.3.2 Determination of age and common Pb correction

U/Pb ages presented here are lower intercept ages of Discordia plotted on $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams. In these diagrams, analyses of purely radiogenic Pb plot on the Concordia and define the U/Pb age for that sample. Discordant analyses represent mixtures between the pure radiogenic composition and the common Pb composition that is defined by the y-intercept of the Discordia. Wolframite U/Pb compositions can be highly dispersed due to mobilisation of U and/or Pb, heterogeneous common Pb and internal dissolution-precipitation zones and these features result in large mean square weighted deviation (MSWD; >10) of Discordia regressions. Therefore, we perform a ‘Model-3’ regression (Ludwig, 2003; available in IsoplotR for U/Pb data; Vermeesch, 2018) on the observed data to obtain the lower intercept age and upper intercept $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$. The ‘Model-3’ regression attributes excess dispersion in U/Pb data to geological heterogeneity instead of analytical uncertainty (as is for ‘Model-1’). This model provides three extra uncertainty terms ($\omega + u / - l$) using a profile log-likelihood method (Vermeesch 2018), where ω is the estimated standard deviation of the assumedly Gaussian geological scatter of the true intercept age, and u and l represent the upper and lower half of a $(1 - \alpha)$ % confidence interval for ω respectively (where $\alpha=0.05$, i.e., 95% confidence interval). Lower intercept ages are presented at two uncertainty levels. The first and smaller value is the 2SD of the isochron determined by IsoplotR that includes the uncertainty in the decay constants of ^{235}U and ^{238}U . This uncertainty can be used when comparing U/Pb data from the same analytical session. The second and larger value in parentheses represents the total measurement uncertainty which includes the 2SD isochron uncertainty, the uncertainty in the age of the MTM-1 wolframite (when used as a reference material; 1.8%), and the long-term reproducibility precision of the 91500 zircon age determined on this system (*ca* 1.5 %), added in quadrature. This uncertainty is used for comparing datasets between analytical sessions and other published data.

4. Results

4.1 Textural and chemical features of wolframite from the Echassières W district

Hand sample photos, μ XRF, and SEM-EDS qualitative element maps are included in Appendix A1 and key maps are presented below. Major and minor element compositions of wolframite samples from the Echassières W district (MTM-1, ECH20-1, ECH20-3, ECH20-4, and ECH20-5) are included in Appendix A2.

Wolframite from the Echassières district has Fe# (where $\text{Fe\#} = \text{Fe}/(\text{Fe} + \text{Mn})_{\text{apfu}}$) values between 0.10 and 0.89, however 75% of analyses have an $\text{Fe\#} > 0.75$, corresponding to the ferberite endmember. The WO_4 content ranges between 68.2 and 78.8 wt.% and is below the stoichiometric composition of 81.7 wt.% for wolframite (Figure 1). The Nb_2O_5 content is up to 4.8 wt.% and the heterovalent substitution of W^{6+} by Nb^{5+} can account for some, but not all the deficiency in W from the stoichiometric composition (e.g., Tindle and Webb 1989). The additional deficit of W could be accounted for by the substitution of Fe^{3+} . Wolframite analysed in this study corresponds to wlf b (MTM-1, ECH20-1, ECH20-3, ECH20-4) and wlf c (ECH20-5) as described by Monnier et al. (2019; Figure 1).

In MTM-1, wolframite is associated with quartz, muscovite, and topaz (Figure 2). Topaz has been selectively replaced by muscovite and this replacement coincides with Mn enrichment in adjacent wolframite, up to crystallization of hübnerite for the most altered zones (Figure 2). The altered zones in wolframite have lower and variable Fe# ranging from 0.78 to 0.40 (“MTM-1 alt” in Figure 1), whilst unaltered wolframite has a consistent Fe# between 0.78 and 0.82 (“MTM-1” in Figure 1). The relationship between wolframite and topaz is obscured by the muscovite alteration overprint. Muscovite alteration does occur within the wolframite aggregate and has been introduced through micro-cracks, although the Mn alteration selvage along these cracks is minimal. Wolframite contained entirely within quartz appears to have been protected from this secondary fluid event and shows no signs of hydrothermal alteration and has high Fe# values.

In sample ECH20-1, wolframite is associated with quartz and muscovite; topaz being absent. Muscovite alteration is widespread and overprints the primary quartz-wolframite association (Figure 3A). Manganese enrichment within wolframite is limited in sample ECH20-1 compared to MTM-1 and the Fe# is correspondingly consistent between 0.85 and 0.79.

Sample ECH20-3 is composed of quartz, topaz, and wolframite (Figure 3B). Topaz overprints and partially replaced wolframite along crystal borders (e.g., Figure 3D). Compared to the other samples, ECH20-3 is the least

altered, with minor muscovite occurring in fine cracks within quartz and topaz, and wolframite having very restricted Fe# between 0.82 and 0.80.

Sample ECH20-4 dominantly contains quartz and wolframite, with rare topaz and muscovite (Figure 3C). Topaz occurs adjacent to wolframite and small fragments of wolframite occur within topaz (Figure 3E). These wolframite fragments likely represent relicts of early wolframite that has been subsequently replaced by topaz, thus indicating that wolframite precipitation predates topaz as proposed by Cuney et al. (1992). Wolframite that occurs adjacent to topaz has an Fe# between 0.89 and 0.82, whereas wolframite occurring within quartz has Fe# between 0.76 and 0.74. Topaz is replaced by muscovite, as shown in the upper right corner of Figure 3C.

Sample ECH20-5, from the Mazet vein that crosscut the Beauvoir granite, contains quartz and wolframite. Wolframite forms acicular crystal habits typical of wlf c of Monnier et al. (2019). Fe# in ECH20-5 is lower than all other samples analysed from Echassières and is comprised between 0.10 and 0.45.

4.2 Downhole fractionation of $^{206}\text{Pb}/^{238}\text{U}$ in wolframite during LA-ICP-MS analysis

Downhole fractionation of $^{206}\text{Pb}/^{238}\text{U}$ in wolframite with a laser spot diameter of 85 μm , repetition rate of 8 Hz and a laser fluence of 7 J/cm² are presented in Figure 4A and B. These ablation pits have aspect ratios of ~0.3. The time resolved $^{206}\text{Pb}/^{238}\text{U}$ ratios during laser ablation of 91500 zircon and MTM-1 wolframite are different (Figure 4A), but similar between the MTM-1 wolframite with other samples of the FMC of variable Fe# (Fe# = 0.3–0.8; Harlaux et al. 2018a,b; Figures 4B–D). This result indicates a minor difference in DHF for the different matrices (zircon vs. wolframite) and similar DHF for the different wolframite endmembers (ferberite vs. hübnerite). We do not perform a DHF correction of $^{206}\text{Pb}/^{238}\text{U}$ data, and instead take the mean $^{206}\text{Pb}/^{238}\text{U}$ of the analysis. Performing a DHF correction will only slightly improve the uncertainty of the $^{206}\text{Pb}/^{238}\text{U}$. For example, the uncorrected and time resolved $^{206}\text{Pb}/^{238}\text{U}$ ratios of the MTM-1 wolframite display 3.6% variation relative to the mean. Applying an exponential log function to these data can reduce the variation about the mean to 3.4%. Cross-calibration of U/Pb ages determined using the Sweet Home Hübnerite (Fe# = 0.001; Yang et al. 2020), MTM-1 (Fe# = 0.8), Xihuashan (Fe# = 0.6; Yang et al. 2020) or YGX-2113 (Fe# = 0.5; Yang et al. 2020) for $^{238}\text{U}/^{206}\text{Pb}$ yield ages within uncertainty of the accepted age for that sample, further indicating that matrix-effects between the wolframite endmembers do not significantly affect LA-ICP-MS data. In general, the relatively low U (<200 ppm) contents commonly found in wolframite yield little radiogenic Pb (particularly ^{207}Pb) and therefore require the use of large diameters of laser ablation which reduce DHF effects (e.g., Paton et al. 2010).

4.3 U and Pb concentrations and U/Pb isotopic composition of wolframite from the Echassières W district

U and Pb concentrations and U/Pb isotopic compositions of the MTM-1 wolframite after normalisation to the Sweet Home Hübnerite, YGX-2113 and Xihuashan wolframites are shown in Table 2. U and Pb concentrations and measured U/Pb isotopic compositions of the MTM-1 used for normalisation of FMC wolframite, including the calculated session correction factors are shown in Table 3. U and Pb concentrations and U/Pb isotopic compositions of the other wolframite samples from the Echassières W district normalised to the MTM-1 wolframite are shown in Table 4. We also report f_{206c} that represents the proportion of common Pb to radiogenic Pb and is calculated according to the following equation shown in Williams (1998):

$$f_{206c} = (\gamma R_m - \gamma R^*) / (\gamma R_c - \gamma R^*) \quad (1)$$

where γR_m is the measured $^{207}\text{Pb}/^{206}\text{Pb}$, γR^* is the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$, and γR_c is the non-radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ (here we estimate the γR_c using the Stacey and Kramers (1972) model, except for the MTM-1 where we assume a $^{207}\text{Pb}/^{206}\text{Pb}_i$ of 0.75 (see below for explanation).

The U concentration is variable between 1.8 and 69 ppm, and this range is comparable to U concentrations reported for the MTM-1 by ID-TIMS of 5.5–68 ppm (Harlaux et al. 2018a). However, we note that primary MTM-1 is more enriched in U compared to the altered components, and to all other wolframite from the Echassières W district (Figure 5A). Similarly, Pb concentrations in MTM-1 wolframite range between 0.18 and 12 ppm, however, the altered components are relatively enriched (Figure 5B). Approximately 60% of analyses of the MTM-1 have $f_{206c} < 0.05$ (equivalent to $< 5\%$ common ^{206}Pb). The remaining wolframite samples (ECH20-1, ECH20-3, and ECH20-4) have a comparable range of U concentrations between 0.4 and 48 ppm (Figure 5A). ECH20- samples are generally more concordant with 84% of analyses with $f_{206c} < 0.05$. Wolframite from the Mazet vein (sample ECH20-5) is relatively depleted in U with between 0.07 and 4.8 ppm, whilst the Pb content (0.01–15.3 ppm) is comparable to the other wolframite samples from Echassières. Correspondingly, $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ data are highly discordant and the minimum f_{206c} is 0.09.

4.3.1 U/Pb age of the MTM-1 wolframite

The $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ compositions of the MTM-1 sample define a lower intercept age 317.0 ± 6.2 Ma after normalisation to the Sweet Home Mine hübnerite, 315.6 ± 6.0 Ma after normalisation to the Yaogangxian wolframite, and 317.4 ± 5.4 Ma after normalisation to the Xihuashan wolframite (Table 2; Figure 6A). These three ages yield a weighted mean age of 316.7 ± 3.3 (5.8) Ma (MSWD = 0.11) that is considered to represent the

crystallisation age of the wolframite. The lower intercept age of primary zones within the MTM-1 is comparable to the altered zones (Figure 6B) indicating that the age of alteration event is within the uncertainty of this method of the initial crystallisation. These new ages for the MTM-1 are significantly different to the previous ID-TIMS U/Pb age of 334.4 ± 1.7 Ma (Harlaux et al. 2018a). Note that in Figure 6A, we show an age of 333.2 ± 0.6 Ma for the 5 aliquots that is slightly different to Fig. 5C of Harlaux et al. (2018a) as we use $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ instead of $^{207}\text{Pb}/^{235}\text{U}$ vs. $^{206}\text{Pb}/^{238}\text{U}$.

4.3.2 Dispersion in highly discordant analyses of the MTM-1 wolframite

Highly discordant data from MTM-1 show much greater dispersion about the Discordia compared to concordant data (Figure 6A). The $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ determined from all data for the MTM-1 in Figure 6A is 0.770 ± 0.009 , but with some analyses falling above and below the Discordia (Figure 6A). The $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ is similar to the free regression of all ID-TIMS data (Discordia 2 in Figure 61; 0.79 ± 0.07), but significantly lower than the value measured in co-existing quartz of 0.87 (Harlaux et al. 2018a) or ca 0.86 predicted by the two-stage terrestrial Pb evolution model of Stacey and Kramers (1975) for 315 Ma. The discrepancy between the $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ determined from LA-ICP-MS analyses of wolframite and in co-existing quartz is discussed further in section 5.2.

4.3.3 U/Pb age of wolframite from the Echassières W district

The ECH20-1, ECH20-3, and ECH20-4 wolframite samples have comparable concordant analyses when compared the MTM-1 wolframite and indicate a similar U/Pb age (Figure 6C). However, data measured for these samples are generally more concordant compared to MTM-1 wolframite and yields $^{207}\text{Pb}/^{206}\text{Pb}_i$ compositions of 0.86 ± 0.01 (Figure 6C) that is different from the MTM-1 wolframite. Hübnerite from the Mazet vein (ECH20-5), which is considered as the third generation of wolframite at Echassières (wlf c of Monnier et al. 2019), contains dominantly discordant U/Pb data and defines a lower intercept age of 279.1 ± 7.1 Ma and $^{207}\text{Pb}/^{206}\text{Pb}_i$ compositions of 0.841 ± 0.004 (Figure 6C).

4.4 U and Pb concentrations and U/Pb isotopic variation measured by LA-ICP-MS in wolframite from the French Massif Central and related ages

The U and Pb concentrations and U/Pb isotopic compositions measured by LA-ICP-MS for wolframite from the six W deposits of the FMC are shown in Table 5. U concentrations in wolframite from the FMC are variable within and across samples (0.15–22 ppm), however, are relatively depleted compared to wolframite from the Echassières W district with 80% of analyses less than 7 ppm. Th is below detection limit for most analyses and when measured is mostly < 0.1 ppm. Total Pb concentrations are predominantly < 1 ppm, however, can be as much as 14 ppm. Figure 7 presents the lower intercept ages of all samples on $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams after normalisation to MTM-1 wolframite using the newly defined $^{238}\text{U}/^{206}\text{Pb}$ age. Rejected analyses are included in Figure 7 and in Table 5. Twelve analyses out of 228 were rejected as they were isolated from the main population of analyses, contain exceptionally high common Pb and or Th concentrations, or have large analytical uncertainties associated with mineral or fluid inclusions.

The distribution of $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios measured by LA-ICP-MS varies within each sample and between samples of the FMC. SM and CFM wolframite have the more concordant data from all samples and the Discordia yields lower intercept ages of 317.1 ± 3.0 (8.0) Ma and 310.6 ± 4.0 (8.3) Ma for ENG and CFM, respectively (Figure 7). $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for ENG and LCP wolframite are comparatively more dispersed but still yield lower intercept $^{238}\text{U}/^{206}\text{Pb}$ ages of 318.3 ± 5.2 (9.1) Ma and 306.8 ± 4.2 (8.3) Ma, respectively. Wolframite from BOS and ML present the most dispersed data. ML wolframite yields a lower intercept age of 307.4 ± 6.1 (9.4) Ma and a $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 1.06. This Discordia is a poor fit for the most Concordant data and the elevated $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ is unrealistic for the Palaeozoic FMC. The upper intercept is dominantly controlled by 5 highly discordant analyses, and the exclusion of these analyses defines a lower intercept age of 298.5 ± 2.9 (7.6) Ma ($^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 0.88 ± 0.1) that better fits the Concordant data and that we interpret to represent the crystallisation age of wolframite. BOS displays significant U/Pb heterogeneity, and the lower intercept age of 367 ± 47 (48) Ma is imprecise but generally too old considering existing geochronological constraints known for this deposit. Rejection of the 20 most discordant analyses ($^{238}\text{U}/^{206}\text{Pb} < 13$) yields a lower intercept age of 307 ± 21 (22) Ma and $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 0.5 ± 0.1 that we consider the crystallisation age of this sample.

Table 5: U/Pb data of the wolframite from the FMC after $^{238}\text{U}/^{206}\text{Pb}$ normalisation to the MTM-1 and $^{207}\text{Pb}/^{206}\text{Pb}$ normalisation to the NIST614.

5. Discussion

5.1 Reassessment of U/Pb and Pb/Pb isotopic ratios of MTM-1 and comparison with published LA-ICP-MS values

Considering the documented chemical and isotopic heterogeneity of the MTM-1 wolframite, and the use of the MTM-1 for normalisation and validation purposes of LA-ICP-MS data (Luo et al. 2019; Deng et al. 2019; Tang et al. 2020; Yang et al. 2020), a re-evaluation of the wolframite crystallisation age is required.

We present a new weighted mean age of 316.7 ± 3.3 Ma (5.8) Ma after U/Pb normalisation to the Sweet Home Mine hübnerite, YGX-2113 and Xihuashan wolframites (Figure 6A). We suggest that the disagreement between the LA-ICP-MS and ID-TIMS age (334.4 ± 1.7 Ma; Harlaux et al. 2018a) results from an inappropriate common Pb correction applied to the Discordant ID-TIMS data (Figure 6A). Harlaux et al. (2018a) measure the common Pb isotopic composition of quartz associated with wolframite and assumes isotopic equilibrium between the two minerals. Note that Harlaux et al. (2018a) prepared aliquots of between 1.202 and 2.635 mg of the MTM-1 wolframite concentrate to be analysed by ID-TIMS, and the authors noted some effects from U- and Pb-rich inclusions on the U/Pb isotopic compositions, which along with variable U and/or Pb mobilisation or $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ (see discussion in Section 5.3) can account for some dispersion of the ID-TIMS data (Figure 6A). A free regression through all ID-TIMS analyses of MTM-1 yields a $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 0.79 ± 0.07 that is similar to the value preferred here, however, dispersion in this dataset yields a relatively inaccurate age of 322 ± 16 Ma (Figure 6A; Discordia 2). Note that we do not consider isotopic heterogeneity due to dissolution-reprecipitation of the MTM-1 wolframite as this is not observed petrographically (Figure 2, Appendix 1). The LA-ICP-MS data reported in Figure 6 suggest a $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of ~ 0.77 that is dissimilar to the value measured in co-existing quartz ($^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 0.87). The $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ determined by LA-ICP-MS is considered more robust as it can avoid the effects of mineral inclusions and alteration zones within wolframite that can strongly influence ID-TIMS data, and the large spread in data better define the upper and lower intercepts of the Discordia.

An important distinction in the LA-ICP-MS data is that MTM-1 and other wolframite from the Echassières deposit have a similar U/Pb age but different $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ (Figure 6C). The relatively enriched U concentration in MTM-1 compared to other wolframite of Echassières indicates that this wolframite was derived or modified by a U-rich fluid that was different to the source fluids of other wolframites. Additionally, the MTM-1 sample appears to be the most affected wolframite by secondary alteration processes indicated by the largest range in Fe# associated with Mn enrichment (Figure 1) and the greatest degree of alteration observed petrographically (Figure 2),

indicating a distinct chemical evolution for this sample. However, although the alteration event has significantly lowered the U concentration in wolframite (Figure 5), it has had little effect on the U/Pb isotopic composition of MTM-1 which display a comparable spread in U/Pb data between the primary and altered zones (Figure 6B).

The 316.5 ± 3.3 (5.8) Ma age for MTM-1 wolframite is more coherent with the local geology and geochronological constraints, and when used as a primary reference material it yields apparently more accurate U/Pb ages for other wolframite of the FMC (discussed in Section 5.2). The wolframite age is within the estimates for the emplacement of phengites from selvages of the quartz-wolframite veins (ca. 325–320 Ma; Merceron et al. 1987) and the emplacement age of the nearby Colettes granite (Rb–Sr isochron age of 317 ± 8 Ma, recalculated from Pin 1991 using the ^{87}Rb decay constant of Villa et al. 2015). It is older than the emplacement age of the Beauvoir granite (^{40}Ar – ^{39}Ar lepidolite age at 308 ± 2 Ma; Cheilletz et al. 1992) and within uncertainty of columbite-tantalite U/Pb age (317 ± 6 Ma; Melleton et al. 2015) that clearly postdates wolframite mineralisation. However, the new wolframite age is younger than a U/Pb age of 335.5 ± 3 Ma of monazite that occurs in the selvage of the ‘La Bosse’ stockwork and is assumed to date W mineralisation (Monnier et al. 2021). The MTM-1 sample of this study was taken from the former open pit site that is adjacent to the Beauvoir rare-metal granite, whilst the other ECH samples originate from beneath the granite. The Beauvoir granite contains magmatic uraninite (Cuney et al. 1992) and fluids derived from its dissolution could generate the radiogenic Pb_c composition observed in MTM-1 wolframite. However, the Beauvoir granite clearly crosscuts the W stockwork at Echassières. It is plausible that the U/Pb isotopic composition of the MTM-1 wolframite was partially reset during the intrusion of the Beauvoir granite whilst the other ECH wolframite from beneath the Beauvoir granite were unaffected by the upward circulating fluids. However, the similar U/Pb age of the MTM-1 and ECH wolframites indicate that initial crystallisation of MTM-1 and partial resetting must have occurred within the age uncertainty presented (ca 5 Ma).

Considering the new age obtained for the MTM-1 wolframite, previously published wolframite ages that have used a wolframite labelled ‘MTM-1’ as an primary reference material (Tang et al. 2020), or for method validation (Luo et al. 2019; Yang et al. 2020) require re-evaluation. The ‘MTM-1’ wolframite presented in Luo et al. (2019), Tang et al. (2020) and Yang et al. (2020) originates from a single crystal purchased from a mineral collector, but its precise provenance (Montmins or La Bosse stockwork) is unknown (Luo *pers comm*). Yang et al. (2020) indicate that the ‘MTM-1’ used in those studies has a Fe# of 0.75 that is within the range the Fe# measured for wlf b by Monnier et al. (2019) and in the present study but differs from Fe# measured in wlf a and c (Monnier et al., 2019). No chemical imaging of that ‘MTM-1’ is available to determine if those samples have been affected by hydrothermal alteration as documented in this work. Interestingly, the $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ determined from U/Pb data

of Tang et al. (2020) is 0.60 ± 0.05 that is unlike the values determined here or in Harlaux et al. (2018a). The ‘MTM-1’ used in those studies obtains a U/Pb age of *ca* 330 Ma when normalised to other primary reference materials (e.g., YGX 2113; Yang et al. 2020), and reproduces U/Pb ages of other well studied wolframite when it is used as a primary reference material with the ID-TIMS age proposed by Harlaux et al. (2018a) for the original MTM-1 sample (e.g., Xihuashan; Tang et al. 2020). Therefore, we suggest that this sample is of a different provenance to the MTM-1 presented here.

The newly defined age for the MTM-1 by LA-ICP-MS has an uncertainty of 1.8% and this is added in quadrature to the uncertainty of the age of the FMC wolframite. This systematic uncertainty in the absolute age of the reference material is the largest source of uncertainty for U/Pb ages of the FMC presented here. A more precise U/Pb age of the MTM-1 wolframite, such as that of the YGX-2113 of 0.12% (Yang et al. 2020) would permit U/Pb ages with a total uncertainty between 20 and 30 % less than reported here. For example, we report a U/Pb age of 318.3 Ma with a total uncertainty of 9.1 Ma (2.9%) for the ENG wolframite.

5.2 Comparison of ID-TIMS and LA-ICP-MS for U/Pb dating of wolframite: the French Massif Central

Table 6 contains a summary of wolframite U/Pb ages and $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ determined from Discordia intercept values of LA-ICP-MS data (this study) and wolframite U/Pb ages and $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of low U/Pb minerals associated with wolframite determined by ID-TIMS (Harlaux et al. 2018a) for the FMC sample set. A comparison of ID-TIMS and LA-ICP-MS ages is presented in Figure 7G.

Based on the U/Pb and Pb/Pb isotopic ratios defined by ID-TIMS on the wolframites in Harlaux et al. (2018a), three W mineralizing events affecting the FMC between *ca.* 335 and 295 Ma were proposed. This study demonstrates that most of these ages were determined from highly discordant data and the corrected ages are potentially biased by the internal heterogeneity of wolframite and its inclusions. Absolute ages determined by LA-ICP-MS here are not sufficiently precise to unravel magmatic-hydrothermal processes in detail, however, do provide improvements on the timing of W mineralisation in the FMC. The new ages presented here are more geologically robust and indicate a maximum period of *ca* 30 Ma (using the total uncertainty of U/Pb ages) for W mineralisation in the FMC.

The 317.1 ± 3.0 (8.0) Ma U/Pb age determined for SM is consistent with the ID-TIMS age of 315 ± 15 Ma (Harlaux et al. 2018a) and within the uncertainty of the emplacement age estimates for the proximal Rocles granite (325 ± 4 to 318 ± 3 Ma; Be Mezeme et al. 2006, 2007), which is the possible fluid source. The 318.3 ± 5.2 (9.1) Ma age from ENG is older than estimated by ID-TIMS (273.7 ± 6.5 Ma Harlaux et al. 2018a), but closer to the

emplacement age for the nearby Margeride granite at *ca* 313 Ma (Laurent et al. 2017) and could indicate the
 magmatic source of W-bearing fluids. Similarly, the 306.8 ± 4.2 (8.3) Ma age of the LCP is significantly older
 than the ID-TIMS age (276.5 ± 2.9 Ma; Harlaux et al. 2018a), but more consistent with the *ca* 306 Ma leucogranite
 dykes intruding nearby the deposit (Monié et al. 2000). The younger ID-TIMS ages for the ENG and LCP likely
 represent partial resetting of the U/Pb in wolframite or the incorporation of secondary inclusions within separates
 as proposed by Harlaux et al. (2018a). Harlaux et al. (2018a) determined an age of 315.9 ± 2.3 Ma for ML that is
 older than the lower intercept age of 298.5 ± 2.9 (7.6) Ma interpreted to represent the crystallisation age of the
 wolframite (Figure 7F). The only external geochronological constraint from this sample comes from an $^{40}\text{Ar}/^{39}\text{Ar}$
 age of muscovite and biotite from the thermal metamorphic aureole of a buried intrusion that yields ages of 300.3
 ± 3.1 and 302.5 ± 3.2 Ma, respectively (Costa 1990), and agrees within uncertainty with the LA-ICP-MS U/Pb
 wolframite age. The BOS has a lower intercept age of 307 ± 21 (22) Ma that we interpret as a crystallisation age.
 The ID-TIMS age for BOS is 332.6 ± 6.1 Ma (Harlaux et al. 2018a). Both the LA-ICP-MS and ID-TIMS age
 estimates are within the error of U/Pb zircon and monazite ages of 324 ± 4 Ma (ID-TIMS age; Holliger et al.
 1986), 328 ± 3 Ma and 324 ± 3 Ma (LA-ICP-MS ages; Villaros et al. 2014) from the nearby St-Sylvestre
 leucogranitic complex. However, the LA-ICP-MS age is more consistent with the $^{40}\text{Ar}/^{39}\text{Ar}$ exhumation age of
ca. 305 Ma from muscovite occurring within the St-Goussaud leucogranite and near quartz-wolframite veins
 (Scaillet et al. 1996). The $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of 0.5 ± 0.1 determined from the LA-ICP-MS data is significantly lower
 than the terrestrial Earth Pb isotope composition for that age ($^{207}\text{Pb}/^{206}\text{Pb}_{(i)} = 0.86$; Stacey and Kramers 1972),
 however, is only slightly lower than defined in quartz from the same deposit ($^{207}\text{Pb}/^{206}\text{Pb}_{(i)} = 0.6$; Harlaux et al.
 2018a). The St-Goussaud leucogranite is associated with significant uraninite mineralisation (Cuney et al. 1990)
 and the mobilisation of the radiogenic Pb from this uraninite can produce the low $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ values seen in BOS
 wolframite. Isotopic heterogeneity in the BOS wolframite is discussed further in section 5.3.

Excluding SM, the U/Pb ages determined by ID-TIMS (Harlaux et al. 2018a) are different from this study and
 geological less plausible, and we suggest this is caused by U and/or Pb mobilisation in wolframite, post-
 crystallization fluid–wolframite interaction zones within wolframite and secondary minerals unintendedly
 included in ID-TIMS aliquots.

5.3 Heterogenous common Pb within wolframite and its inclusions

Wolframite commonly has abundant mineral inclusions including sulphides, scheelite, and Nb-Ta minerals that
 may be rich in Pb and/or U and will affect the U/Pb system of the bulk sample analysed by ID-TIMS. Most
 commonly, ID-TIMS work on wolframite is affected by Pb-rich inclusions and the bulk samples have markedly

lower measured $^{206}\text{Pb}/^{204}\text{Pb}$ and higher $^{207}\text{Pb}/^{206}\text{Pb}$ compared to LA-ICP-MS (Figure 7). To obtain more precise U/Pb ages from ID-TIMS analyses with high Pb_c , the common Pb isotopic composition must be known from independent analyses, such as cogenetic low- $^{238}\text{U}/^{204}\text{Pb}$ minerals. Most wolframite samples from the FMC measured by ID-TIMS have low $^{206}\text{Pb}/^{204}\text{Pb}$ (as low as 24 in Harlaux et al. 2018a) and, therefore, the obtained age depends strongly on the Pb_c composition used for correction. Traditionally, the most robust approach to estimate the Pb_c composition is to analyse low U/Pb minerals from the same paragenesis. However, for the wolframite samples of the FMC, this approach is not always suitable as demonstrated for MTM-1. Additionally, secondary mineral inclusions occurring along fracture surfaces, within veins or on the exterior of the wolframite can be included in wolframite concentrates. These minerals can have precipitated immediately following the wolframite (e.g., sulphide mineralisation is a common late-stage feature in these deposits), but with a different common Pb composition.

For LA-ICP-MS, it is possible to avoid inclusions with careful placement of spots after small-scale mineralogical and chemical characterization and therefore, data plot closer to the lower intercept in $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams compared to ID-TIMS data (Figure 7). The LA-ICP-MS also enables the acquisition of a significantly larger number of data which are globally more dispersed in their $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios but define a Discordia that can be more accurate and precise than from ID-TIMS data (exemplified by CFM, SM, ENG or LCP samples; Figure 7). Additionally, LA-ICP-MS data can better highlight heterogeneity in both U/Pb and apparent $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ within wolframite as shown in the MTM-1 and BOS wolframite.

Common Pb in a granite is typically relatively little radiogenic and homogeneous as the Pb composition is dominated by feldspar (Hogan and Sinha 1991). Such little radiogenic Pb is seen by ID-TIMS and LA-ICP-MS in most wolframite samples from the FMC (including with $^{207}\text{Pb}/^{206}\text{Pb}$ in the range 0.83 to 0.90 and $^{206}\text{Pb}/^{204}\text{Pb}$ in the range 17.8 to 18.8, as indicated by sulphide and scheelite-bearing samples; Harlaux et al. 2018a). However, some of granites within the FMC are U-rich and a significant portion of U is hosted in uraninite or U-rich minerals (e.g., St-Sylvestre leucogranite; Cuney et al. 1990 and Beauvoir granite; Cuney et al. 1992). Uraninite readily reacts with oxidized fluids, mobilizing U and radiogenic Pb that formed after uraninite crystallization. Uraninite has very high $^{238}\text{U}/^{204}\text{Pb}$ and will develop notably radiogenic Pb isotopic compositions after few thousand years. Mobilisation of Pb from feldspar and uraninite may result in fluids that have isotopically variable Pb isotopic composition both in time and space, depending on the relative contribution of Pb from feldspar and uraninite. Crystallization by such fluid may account for the low $^{207}\text{Pb}/^{206}\text{Pb}_i$ (and high $^{206}\text{Pb}/^{204}\text{Pb}_i$) observed for some wolframite samples such as MTM-1 and BOS. Yang et al. (2020) also find a low $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ (0.39) in wolframite

from the Nanling Range (YGX2107). Similarly low $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ has also been inferred for cassiterite (Carr et al. 2020) that is commonly associated with wolframite.

5.4 Post-crystallisation fluid–wolframite interaction

In addition to Pb isotopic heterogeneity introduced from mineral inclusion or variable common Pb within wolframite, wolframite can be strongly affected by post-crystallization fluids (particularly those containing Fe and/or Mn; Lecumberri-Sanchez et al. 2017), as exemplified by MTM-1 sample (see 5.1.1). Post-crystallization fluid–mineral interaction can result in multiple events being recorded in individual crystals (e.g., Deng et al. 2019; Legros et al. 2020) or the replacement of wolframite by secondary minerals such as hübnerite, ferberite, and/or scheelite with different U/Pb compositions (e.g., Harlaux et al. 2018a and Figure 2). Dissolution-precipitation of wolframite may result in a partial resetting of U/Pb decay system and modification of the $\text{Pb}/\text{Pb}_{(i)}$ ratio for the affected zones such as seen in the BOS wolframite, leading to a heterogeneous distribution of the isotopic ratios at the crystal scale (Figure 8). Bulk analyses that include material affected by such secondary processes will result in mixed ages that fall between the crystallisation and alteration age and changes in $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$. The origin of U/Pb isotopic variability in the BOS wolframite is therefore thought to result from the replacement of primary wolframite by ferberite during hydrothermal alteration (e.g., ferberitisation; Figure 8). Time resolved $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for two analyses of the BOS with high Pb_c analyses show contrasting behaviour (Figure 8A). $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ in analysis I is erratic and indicates the ablation of mineral inclusions. In contrast, analysis III has a relatively stable $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ signal and more indicative that U and Pb are structure bound in wolframite. However, analysis III is isolated relative to the other data and the significance of the very low $^{207}\text{Pb}/^{206}\text{Pb}$ (0.36) is unclear. Analyses II and IV, which occur along the ID-TIMS Discordia, have initial peaks associated with surficial Pb_c , but subsequently are relatively stable indicating that no mineral inclusions were ablated. We therefore attribute this isotopic heterogeneity to oxide mineral inclusions (Figure 8B) and secondary ferberitisation (Figure 8C) present in the BOS. ENG, CFM and LCP are affected by similar processes, leading to erroneous ID-TIMS U/Pb ages. Several LA-ICP-MS analyses plot to the right of the Discordia in Figure 7 (these analyses were rejected from age calculations). These data indicate that some zones within these samples have been affected by Pb-loss (or a second generation of wolframite crystallisation), which can also explain the large disparity between LA-ICP-MS and the younger ID-TIMS ages of these samples.

5.5 U-Th-Pb isotopic and chemical heterogeneity in wolframite

The concentration of U, Th, and Pb in wolframite samples from the FMC is variable from below the detection limits and up to 152, 3.3, and 28 ppm, respectively (Figure 9). Several studies have questioned whether isotopic

heterogeneity in wolframite is caused by primary changes of its chemical composition or whether results from mineral and/or fluid inclusions (Harlaux et al. 2018a; Legros et al. 2020). Compositional heterogeneity can result in large variation in the concentration of U reflecting the primary growth zoning as visible on the BSE image (Figure 10B). In contrast, LA-ICP-MS line scans across large grains that appear homogeneous in BSE imagery can exhibit U variations by an order of magnitude (Figure 10A). These data indicate large internal heterogeneity of U within the wolframite structure that is unrelated to mineral or fluid inclusions. Deng et al. (2019) suggest that U substitution into the wolframite structure is aided by Nb^{5+} , however, Nb is not a significant contributor to BSE, and therefore cannot be easily mapped by this method.

Generally, Th/U within wolframite from the FMC is low (< 0.1) compared to the available data from the Nanling Range (Deng et al. 2019 and Tang et al. 2020). Th and U are rarely correlated (Figure 9), and this is unsurprisingly considering that Th is incompatible within wolframite (Harlaux et al. 2018b) and is generally less soluble in fluids associated with magmatic-hydrothermal W deposits (e.g., Audétat et al. 2000). However, a correlation between U and Th occurs within SM and suggests that Th is structurally bounded within wolframite (Figure 9). This variable correlation between Th and U, and the potential for Th to approach 1 ppm (Figure 9) justify monitoring ^{232}Th for potential samples appropriate for $^{208}\text{Pb}/^{232}\text{Th}$ dating, and the use of 208-common Pb corrections (discussed below).

5.5.1 Assessment of common Pb in wolframite and correction procedures

Mean weighted averages of Pb_c corrected $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ or $^{207}\text{Pb}/^{206}\text{Pb}$ ages are commonly used in zircon geochronology to provide more precise age constraints (e.g., Spencer et al. 2016). This Pb_c correction is ideally applied using measured $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ in the sample, as ^{204}Pb is the only non-radiogenic Pb isotope. However, the measurement of ^{204}Pb by LA-ICP-MS is frequently hindered by low signal, and an isobaric interference with ^{204}Hg which is a common contaminant in the Ar gas used to transport the sample (e.g., Hirata et al. 2005). Additionally, there is a major isobaric interference between ^{204}Pb and $^{186}\text{W}^{18}\text{O}$ during ablation of wolframite requiring a mass resolution of $\sim 12,000$ (e.g., Carr et al. 2017), which is significantly higher than the 300 used in this study. Achieving such a high mass resolution will inherently reduce signal intensity and is not feasible for U/Pb dating application of wolframite by LA-ICP-MS. The contribution of $^{186}\text{W}^{18}\text{O}$ to AMU 204 can be estimated by monitoring $^{186}\text{W}^{16}\text{O}$ on AMU 202 and assuming a $^{18}\text{O}/^{16}\text{O}$ of 0.002. In Figure 11A, we show that counts on AMU 204 are linearly correlated with counts on AMU 202, indicating that the signal on AMU 204 is dominated by $^{186}\text{W}^{18}\text{O}$. Note that these data have been corrected for the large background signal introduced from

Hg contamination on both AMU 202 and 204. The analyses that occur above this linear relationship contain high ^{204}Pb or ^{204}Hg .

The overall low signal of ^{204}Pb from LA-ICP-MS data of wolframite from FMC and the two isobaric interferences render Pb_c correction using ^{204}Pb difficult. Instead, most LA-ICP-MS studies of Pb_c bearing minerals apply Pb_c corrections using the 207- and 208- methods (e.g., Williams 1998). All wolframite from the FMC measured in this study have a Th/U of <0.1 (Figure 9) indicating a small proportion of radiogenic ^{208}Pb and that the $^{208}\text{Pb}/^{206}\text{Pb}$ can be used to estimate the proportion of Pb_c . In minerals with low Th/U like wolframite, the 208-correction method is preferred because ^{208}Pb is the most abundant Pb_c isotope. In Figure 11B, we show that after a mass interference correction on AMU 204 to remove the $^{186}\text{W}^{18}\text{O}$ component, ^{204}Pb cps correlate linearly with ^{208}Pb cps at high signal intensity (Figure 11B). ^{208}Pb is 38.5 times greater than ^{204}Pb which is comparable to the $^{208}\text{Pb}/^{204}\text{Pb}$ reported in Harlaux et al. (2018a) in low U/Pb minerals. Analyses with relatively high Th remain on this linear trend and highlight that radiogenic ^{208}Pb is insignificant in the FMC. At low ^{204}Pb ($<1,000$ cps) the relationship with ^{208}Pb is no longer linear (Figure 10).

A comparison of the 207- and 208- Pb_c correction methods applied to CFM wolframite is shown in Figure 12A and B and using the following common Pb compositions: $^{207}\text{Pb}/^{206}\text{Pb} = 0.86$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$. Data excluded from Figure 7C are also excluded here. Only the internal error is included in the mean weighted age as data are not being compared intra-session. Both the 207- and 208- correction methods yield a comparable range of Pb_c corrected $^{206}\text{Pb}/^{238}\text{U}$ ages between *ca* 330 Ma and 290 Ma, and both methods yield similar mean weighted ages with high MSWD. In this study, the CFM yields the least dispersion in common Pb corrected ages. The Pb isotopic heterogeneity within wolframite from other deposits of the FMC yields significant dispersion in Pb_c corrected ages with higher MSWD and precludes more accurate Pb/U ages by these methods. However, despite this dispersion, both the 207- Pb_c and 208- Pb_c produce similar results.

5.6 Suggested procedures for U/Pb wolframite geochronology by LA-ICP-MS

With the increasing number of publications on U/Pb wolframite geochronology by LA-ICP-MS, standardised data treatment and interpretation procedures are required. We suggest the guidelines outlined by Horstwood et al. (2016) and emphasise the following for wolframite:

- Compositional imaging of wolframite coupled to small-scale mineralogical analysis prior to U/Pb dating is a pre-requisite to avoid inclusions and/or alteration zones during LA-ICP-MS analysis. Element

distribution maps (e.g., SEM-EDS or μ XRF) can be also used to target internal zones, or to exclude samples for ID-TIMS analyses. Near-infrared microscopy (e.g., Ortelli et al. 2018; Harlaux et al. 2021) and X-ray computed tomography (CT; Harlaux et al. 2018a) are also promising tools to investigate the textures of wolframite and to provide 3D information about the relative proportions and the spatial distribution of micro-inclusions and/or alteration zones.

- We suggest a well-characterised matrix-matched reference material is used for normalisation of $^{238}\text{U}/^{206}\text{Pb}$ ratios and a NIST synthetic glass for normalisation of Pb isotope ratios. We prefer the NIST 614 as it has a Pb concentration of 2.32 ppm similar to the values typically observed in wolframite, and its Pb isotopic composition is known with precision (Woodhead and Hergt 2001). Well characterised, non-matrix-matched reference materials such as 91500 zircon (Wiedenbeck et al. 1995) can be included in the analytical procedure to quantify the session excess variance of $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ and to monitor instrumental drift. As secondary wolframite U/Pb reference materials are currently unavailable to assess age reproducibility, we recommend using the long-term reproducibility of other minerals that are commonly dated by LA-ICP-MS (e.g., 91500 zircon used here) to give more realistic estimates of the wolframite age reproducibility.
- Wolframite can show heterogeneity in apparent U/Pb age and common Pb composition due to U and/or Pb mobilisation, heterogenous common Pb, or dissolution-reprecipitation. Importantly, the common Pb composition is not always in isotopic equilibrium with low U/Pb minerals associated with wolframite, nor terrestrial Pb evolution models (e.g., Stacey and Kramers 1972). For such samples, anchoring Discordia to a fixed $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ or performing Pb_c corrections may give incorrect ages.

6. Conclusions

A new age of 316.7 ± 3.3 (5.8) Ma is proposed for the MTM-1 wolframite. This age is different to the previous ID-TIMS age of 334.4 ± 1.7 Ma that was derived from an inappropriate common Pb correction of Discordant data. Using MTM-1 and the newly defined age for normalisation of LA-ICP-MS U/Pb data for six wolframite samples from the FMC, we determine new U/Pb wolframite ages that are more robust and geologically plausible compared to ID-TIMS ages of the same samples. LA-ICP-MS data are more widely distributed on a $^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ diagram compared to ID-TIMS and can better define a Discordia lower intercept U/Pb ages and upper intercept $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$. LA-ICP-MS wolframite ages define a period of mineralisation between *ca* 325 Ma and 295 Ma which is 10 Ma shorter than previously defined by ID-TIMS of the same samples. The highly variable U, Th and Pb concentrations and U/Pb and Pb/Pb isotopic ratios in wolframite can be attributed to natural

variability in the crystal structure, alteration of primary compositions, and/or mineral and fluid inclusions that were unintentionally analysed during laser ablation. This variability warrants the use of in-situ methods, such as LA-ICP-MS, and compositional maps (such as μ XRF or SEM) for targeting purposes. We propose new guidelines for the U/Pb dating of wolframite by LA-ICP-MS that will permit more accurate wolframite ages and more realistic uncertainties.

Appendix

A1 – Hand sample photos and μ XRF and EDS maps

A2 – EPMA data

Acknowledgements

P.C. was funded by Institut Carnot ICEEL and the French National Agency through the national programme “Investissements d’avenir” of the Labex Ressources 21 (Reference ANR-10-LABX-21-RESSOURCES21). This research was funded by an OSU OTELo grant to J.M. “Développement du traçage géochimique et de la datation U-Th-Pb in-situ des colombo-tantalites, cassitérites et wolframites par couplage LA-ICP-MS et SIMS” and a CNRS-INSU-CESSUR grant to J.M. “développement du traçage géochimique et de la datation U-Th-Pb in-situ Colombo-tantalites, cassitérites et wolframites par couplage LA-ICP-MS et SIMS”. L. Monnier is thanked for providing samples from the Echassières deposit and discussions. M. Yang is thanked for providing the YGX-2113 wolframite. Balz Kamber is thanked for editorial handling, and David Chew and an anonymous reviewer for their constructive comments.

Figures Captions

Figure 1: Chemical compositions of wolframite from the Echassières district, French Massif Central, determined by EPMA. All compositions of the MTM-1 measured in this study are shown in coloured triangles; primary MTM-1 is in yellow and altered zones in red. Data from samples considered to be MTM-1 of Yang et al. (2020) are shown as open triangles. Other wolframite samples from Echassières are shown as squares including ECH20-1 (blue), ECH20-3 (green), ECH20-4 (grey), and ECH20-5 (cyan). The grey arrow shows the effect of hydrothermal alteration on the composition of MTM-1 wolframite (i.e., hübneritization; see text for discussion) towards values with lower Fe#. The three generations of wolframite (wlf a, b, c) at Echassières reported by Aïssa et al. (1987) and Monnier et al. (2019) are shown as open circles. Wolframite used in this study is from wlf b and c.

Figure 2: Petrographic characteristics of MTM-1 wolframite sample. A) Transmitted light microscope image of the MTM-1 in thin section. B) SEM-EDS composite element map (Si – turquoise, Al - pink, K – dark blue, W - yellow, Mn – green, Fe - red) highlighting the dominant quartz-topaz-wolframite-muscovite association. C) SEM-EDS intensity map of Mn in wolframite highlighting zones of enrichment (bright color) associated with muscovite replacing topaz. Abbreviations: Ms = muscovite, Qtz = quartz, Tpz = topaz, Wlf = wolframite.

$$Fe\# = (Fe + Mn) / Mn_{apfu}$$

Figure 3: SEM-EDS composite elemental maps for wolframite-bearing samples from the Echassières district (A–C). Same colour scheme as Figure 2. D) and E) are high resolution images of regions labelled in B) and C), respectively. Abbreviations: Ms = muscovite, Qtz = quartz, Tpz = topaz, Wlf = wolframite.

Figure 4: A) Comparison of downhole fractionation of $^{206}\text{Pb}/^{238}\text{U}$ ratio between MTM-1 wolframite and 91500 zircon, based on 85 μm spot diameter 8 Hz repetition rate and 7 J/cm^2 laser energy density. B–D) Comparison of downhole fractionation of $^{206}\text{Pb}/^{238}\text{U}$ ratio between MTM-1 wolframite (dark grey) and other wolframites from the French Massif Central with variable Fe# values. Despite variable Fe#, downhole fractionation of $^{206}\text{Pb}/^{238}\text{U}$ is comparable between all wolframites of this study. Note that the BOS is offset from the MTM-1 due to minor common Pb. E) $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ of the ECH20-4 wolframite after U/Pb normalisation to the MTM-1 and 91500 zircon showing a 5% matrix-bias during LA-ICP-MS. Note that these data were collected with the same analytical conditions as for the data in A–D.

Figure 5: Box and whisker plot of: A) U and B) total Pb concentration (in ppm) in primary and altered MTM-1 wolframite and other wolframite samples from the Echassières W deposit. Circles represent individual measurements.

Figure 6: A) Comparison of $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios and related U/Pb ages of the MTM-1 wolframite determined by LA-ICP-MS and after normalisation to the Sweet Home hübnerite (red), YGX-2113 (green) and Xihuashan (blue). The ID-TIMS data of MTM-1 (yellow stars) and ECH (grey stars) of Harlaux et al. (2018a) are shown here and the following panels for comparison. Note that the uncertainties of the ID-TIMS analyses are smaller than the star symbols. Three regressions of the data are shown; 1) LA-ICP-MS data after normalisation to the Sweet Home Mine hübnerite (largest dataset when compared to normalisation by YGX-2113 and Xihuashan), 2) a free regression through all ID-TIMS data of Harlaux et al. (2018a), and 3) an anchored regression through a selection of ID-TIMS data and using a $^{207}\text{Pb}/^{206}\text{Pb}_i$ determined within quartz associated with the wolframite. B) $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ of primary (red) and altered (green) zones of MTM-1 wolframite. C) $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ data and related U/Pb ages of wolframite from the Echassières deposit and normalised to the MTM-1. These data indicate that MTM-1 and wlf b are of similar age but different apparent $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$. The grey ellipses are the MTM-1 data from panel A.

Figure 7: A–F) $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ diagrams and related U/Pb ages of wolframite from the French Massif Central measured by LA-ICP-MS and normalised using new U/Pb age of MTM-1 wolframite. ID-TIMS data of Harlaux et al. (2018a) are shown in black dots and the errors have been exaggerated so they can be easily seen. A ‘Model-3’ regression through all data is represented by the solid line and grey field. Disp = dispersion as discussed in Vermeesch (2018). For BOS and ML samples, we also show the ‘Model-3’ regressions through the observed data with and without filtering the most discordant data as described in the text. G) Lower intercept ages of wolframite by LA-ICP-MS compared with ID-TIMS ages of the same samples as presented in Harlaux et al. (2018a). The two uncertainties show for LA-ICP-MS ages represent the propagated uncertainty without (small value) and with the added uncertainty introduced from the new defined age of the MTM-1 reference material.

Figure 8: $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ of the BOS wolframite. Ellipses represent LA-ICP-MS data and are coloured by their analytical session (3 in total). The Discordia defined by ID-TIMS analysis of the BOS by Harlaux et al. (2018a) is included. Selected time resolved signals for four analyses are shown in the insets (I, II, III and IV). Each inset is a 30 second ablation spectrum. This time resolved data has not be corrected for background signal

or instrument drift and has not been normalised and are not directly comparable to the compositions defined in the Tera-Wasserburg diagram. (B) SEM EDS map of a BOS wolframite grain showing relatively abundance of Mn, Fe and O. Mn is highly variable in BOS, and oxide mineral inclusions are common. Images were taken on a JEOL JSM-7600F SEM with a Oxford Instruments EDS X-Max 20mm2/WDS Wave detector (C) SEM BSE image of the BOS wolframite showing secondary ferberitisation of the wolframite (after Harlaux et al. 2018b).

Figure 9: U content vs. Th content (A) and $^{208}\text{Pb}/^{206}\text{Pb}$ (B) in wolframite from the French Massif Central. The low Th in wolframite indicates that $^{208}\text{Pb}/^{206}\text{Pb}$ is a good proxy for the proportion of Pb_c . U-Th data from wolframite in the Nanling Range, China is included for comparison (data from Deng et al. 2019 and Tang et al. 2020).

Figure 10: In situ U/Pb isotopic heterogeneity in wolframite from the French Massif Central. A-B) Backscattered electron images of wolframite from the Vaulry (CFM sample, A) and St-Mélany (SM sample, B) deposits (modified from Harlaux et al. 2018b). The red lines correspond to LA-ICP-MS scans performed along transects in wolframite which are shown in (C) and (D). All isotopes were measured on a Agilent 7500c quadrupole ICP-MS coupled with a 193 nm GeoLas ArF excimer laser at the GeoRessources laboratory (Université de Lorraine, Nancy) and reported in Harlaux et al. (2018b). U content and $^{238}\text{U}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios can vary significantly within wolframite whilst $\text{Fe}/(\text{Fe}+\text{Mn})$ remains stable.

Figure 11: A) Isobaric mass interference on AMU 204 between ^{204}Pb and $^{186}\text{W}^{18}\text{O}$. Data correspond to all wolframite from the French Massif Central (FMC) analysed during a single LA-ICP-MS session. Wolframite data from the Vaulry deposit (CFM) are shown for comparison. The predicted cps on AMU 204 contributed by $^{186}\text{W}^{18}\text{O}$ are shown along the linear trend that is defined by intensity on AMU 202 from $^{186}\text{W}^{16}\text{O}$ and a $^{18}\text{O}/^{16}\text{O}$ of 0.002. Covariation of $^{186}\text{W}^{16}\text{O}$ and $^{186}\text{W}^{18}\text{O}$ along this linear trend is due to a shift of sensitivity of the ICP-MS with time. Data that fall above this linear trend are due to ^{204}Pb within wolframite. All data have been corrected for the large background signal introduced from Hg contamination on both AMU 202 and 204. B) The intensity of ^{204}Pb (corrected for $^{186}\text{W}^{18}\text{O}$) correlates strongly with the ^{208}Pb and this relationship is defined as a slope of 38.5 which is equal to the $^{208}\text{Pb}/^{206}\text{Pb}_{(i)}$ ratio of wolframite from the French Massif Central (Harlaux et al. 2018a). This linear correlation for high ^{204}Pb (>500 cps) indicates that nearly all ^{208}Pb is non-radiogenic. For ^{204}Pb <500 cps the correlation no longer exists.

Figure 12: Comparison between a 207-corrected and 208-corrected $^{206}\text{Pb}/^{238}\text{U}$ ages for the CFM wolframite.

Tables

Table 1: Analytical settings used for EPMA analysis of wolframite.

Element	Crystal detector	Peak counting time/background counting time	Detection limit (ppm)	Calibration standard
Analytical settings #1				
W	LIF	10/5	4500	Scheelite
Fe	LIF	10/5	1300	Hematite
Mn	LIF	10/5	1200	Pyrophanite
Analytical settings #2				
F	PC1	120/60	800	Topaz
Sc	PET	60/30	380	Sc metal
Ti	PET	100/50	230	Pyrophanite
Nb	PET	120/60	1200	Synthetic LiNbO ₃
Sn	PET	100/50	850	Cassiterite
Ta	LIF	120/60	1300	Synthetic LiTaO ₃
U	LPET	120/60	1000	Synthetic UO ₂

Table 2: U/Pb data of the MTM-1 wolframite after $^{238}\text{U}/^{206}\text{Pb}$ normalisation to three wolframites and $^{207}\text{Pb}/^{206}\text{Pb}$ normalisation to the NIST614. (see attached .xlsx)

Table 3: Measured U/Pb data of the MTM-1 wolframite and Pb/Pb data normalised to the NIST614. (see attached .xlsx)

Table 4: U/Pb data of the Echassières wolframite after $^{238}\text{U}/^{206}\text{Pb}$ normalisation to the MTM-1 and Pb/Pb data normalised to the NIST614. (see attached .xlsx)

Table 5: Measured U/Pb data of wolframite from the French Massif Central. (see attached .xlsx)

Table 6: Comparison of U/Pb ages for wolframite from the French Massif Central obtained by LA-ICP-MS (this study) and ID-TIMS (Harlaux et al. 2018a). All data are shown on Figure 7. *The BOS and ML ages are determined from filtering out the most discordant analyses as described in the text. LA-ICP-MS $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ ratios were determined from the upper intercept values in Figure 7, and from ID-TIMS analyses of low U/Pb phases such as pyrite and scheelite (Harlaux et al. 2018a). For samples without appropriate Pb-rich phases, quartz (Pb in fluid inclusions) associated with wolframite was used (Harlaux et al. 2018a). The average $^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of up to 4 analyses (2SD shown for multiple analyses) determined by ID-TIMS. Note that MTM-1 and ECH occur in the same deposit (La Bosse) and a single quartz sample was analysed from this deposit.

Sample	LA-ICP-MS (this study)		ID-TIMS (Harlaux et al. 2018a)	
	Lower intercept age (Ma)	$^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$	Age (Ma)	$^{207}\text{Pb}/^{206}\text{Pb}_{(i)}$ of low U/Pb minerals
MTM	316.5 ± 5.3	0.770 ± 0.009	334.4 ± 1.7	0.87
ECH			333.4 ± 2.4	0.87
BOS	307 ± 21 (22)*	0.5 ± 0.1	332.6 ± 6.1	0.60
ENG	318.3 ± 5.2 (9.1)	0.90 ± 0.01	273.7 ± 6.5	0.859 ± 0.006
SM	317.1 ± 3.0 (8.3)	0.84 ± 0.004	315 ± 15	0.857 ± 0.003
CFM	310.6 ± 4.0 (9.2)	0.83 ± 0.5	298.0 ± 1.2	0.80
ML	298.5 ± 2.9 (7.6)*	0.88 ± 0.06	315.9 ± 2.3	0.86
LCP	306.8 ± 4.2 (9.3)	0.842 ± 0.006	276.5 ± 2.9	0.86 ± 0.02

References

- Aïssa, M.; Marignac, C.; Weisbrod, A. Le stockwerk à ferbérîte d'Echassières: Évolution spatiale et temporelle; cristalochimie des ferbérîtes. *Géol. Fr.* 1987, 2, 311–333
- Audétat, A, Günther, D and Heinrich, CA, 2000. Causes for large-scale metal zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Economic Geology*, 95(8): 1563-1581. <https://doi.org/10.2113/gsecongeo.95.8.1563>
- Barbá, KE, Nelson, EP, Misantoni, D, Hitzman, M.W, and Layer, PW, 2005. Structural controls on mineralized veins in the Sweet Home mine, Alma district, Colorado. In: Rhoden, H.N., Steininger, R.C., Vikre, P.G. (Eds.), *Geol. Soc. Nevada Symp.* 2005: 698–708.
- Be Mezeme E, Cocherie A, Faure M, Legendre O, Rossi P (2006) Electron microprobe monazite geochronology of magmatic events: examples from Variscan migmatites and granitoids, Massif Central, France. *Lithos* 87:276-288.
- Be Mezeme E, Faure M, Chen Y, Cocherie A, Talbot JY (2007) Structural, AMS and geochronological study of a laccolith emplaced during Late Variscan orogenic extension: the Rocles pluton (SE French Massif Central). *Int J Earth Sci* 96:215-228.
- Carr, P.A., Norman, M.D., and Bennett, V.C., 2017. Assessment of crystallographic orientation effects on secondary ion mass spectrometry (SIMS) analysis of cassiterite. *Chemical Geology*, 467, 122-133. <https://doi.org/10.1016/j.chemgeo.2017.08.003>
- Carr, PA, Zink, S, Bennett, VC, Norman, MD, Amelin, Y, and Blevin, PL, 2020. A new method for U/Pb geochronology of cassiterite by ID-TIMS applied to the Mole Granite polymetallic system, eastern Australia. *Chemical Geology*, 539: 119539. <https://doi.org/10.1016/j.chemgeo.2020.119539>
- Cheilletz A, Archibald D, Cuney M, and Charoy B, 1992. Ages $^{40}\text{Ar}/^{39}\text{Ar}$ du leucogranite à topaze-lépidolite de Beauvoir et des pegmatites sodolithiques de Chédeville (Nord Massif Central, France). Significations pétrologique et géodynamique. *Comptes Rendus de l'Académie des Sciences*, 315: 329–336
- Chew, DM, Petrus, JA, and Kamber, BS, 2014. U/Pb LA-ICPMS dating using accessory mineral standards with variable common Pb. *Chemical Geology*, 363, 185-199. <https://doi.org/10.1016/j.chemgeo.2013.11.006>

840 Costa S, 1990. De la collision continentale à l'extension tardiorogénique: 100 millions d'années d'histoire
 841 varisque dans le Massif Central Français. Une étude chronologique par la méthode ^{40}Ar - ^{39}Ar . Unpublished Ph.D.
 842 thesis, Université de Montpellier, France, 441p

843 Cuney M, Friedrich M, Blumenfeld P, Bourguignon A, Boiron MC, Vigneresse JL, and Poty B, 1990.
 844 Metallogenesis in the French part of the Variscan orogen. Part I: U preconcentrations in pre-Variscan and Variscan
 845 formations—a comparison with Sn, W and Au. *Tectonophysics* 177:39–57. [https://doi.org/10.1016/0040-](https://doi.org/10.1016/0040-1951(90)90273-B)
 846 [1951\(90\)90273-B](https://doi.org/10.1016/0040-1951(90)90273-B)

847 Cuney, M, Marignac, C and Weisbrod, A, 1992. The Beauvoir topaz-lepidolite albite granite (Massif Central,
 848 France); the disseminated magmatic Sn-Li-Ta-Nb-Be mineralisation. *Economic Geology*, 87(7): 1766-1794.
 849 <https://doi.org/10.2113/gsecongeo.87.7.1766>

850 Deng, XD, Luo, T, Li, JW and Hu, ZC, 2019. Direct dating of hydrothermal tungsten mineralisation using in situ
 851 wolframite U/Pb chronology by laser ablation ICP-MS. *Chemical Geology*, 515:94-104.
 852 <https://doi.org/10.1016/j.chemgeo.2019.04.005>

853 Frei R, Nagler TF, Schonberg R, and Kramers JD, 1998. Re-Os, Sm-Nd, UPb, and stepwise lead leaching isotope
 854 systematics in shear-zone hosted gold mineralisation: genetic tracing and age constraints of crustal hydrothermal
 855 activity. *Geochimica Cosmochimica Acta* 62:1925–1936. [https://doi.org/10.1016/S0016-7037\(98\)00111-2](https://doi.org/10.1016/S0016-7037(98)00111-2)

856 Guillong, M., and Gunther, D. 2002. Effect of particle size distribution on ICP-induced elemental fractionation in
 857 laser ablation-inductively coupled plasma-mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 17(8),
 858 831-837. <https://doi.org/10.1039/B202988J>

859 Guillong, M., Wotzlaw, J. F., Looser, N., and Laurent, O. 2020. Evaluating the reliability of U/Pb laser ablation
 860 inductively coupled plasma mass spectrometry (LA-ICP-MS) carbonate geochronology: matrix issues and a
 861 potential calcite validation reference material. *Geochronology*, 2(1), 155-167. [https://doi.org/10.5194/gchron-2-](https://doi.org/10.5194/gchron-2-155-2020)
 862 [155-2020](https://doi.org/10.5194/gchron-2-155-2020)

863 Harlaux, M, Mercadier, J, Bonzi, WME, Kremer, V, Marignac, C and Cuney, M, 2017. Geochemical signature of
 864 magmatic-hydrothermal fluids exsolved from the Beauvoir rare-metal granite (Massif Central, France): Insights
 865 from LA-ICPMS analysis of primary fluid inclusions. *Geofluids*, 2017. <https://doi.org/10.1155/2017/1925817>

866 Harlaux, M, Romer, RL, Mercadier, J, Morlot, C, Marignac, C and Cuney, M, 2018a. 40 Ma of hydrothermal W
867 mineralisation during the Variscan orogenic evolution of the French Massif Central revealed by U/Pb dating of
868 wolframite. *Mineralium Deposita*, 53(1): 1-51. <https://doi.org/10.1007/s00126-017-0742-8>

869 Harlaux, M., Mercadier, J., Marignac, C., Peiffert, C., Cloquet, C. and Cuney, M., 2018b. Tracing metal sources
870 in peribatholithic hydrothermal W deposits based on the chemical composition of wolframite: The example of the
871 Variscan French Massif Central. *Chemical Geology*, 479: 58-85. <https://doi.org/10.1016/j.chemgeo.2017.12.029>

872 Harlaux, M., Marignac, C., Mercadier, J., Poujol, M., Boiron, M.C., Kouzmanov, K., Camacho, A., Alikouss, S.,
873 Roméo, B., Mouthier, B. and Cuney, M., 2021. Multistage development of a hydrothermal W deposit during the
874 Variscan late-orogenic evolution: the Puy-les-Vignes breccia pipe (Massif Central, France). *BSGF-Earth Sciences*
875 *Bulletin*, 192, p.33. <https://doi.org/10.1051/bsgf/2021023>

876 Hiess, J., Condon, D.J., McLean, N. and Noble, S.R., 2012. 238U/235U systematics in terrestrial uranium-bearing
877 minerals. *Science*, 335(6076), pp.1610-1614. <https://doi.org/10.1126/science.1215507>

878 Hogan, J.P., Sinha, A.K., 1991. The effect of accessory minerals on the redistribution of lead isotopes during
879 crustal anatexis: A model. *Geochim. Cosmochim. Acta* 55. [https://doi.org/10.1016/0016-7037\(91\)90422-2](https://doi.org/10.1016/0016-7037(91)90422-2)

880 Holliger P, Cuney M, Friedrich M, and Turpin L, 1986. Age Carbonifère de l'unité de Brême du complexe
881 granitique peralumineux de Saint Sylvestre (N.O. Massif Central) défini par les données isotopiques U/Pb sur
882 zircon et monazite. *Comptes Rendus des Seances de l'Academie des Sciences* 303:1309–1314

883 Horstwood, MS, Košler, J, Gehrels, G, Jackson, SE, McLean, NM, Paton, C, Pearson, NJ, Sircombe, K, Sylvester,
884 P, Vermeesch, Bowring, JF, Condon, DJ, and Shoen B, 2016. Community- derived standards for LA- ICP- MS
885 U- (Th-) Pb geochronology–Uncertainty propagation, age interpretation and data reporting. *Geostandards and*
886 *Geoanalytical Research*, 40(3): 311-332. <https://doi.org/10.1111/j.1751-908X.2016.00379.x>

887 Jochum, K.P., Weis, U., Stoll, B., Kuzmin, D., Yang, Q., Raczek, I., Jacob, D.E., Stracke, A., Birbaum, K., Frick,
888 D.A., Günther, D. and Enzweiler, J., 2011. Determination of reference values for NIST SRM 610–617 glasses
889 following ISO guidelines. *Geostandards and Geoanalytical Research*, 35(4), 397-429.
890 <https://doi.org/10.1111/j.1751-908X.2011.00120.x>

891 Laurent, O., Couzinié, S., Zeh, A., Vanderhaeghe, O., Moyen, J. F., Villaros, A., Gardien, V., Chelle-Michou, C.,
892 2017. Protracted, coeval crust and mantle melting during Variscan late-orogenic evolution: U/Pb dating in the

893 eastern French Massif Central. *International Journal of Earth Sciences*, 106(2), 421–451.
 894 <https://doi.org/10.1007/s00531-016-1434-9>

895 Lecumberri-Sanchez P, Romer RL, Lüders V, Bodnar RJ, 2014. Genetic relationship between silver-lead-zinc
 896 mineralisation in the Wutong deposit, Guangxi Province and Mesozoic granitic magmatism in the Nanling belt,
 897 southeast China. *Mineralium Deposita* 49:353–369. <https://doi.org/10.1007/s00126-013-0494-z>

898 Legros, H, Harlaux, M, Mercadier, J, Romer, RL, Poujol, M, Camacho, A, Marignac, C, Cuney, M, Wang, RC,
 899 Charles, N, and Lespinasse, MY, 2020. The world-class Nanling metallogenic belt (Jiangxi, China): W and Sn
 900 deposition at 160 Ma followed by 30 my of hydrothermal metal redistribution. *Ore Geology Reviews*, 117:
 901 103302. <https://doi.org/10.1016/j.oregeorev.2019.103302>

902 Li, QL, Li, XH, Lan, ZW, Guo, CL, Yang, YN, Liu, Y. and Tang, GQ, 2013. Monazite and xenotime U–Th–Pb
 903 geochronology by ion microprobe: dating highly fractionated granites at Xihuashan tungsten mine, SE China.
 904 *Contributions to Mineralogy and Petrology*, 166(1): 65–80. <https://doi.org/10.1007/s00410-013-0865-6>

905 Li, Q, Parrish, RR, Horstwood, MSA, and McArthur, JM, 2014. U/Pb dating of cements in Mesozoic ammonites,
 906 *Chemical Geology*, 376: 76–83, 2014. <https://doi.org/10.1016/j.chemgeo.2014.03.020>

907 Li, ST, Wang, JB, Zhu, XY and Li, C, 2011. Re-Os dating of molybdenite and sulfur isotope analysis of the
 908 Yaogangxiang tungsten polymetallic deposits in Hunan Province and their geological significance. *Geoscience*,
 909 25(2), pp.228–235.

910 Ludwig, K.R., 2003. User's manual for isoplot 3.00, a geochronological toolkit for microsoft excel. Berkeley
 911 *Geochronl. Cent. Spec. Publ.*, 4, 25–32.

912 Luo, T, Deng, X., Li, J. Hu, Z., Zhang, W., Liu, Y and Zhang, J. 2019. U–Pb geochronology of wolframite by
 913 laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 34(7):
 914 1439–1446. <https://doi.org/10.1039/C9JA00139E>

915 Mao, JW, 2007. Largescale tungsten-tin mineralization in the Nanling region, South China: metallogenic ages and
 916 corresponding geodynamic processes. *Acta Petrol. Sin.*, 23, pp.2329–2338.

917 Melleton J, Gloaguen E, and Frei D, 2015. Rare-elements (Li-Be-Ta-Sn-Nb) magmatism in the European Variscan
 918 Belt, a review. In *Proceedings of the 13th Biennial SGA Meeting*, 24–27 August 2015, Nancy, France (eds. A. S.
 919 André-Mayer, M. Cathelineau, P. Muchez, E. Pirard and S. Sindern), Vol. 2, 807–810

920 Monié P, Respaut JP, Brichaud S, Bouchot V, Faure M, and Roig JY, 2000. $^{40}\text{Ar}/^{39}\text{Ar}$ and U/Pb geochronology
 921 applied to Au-W-Sb metallogenesis in the Cévennes and Châtaigneraie districts (Southern Massif Central,
 922 France). In A Geode-GeoFrance 3D Workshop on Orogenic Gold Deposits in Europe with emphasis on the
 923 Variscides (eds. V. Bouchot and R. Moritz). Doc BRGM, 297, 77–79

924 Monnier, L, Salvi, S, Melleton, J, Bailly, L, Béziat, D, de Parseval, P, Gouy, S, and Lach, P, 2019. Multiple
 925 Generations of Wolframite Mineralisation in the Echassieres District (Massif Central, France). *Minerals*, 9(10):
 926 637. <https://doi.org/10.3390/min9100637>

927 Monnier, L, Salvi, S, Jourdan, V, Sall, S, Bailly, L, Melleton, J, and Béziat, D, 2020. Contrasting fluid behavior
 928 during two styles of greisen alteration leading to distinct wolframite mineralisations: the Echassières district
 929 (Massif Central, France). *Ore Geology Reviews*, 124: 103648. <https://doi.org/10.1016/j.oregeorev.2020.103648>

930 Monnier, L., Melleton, J., Vanderhaeghe, O., Salvi, S., Lach, P., Bruguier, O., Benmammar, A., Bailly, L., Béziat,
 931 D., Gloaguen, E, 2021. Episodic Precipitation of Wolframite during An Orogen: The Echassières District, Variscan
 932 Belt of France. *Minerals*, 11, 923. <https://doi.org/10.3390/min11090923>

933 Orтели, M., Kouzmanov, K., Wälle, M., Ubrig, N. and Casanova, V., 2018. Fluid inclusion studies in opaque ore
 934 minerals: I. Trace element content and physical properties of ore minerals controlling textural features in
 935 transmitted near-infrared light microscopy. *Economic Geology*, 113(8), pp.1845-1860.

936 Paton, C, Woodhead, JD, Hellstrom, JC, Hergt, JM, Greig, A, and Maas, R, 2010. Improved laser ablation U- Pb
 937 zircon geochronology through robust downhole fractionation correction. *Geochemistry, Geophysics, Geosystems*,
 938 11(3). <https://doi.org/10.1029/2009GC002618>

939 Peng, J, Zhou, MF, Hu, R, Shen, N, Yuan, S, Bi, X, Du, A and Qu, W, 2006. Precise molybdenite Re–Os and
 940 mica Ar–Ar dating of the Mesozoic Yaogangxian tungsten deposit, central Nanling district, South China.
 941 *Mineralium Deposita*, 41(7), pp.661-669.

942 Pfaff K, Romer RL, and Markl G, 2009. U/Pb ages of ferberite, chalcedony, agate, ‘U-mica’ and pitchblende:
 943 constraints on the mineralisation history of the Schwarzwald ore district. *European Journal of Mineralogy*,
 944 21:817–836. <https://doi.org/10.1127/0935-1221/2009/0021-1944>

945 Pietruszka A.J., and Neymark L.A., 2017. Evaluation of laser ablation double-focussing SC-ICPMS for
 946 “common” lead isotopic measurements in silicate glasses and minerals. *Journal of Analytical Atomic*
 947 *Spectrometry*, 32:1135-1154. <https://doi.org/10.1039/C7JA00005G>

948 Pietruszka, A.J. and Neymark, L.A., 2017. Evaluation of laser ablation double-focusing SC-ICPMS for “common”
 949 lead isotopic measurements in silicate glasses and minerals. *Journal of Analytical Atomic Spectrometry*, 32(6),
 950 pp.1135-1154. <https://doi.org/10.1039/C7JA00005G>

951 Pin, C, 1991. Sr–Nd isotopic study of igneous and metasedimentary enclaves in some hercynian granitoids from
 952 the Massif Central, France. In: Didier, J., Barbarin, B. (Eds.), *Enclaves and granite petrology (Developments in*
 953 *Petrology)*, 13. Elsevier, pp. 333–343.

954 Poitrenaud, T, Poujol, M, Augier, R and Marcoux, E, 2019. The polyphase evolution of a late Variscan W/Au
 955 deposit (Salau, French Pyrenees): insights from REE and U/Pb LA-ICP-MS analyses. *Mineralium Deposita*, pp.1-
 956 21. <https://doi.org/10.1007/s00126-019-00923-2>

957 Raimbault, L, Cuney, M, Azencott, C, Duthou, JL, and Joron, JL, 1995. Geochemical evidence for a multistage
 958 magmatic genesis of Ta-Sn-Li mineralisation in the granite at Beauvoir, French Massif Central. *Economic*
 959 *Geology*, 90(3): 548-576. <https://doi.org/10.2113/gsecongeo.90.3.548>

960 Romer RL, and Lüders V, 2006. Direct dating of hydrothermal W mineralisation: U/Pb age for hübnerite
 961 (MnWO₄), Sweet Home Mine mine, Colorado. *Geochimica et Cosmochimica Acta* 70:4725–4733.
 962 <https://doi.org/10.1016/j.gca.2006.07.003>

963 Schärer, U., 1984. The effect of initial ²³⁰Th disequilibrium on young UPb ages: the Makalu case, Himalaya.
 964 *Earth and Planetary Science Letters*, 67(2), pp.191-204. [https://doi.org/10.1016/0012-821X\(84\)90114-6](https://doi.org/10.1016/0012-821X(84)90114-6)

965 Scaillet S, Cheilletz A, CuneyM, Farrar E, and Archibald DA, 1996. Cooling pattern and mineralisation history
 966 of the saint Sylvestre and western Marche leucogranite pluton, French massif central: I. ⁴⁰Ar/³⁹Ar isotopic
 967 constraints. *Geochimica et Cosmochimica Acta*, 60:4653–4671. [https://doi.org/10.1016/S0016-7037\(96\)00291-8](https://doi.org/10.1016/S0016-7037(96)00291-8)

968 Stacey, J.T., and Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model.
 969 *Earth and planetary science letters*, 26(2), 207-221. [https://doi.org/10.1016/0012-821X\(75\)90088-6](https://doi.org/10.1016/0012-821X(75)90088-6)

970 Tang, Y, Cui, K, Zheng, Z, Gao, J, Han, J, Yang, J and Liu, L, 2020. LA-ICP-MS U-Pb geochronology of
 971 wolframite by combining NIST series and common lead-bearing MTM as the primary reference material:
 972 Implications for metallogenesis of South China. *Gondwana Research*, 83: 217-231.
 973 <https://doi.org/10.1016/j.gr.2020.02.006>

974 Tera, F, and Wasserburg, GJ, 1972. U-Th-Pb systematics in three Apollo 14 basalts and the problem of initial Pb
 975 in lunar rocks. *Earth and planetary science letters*, 14(3), pp.281-304. [https://doi.org/10.1016/0012-](https://doi.org/10.1016/0012-821X(72)90128-8)
 976 [821X\(72\)90128-8](https://doi.org/10.1016/0012-821X(72)90128-8)

977 Tindle, A.G., and Webb, P.C., 1989. Niobian wolframite from Glen Gairn in the Eastern Highlands of Scotland:
 978 A microprobe investigation. *Geochimica et Cosmochimica Acta*, 53(8), 1921-1935. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(89)90313-X)
 979 [7037\(89\)90313-X](https://doi.org/10.1016/0016-7037(89)90313-X)

980 Vermeesch, P, 2018. IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers*, 9(5): 1479-
 981 1493. <https://doi.org/10.1016/j.gsf.2018.04.001>

982 [Villa, I.M., De Bièvre, P., Holden, N.E., and Renne, P.R., 2015\). IUPAC-IUGS recommendation on the half life](https://doi.org/10.1016/j.gsf.2018.04.001)
 983 [of 87Rb. *Geochimica et Cosmochimica Acta*, 164, 382-385. <https://doi.org/10.1016/j.gca.2015.05.025>](https://doi.org/10.1016/j.gsf.2018.04.001)

984 Villa, I. M., De Bièvre, P., Holden, N. E., and Renne, P. R. 2015. IUPAC-IUGS recommendation on the half life
 985 of 87Rb. *Geochimica et Cosmochimica Acta*, 164, 382-385.

986 Villaros A, Laurent O, Pichavant M, Zeh A, Cuney M, and Deveaud S, 2014. Source variability in a single granitic
 987 pluton : Example from the St Sylvestre Leucogranite complex. 24ème Réunion des Sciences de la Terre, Oct 2014,
 988 Pau, France, 141

989 Wang, DH, Li, HQ, Qin, Y, Mei, YP, Chen, ZH, Qu, WJ., WANG, YB, Cai, H., Gong, SQ and He, XP, 2009.
 990 Rock-forming and ore-forming ages of the Yaogangxian tungsten deposit of Hunan Province. *Rock and mineral*
 991 *analysis*, 28(3), pp.201-208.

992 Wang, FY, Li, CY, Ling, MX, Zhang, H, Sun, YL, and Sun, W, 2011. Geochronology of the Xihuashan tungsten
 993 deposit in southeastern China: constraints from Re–Os and U/Pb dating. *Resource geology*, 61(4): 414-423.
 994 <https://doi.org/10.1111/j.1751-3928.2011.00176.x>

995 Wetherill, GW, 1956. Discordant uranium- lead ages, I. Eos, *Transactions American Geophysical Union*, 37(3):
 996 320-326. <https://doi.org/10.1029/TR037i003p00320>

997 Wiedenbeck, M, Alle, P, Corfu, F, Griffin, WL, Meier, M, Oberli, F, von Quadt, A, Roddick, JC, and Spiegel, W,
 998 1995. Three natural zircon standards for U- Th- Pb, Lu- Hf, trace element and REE analyses. *Geostandards*
 999 *newsletter*, 19(1): 1-23. <https://doi.org/10.1111/j.1751-908X.1995.tb00147.x>

1000 Williams, IS, 1998. U-Th-Pb geochronology by ion microprobe. *Reviews in economic geology*, 7:1-35.
 1001 <https://doi.org/10.5382/Rev.07.01>

1002 Woodhead, JD, and Hergt, JM, 2001. Strontium, neodymium and lead isotope analyses of NIST glass certified
 1003 reference materials: SRM 610, 612, 614. *Geostandards Newsletter*, 25(2- 3): 261-266.
 1004 <https://doi.org/10.1111/j.1751-908X.2001.tb00601.x>

1005 Yang, M, Yang, YH, Wu, ST, Romer, R, Che, X, Zhao, ZF, Yang, JH, Wu, FY, Xie, LW, Huang, C, and Zhang,
 1006 D. 2020. Accurate and precise in situ U/Pb isotopic dating of wolframite series minerals via LA-SF-ICP-MS.
 1007 *Journal of Analytical Atomic Spectrometry*. <https://doi.org/10.1039/D0JA00248H>

1008 Zhang, R, Lehmann, B, Seltmann, R, Sun, W, Li, C. 2017. Cassiterite U/Pb geochronology constrains magmatic-
 1009 hydrothermal evolution in complex evolved granite systems: The classic Erzgebirge tin province (Saxony and
 1010 Bohemia). *Geology* 45, 1095–1098. <https://doi.org/10.1130/G39634.1>

1011

Figure 1

[Click here to access/download;Figure;Figure 1jpg.jpg](#)

Figure 3

[Click here to access/download;Figure;Figure 3.png](#)

Figure 4

[Click here to access/download;Figure;Figure 4.png](#)

Figure 5

[Click here to access/download;Figure;Figure 5.png](#)

Figure 8

[Click here to access/download;Figure;Figure 8.jpg](#)

Figure 10 [Click here to access/download;Figure;Figure 10.png](#)

Figure 11

Figure 12

[Click here to access/download;Figure;Figure 12.png](#)

Session 1Pb ppm1 232Thppr238U ppnf206c					238U/ ²⁰⁶ F 2SE		207Pb/ ²⁰⁶ 2SE		208Pb/ ²⁰⁶ F 2SE	
Normaliation of 238U/206Pb to YGX-2113										
7405	0.32	0.01	5.24	0.005	19.5	0.6	0.057	0.002	0.0394	0.0359
7405	0.51	0.01	9.49	0.004	20.1	0.8	0.056	0.002	0.0048	0.0013
7405	0.80	0.04	14.86	0.003	19.7	0.8	0.055	0.001	0.0071	0.0011
7405	0.23	0.04	3.40	0.018	18.6	0.7	0.067	0.004	0.0542	0.0100
7405	0.54	0.02	9.65	0.029	20.3	0.8	0.075	0.002	0.0588	0.0044
7405	5.63	0.06	84.40	0.065	18.3	0.8	0.105	0.002	0.1409	0.0031
7405	1.35	0.04	27.14	0.003	19.9	0.9	0.055	0.001	0.0037	0.0011
7405	0.22	0.00	3.35	0.012	18.7	0.5	0.063	0.005	0.0106	0.0055
7405	5.73	0.09	96.47	0.032	18.9	0.8	0.078	0.001	0.0721	0.0009
7405	16.09	0.63	197.64	0.130	17.2	0.7	0.157	0.002	0.2822	0.0012
7405	0.64	0.02	12.73	0.003	20.5	0.9	0.055	0.002	0.0076	0.0123
7405	0.13	0.00	2.02	0.016	19.4	0.8	0.066	0.006	0.0073	0.0067
7405	14.37	0.57	176.00	0.129	17.2	0.7	0.155	0.003	0.2757	0.0060
7405	11.87	0.31	189.20	0.054	19.0	0.8	0.096	0.002	0.1182	0.0009
7405	1.00	0.03	17.71	0.023	19.7	0.8	0.071	0.002	0.0474	0.0022
7405	0.78	0.01	11.71	0.037	18.0	0.7	0.083	0.003	0.0807	0.0062
7405	0.14	0.00	2.23	0.019	20.4	1.0	0.067	0.004	0.0221	0.0073
7405	0.23	0.00	3.84	0.014	19.2	0.9	0.064	0.006	0.0125	0.0040
7405	0.85	0.01	14.04	0.029	19.0	0.8	0.076	0.004	0.0567	0.0086
7405	0.17	0.00	2.86	0.012	20.4	0.9	0.062	0.004	-0.0004	0.0050
7405	0.96	0.02	18.63	0.000	20.5	0.9	0.052	0.001	0.0014	0.0009
7405	1.01	0.03	19.57	0.000	20.6	0.9	0.053	0.001	0.0025	0.0008
7405	0.42	0.02	6.90	0.030	19.0	0.7	0.077	0.004	0.0417	0.0051
7405	0.61	0.08	8.70	0.062	18.8	0.8	0.102	0.007	0.1303	0.0180
7405	1.08	0.04	20.01	0.005	19.9	0.8	0.057	0.003	0.0033	0.0017
7405	1.95	0.07	36.33	0.002	19.6	0.8	0.054	0.001	0.0040	0.0012
7405	2.54	0.10	45.46	0.018	19.8	0.8	0.067	0.001	0.0386	0.0013
7405	1.11	0.03	20.43	0.006	19.7	0.8	0.058	0.001	0.0123	0.0010
7405	1.95	0.03	37.06	0.001	20.0	0.8	0.053	0.001	0.0008	0.0004
7405	2.16	0.03	40.79	0.007	20.0	0.8	0.059	0.002	0.0083	0.0027
Normaliation of 238U/206Pb to Xihuashan										
6668	0.26	0.01	4.77	0.019	19.8	0.7	0.068	0.002	0.0299	0.0022
6668	0.20	0.02	3.50	0.019	19.2	0.6	0.068	0.002	0.0328	0.0028
6668	0.51	0.04	5.25	0.185	15.5	0.5	0.201	0.004	0.3893	0.0101
6668	0.25	0.02	4.71	0.018	19.6	0.6	0.067	0.002	0.0300	0.0022
6668	0.22	0.01	3.93	0.024	19.4	0.6	0.072	0.002	0.0473	0.0033
6668	0.43	0.01	8.43	0.011	19.8	0.6	0.061	0.001	0.0183	0.0012
6668	0.35	0.02	6.57	0.014	19.7	0.6	0.064	0.001	0.0232	0.0019

6668	0.54	0.02	10.80	0.006	19.9	0.6	0.058	0.001	0.0111	0.0008
6668	0.76	0.01	14.91	0.008	19.6	0.6	0.059	0.001	0.0135	0.0012
6668	0.95	0.01	19.11	0.002	19.6	0.6	0.054	0.001	0.0022	0.0004
6668	0.84	0.01	16.88	0.002	19.8	0.6	0.054	0.001	0.0022	0.0004
6668	1.01	0.01	20.75	0.002	19.9	0.6	0.054	0.001	0.0020	0.0004
6668	1.18	0.02	24.05	0.001	19.7	0.6	0.054	0.001	0.0014	0.0003
6668	1.90	0.03	38.44	0.001	19.6	0.6	0.053	0.001	0.0011	0.0002
7405	0.32	0.01	5.24	0.005	19.6	0.8	0.057	0.002	0.0394	0.0359
7405	0.51	0.01	9.49	0.004	20.2	1.1	0.056	0.002	0.0048	0.0013
7405	0.80	0.04	14.86	0.003	19.8	1.0	0.055	0.001	0.0071	0.0011
7405	0.22	0.05	3.29	0.009	18.8	0.8	0.060	0.004	0.0293	0.0090
7405	5.63	0.06	84.58	0.065	18.3	0.9	0.105	0.002	0.1408	0.0031
7405	1.33	0.04	26.61	0.003	20.4	1.1	0.055	0.001	0.0039	0.0011
7405	0.22	0.00	3.35	0.012	18.7	0.6	0.063	0.005	0.0106	0.0055
7405	5.73	0.09	96.47	0.032	18.8	1.0	0.078	0.001	0.0721	0.0009
7405	16.09	0.63	197.64	0.130	17.2	0.9	0.157	0.002	0.2822	0.0012
7405	0.64	0.02	12.73	0.003	20.8	1.1	0.055	0.002	0.0076	0.0123
7405	0.13	0.00	2.02	0.016	19.3	1.0	0.066	0.006	0.0073	0.0067
7405	14.37	0.57	176.00	0.129	17.1	0.9	0.155	0.003	0.2757	0.0060
7405	11.87	0.31	189.20	0.054	18.8	0.9	0.096	0.002	0.1182	0.0009
7405	1.00	0.03	17.71	0.023	19.5	1.0	0.071	0.002	0.0474	0.0022
7405	0.78	0.01	11.71	0.037	17.8	0.8	0.083	0.003	0.0807	0.0062
7405	0.14	0.00	2.23	0.019	20.1	1.2	0.067	0.004	0.0221	0.0073
7405	0.23	0.00	3.84	0.014	18.9	1.0	0.064	0.006	0.0125	0.0040
7405	0.17	0.00	2.86	0.012	20.1	1.0	0.062	0.004	-0.0004	0.0050
7405	0.96	0.02	18.63	0.000	20.2	1.0	0.052	0.001	0.0014	0.0009
7405	1.01	0.03	19.57	0.000	20.3	1.1	0.053	0.001	0.0025	0.0008
7405	0.41	0.02	6.67	0.019	18.5	0.9	0.068	0.003	0.0308	0.0036
7405	1.08	0.04	20.01	0.005	19.5	0.9	0.057	0.003	0.0033	0.0017
7405	1.95	0.07	36.33	0.001	19.2	1.0	0.054	0.001	0.0040	0.0012
7405	2.54	0.10	45.46	0.018	19.3	1.0	0.067	0.001	0.0386	0.0013
7405	1.11	0.03	20.43	0.006	19.2	1.0	0.058	0.001	0.0123	0.0010
7405	1.95	0.03	37.06	0.001	19.5	1.0	0.053	0.001	0.0008	0.0004
7405	2.12	0.03	41.59	0.002	19.7	1.0	0.054	0.001	0.0023	0.0006
Normaliation of 238U/206Pb to Sweet Home Hübnerite										
6949	0.16	0.01	2.92	0.014	19.5	0.7	0.060	0.002	0.0077	0.0018
6949	0.59	0.01	10.70	0.035	19.0	0.7	0.074	0.001	0.0529	0.0018
6949	1.61	0.06	27.20	0.069	18.5	0.7	0.098	0.002	0.1205	0.0043
6949	0.24	0.01	4.22	0.031	18.6	0.7	0.072	0.002	0.0476	0.0026
6949	6.08	1.80	43.27	0.354	13.5	0.5	0.298	0.010	0.6531	0.0261

6949	3.14	0.16	63.52	0.009	19.6	0.7	0.056	0.001	0.0106	0.0003
6949	1.03	0.07	21.39	0.007	19.8	0.7	0.055	0.001	0.0058	0.0007
6949	2.90	0.17	57.03	0.022	19.5	0.7	0.065	0.001	0.0329	0.0017
6949	2.88	0.35	53.52	0.028	18.9	0.7	0.070	0.001	0.0468	0.0009
6949	3.75	0.15	61.42	0.076	18.4	0.6	0.103	0.004	0.1306	0.0087
6949	2.99	0.12	59.81	0.016	19.7	0.7	0.061	0.001	0.0226	0.0009
6949	2.92	0.15	57.72	0.012	19.2	0.7	0.059	0.001	0.0158	0.0009
6949	3.10	1.27	58.20	0.025	18.7	0.7	0.067	0.001	0.0389	0.0011
6949	3.34	0.23	66.94	0.012	19.4	0.7	0.058	0.001	0.0162	0.0007
6949	2.34	0.19	44.91	0.025	19.3	0.7	0.068	0.001	0.0386	0.0018
6949	1.80	0.09	35.77	0.014	19.3	0.7	0.060	0.001	0.0185	0.0012
6949	0.98	0.03	19.57	0.013	19.5	0.7	0.059	0.001	0.0155	0.0014
6949	3.33	0.31	9.98	0.609	7.2	0.3	0.476	0.006	1.1343	0.0110
6949	2.57	0.09	53.20	0.006	19.8	0.7	0.054	0.001	0.0040	0.0002
6949	1.32	0.20	27.28	0.005	19.7	0.7	0.053	0.001	0.0043	0.0003
6949	9.24	0.34	99.28	0.213	15.4	0.6	0.199	0.002	0.3894	0.0051
6949	2.03	0.11	33.87	0.071	18.6	0.7	0.099	0.001	0.1243	0.0018
6949	13.74	0.35	140.59	0.242	15.3	0.6	0.219	0.002	0.4422	0.0046
6949	11.71	0.34	117.89	0.251	15.3	0.5	0.226	0.002	0.4616	0.0019
6949	10.56	0.24	113.19	0.230	15.8	0.6	0.211	0.002	0.4214	0.0028
6949	8.39	0.25	101.28	0.179	16.1	0.6	0.175	0.002	0.3258	0.0052
6949	16.59	0.33	98.17	0.364	13.2	0.8	0.305	0.025	0.6689	0.0662
6949	5.72	0.30	51.85	0.272	14.2	0.5	0.240	0.003	0.4983	0.0057
6949	11.35	0.33	113.01	0.245	15.2	0.5	0.222	0.003	0.4482	0.0053
6949	3.30	0.15	16.56	0.458	9.9	0.4	0.371	0.005	0.8452	0.0131
6949	7.18	0.22	89.00	0.177	16.6	0.6	0.174	0.002	0.3187	0.0023
6949	10.97	0.23	108.70	0.229	15.4	0.5	0.211	0.011	0.4194	0.0279
6949	5.50	0.18	100.34	0.044	18.9	0.7	0.081	0.001	0.0739	0.0023
6949	2.74	0.10	43.10	0.084	17.9	0.7	0.109	0.002	0.1478	0.0033
6949	8.95	0.22	112.91	0.168	16.7	0.7	0.167	0.010	0.3076	0.0270
6949	7.15	0.21	109.31	0.100	17.7	0.7	0.120	0.001	0.1787	0.0019
6949	3.68	0.13	70.27	0.027	18.9	0.7	0.069	0.001	0.0417	0.0005
6949	5.37	0.15	92.73	0.059	18.4	0.7	0.091	0.001	0.1032	0.0009
6949	2.70	0.10	54.51	0.011	19.4	0.7	0.057	0.001	0.0120	0.0004
6949	2.54	0.15	35.83	0.115	17.1	0.6	0.130	0.001	0.2059	0.0020
6949	3.73	0.19	56.18	0.093	18.1	0.5	0.115	0.006	0.1662	0.0168
6949	2.03	0.10	26.03	0.153	16.3	0.6	0.157	0.008	0.2764	0.0205
6949	6.32	0.24	101.08	0.066	17.5	0.7	0.096	0.003	0.1168	0.0071
6949	1.29	0.08	5.91	0.512	10.2	0.4	0.408	0.012	0.9115	0.0229
6949	1.06	0.03	5.63	0.457	10.8	0.4	0.370	0.005	0.8456	0.0116

6949	1.21	0.06	4.34	0.614	8.9	0.3	0.480	0.007	1.1359	0.0146
6949	2.08	0.18	4.25	0.763	5.7	0.3	0.584	0.007	1.4159	0.0142
6949	2.87	0.16	57.51	0.010	19.2	0.7	0.057	0.001	0.0116	0.0011
6949	0.17	0.02	3.35	0.011	19.6	0.7	0.058	0.002	0.0083	0.0019
6949	10.23	0.79	5.61	0.924	1.8	0.1	0.697	0.006	1.7129	0.0072
6949	0.36	0.04	4.32	0.151	17.1	0.7	0.156	0.019	0.2634	0.0475
6949	0.29	0.01	5.67	0.015	19.5	0.7	0.060	0.001	0.0166	0.0017
6949	0.39	0.02	7.71	0.021	19.8	0.7	0.064	0.001	0.0265	0.0018
6949	0.54	0.07	10.82	0.007	20.3	0.8	0.055	0.001	0.0071	0.0007
6949	1.27	0.09	10.53	0.286	13.8	0.6	0.250	0.007	0.5367	0.0174
6949	1.13	0.49	7.75	0.305	14.0	0.8	0.263	0.020	0.5764	0.0515
6949	1.31	0.21	22.67	0.056	19.1	0.7	0.089	0.001	0.0992	0.0030
6949	0.60	0.10	10.58	0.050	19.3	0.7	0.085	0.004	0.0874	0.0100
6949	1.18	0.19	12.87	0.201	16.0	0.6	0.191	0.005	0.3815	0.0108
6949	1.85	0.16	11.33	0.394	11.6	0.5	0.326	0.005	0.7344	0.0116
6949	0.87	0.05	17.59	0.009	19.9	0.7	0.056	0.001	0.0088	0.0006
6949	0.91	0.08	18.17	0.009	19.7	0.7	0.056	0.001	0.0102	0.0006
6949	1.06	0.08	15.67	0.099	17.6	0.6	0.119	0.002	0.1772	0.0043
6949	0.84	0.08	16.87	0.008	19.8	0.7	0.056	0.001	0.0093	0.0005
6949	0.74	0.03	14.20	0.018	19.3	0.7	0.063	0.001	0.0293	0.0011
6949	0.72	0.04	14.76	0.006	19.9	0.7	0.054	0.001	0.0026	0.0004
6949	0.61	0.01	12.38	0.007	19.8	0.7	0.055	0.001	0.0039	0.0006
6949	0.49	0.02	9.63	0.006	19.6	0.7	0.054	0.001	0.0038	0.0007
6949	0.78	0.02	16.06	0.005	20.0	0.7	0.053	0.001	0.0023	0.0003
6949	0.73	0.05	14.67	0.010	19.7	0.7	0.057	0.001	0.0107	0.0007
6949	0.66	0.01	12.53	0.025	19.5	0.7	0.067	0.001	0.0382	0.0015
6949	0.53	0.01	10.46	0.009	19.7	0.7	0.056	0.001	0.0091	0.0007
6949	0.77	0.01	10.88	0.117	17.5	0.6	0.132	0.002	0.2099	0.0035
6949	0.38	0.01	7.22	0.020	19.5	0.8	0.064	0.001	0.0292	0.0020
6949	0.43	0.01	8.08	0.024	18.9	0.8	0.067	0.001	0.0356	0.0017
6949	2.53	0.22	14.45	0.440	11.5	0.5	0.358	0.005	0.8186	0.0103
6949	1.58	0.04	32.95	0.005	20.0	0.8	0.054	0.001	0.0024	0.0002
6949	0.86	0.01	17.49	0.007	19.7	0.7	0.055	0.001	0.0056	0.0004
6949	0.74	0.09	14.78	0.014	19.9	0.7	0.060	0.001	0.0178	0.0008
6949	0.86	0.03	17.90	0.005	20.1	0.7	0.054	0.001	0.0022	0.0003
6949	1.15	0.14	23.99	0.005	20.1	0.7	0.054	0.001	0.0031	0.0003
6949	1.04	0.02	21.80	0.004	20.1	0.7	0.053	0.001	0.0010	0.0002
6949	0.57	0.02	11.66	0.010	20.2	0.7	0.057	0.001	0.0105	0.0016
6949	0.86	0.04	12.40	0.108	17.5	0.7	0.126	0.003	0.1993	0.0065
6949	1.32	0.12	15.04	0.207	16.8	0.6	0.195	0.005	0.3868	0.0128

6949	0.72	0.10	14.98	0.007	20.2	0.7	0.055	0.001	0.0070	0.0005
6949	0.82	0.12	16.71	0.009	20.1	0.8	0.056	0.001	0.0109	0.0006
6949	3.26	0.45	20.98	0.316	14.2	0.8	0.271	0.025	0.5886	0.0669
6949	1.26	0.04	13.91	0.191	15.8	0.6	0.184	0.003	0.3527	0.0077
6949	2.12	0.04	12.62	0.412	11.5	0.4	0.338	0.005	0.7584	0.0098
6949	0.56	0.01	11.11	0.014	19.8	0.7	0.060	0.001	0.0215	0.0010
6949	0.98	0.06	13.85	0.126	18.1	0.6	0.138	0.007	0.2275	0.0179
6949	0.77	0.03	12.28	0.086	18.4	0.7	0.110	0.002	0.1535	0.0037
6949	1.67	0.28	11.15	0.435	13.2	0.5	0.354	0.005	0.8083	0.0103
6949	0.90	0.04	18.49	0.008	20.0	0.7	0.055	0.001	0.0082	0.0005
6949	0.88	0.04	17.97	0.009	19.9	0.7	0.057	0.001	0.0091	0.0006
6949	0.93	0.26	12.21	0.144	17.2	0.6	0.151	0.003	0.2685	0.0087
6949	0.79	0.17	16.11	0.011	19.8	0.7	0.058	0.001	0.0187	0.0009
6949	0.95	0.10	19.69	0.007	20.2	0.7	0.055	0.001	0.0058	0.0004
6949	0.19	0.03	3.60	0.011	19.7	0.7	0.058	0.002	0.0137	0.0020
6949	1.41	0.24	9.72	0.369	13.6	0.6	0.309	0.015	0.6918	0.0410
6949	1.61	0.32	26.93	0.064	18.5	0.7	0.094	0.002	0.1134	0.0057
6949	0.37	0.05	5.11	0.123	17.4	0.6	0.136	0.003	0.2195	0.0068
6949	0.99	0.11	11.91	0.179	17.1	0.6	0.175	0.010	0.2997	0.0222
6949	1.12	0.32	13.82	0.172	16.9	0.6	0.170	0.002	0.3199	0.0044
6949	0.71	0.21	10.63	0.102	18.1	0.6	0.121	0.002	0.1879	0.0029
6949	0.62	0.11	11.73	0.021	19.4	0.7	0.064	0.001	0.0335	0.0012
6949	2.64	0.28	4.08	0.779	4.3	0.2	0.596	0.006	1.4417	0.0102
6949	2.42	0.35	7.59	0.646	7.9	0.3	0.502	0.005	1.1960	0.0092
6949	0.89	0.05	17.39	0.009	19.5	0.7	0.056	0.001	0.0114	0.0009
6949	0.85	0.06	16.57	0.010	19.3	0.7	0.057	0.001	0.0119	0.0012
6949	1.54	0.28	22.49	0.104	17.3	0.6	0.123	0.003	0.1907	0.0067
6949	0.97	0.05	13.93	0.128	18.3	0.7	0.140	0.003	0.2401	0.0091
7405	0.32	0.01	5.24	0.005	19.8	0.4	0.057	0.002	0.0394	0.0359
7405	0.51	0.01	9.49	0.004	20.4	0.5	0.056	0.002	0.0048	0.0013
7405	0.80	0.04	14.86	0.003	20.0	0.5	0.055	0.001	0.0071	0.0011
7405	0.22	0.05	3.29	0.009	19.2	0.5	0.060	0.004	0.0293	0.0090
7405	5.63	0.06	84.58	0.065	18.5	0.5	0.105	0.002	0.1408	0.0031
7405	1.33	0.04	26.61	0.003	20.1	0.5	0.055	0.001	0.0039	0.0011
7405	0.22	0.00	3.35	0.012	18.8	0.4	0.063	0.005	0.0106	0.0055
7405	5.73	0.09	96.47	0.032	19.0	0.5	0.078	0.001	0.0721	0.0009
7405	16.09	0.63	197.64	0.130	17.3	0.4	0.157	0.002	0.2822	0.0012
7405	0.64	0.02	12.73	0.003	20.6	0.6	0.055	0.002	0.0076	0.0123
7405	0.13	0.00	2.02	0.016	19.5	0.6	0.066	0.006	0.0073	0.0067
7405	14.37	0.57	176.00	0.129	17.2	0.4	0.155	0.003	0.2757	0.0060

7405	11.87	0.31	189.20	0.054	19.0	0.5	0.096	0.002	0.1182	0.0009
7405	1.00	0.03	17.71	0.023	19.6	0.5	0.071	0.002	0.0474	0.0022
7405	0.78	0.01	11.71	0.037	17.9	0.4	0.083	0.003	0.0807	0.0062
7405	0.14	0.00	2.23	0.019	20.2	0.7	0.067	0.004	0.0221	0.0073
7405	0.23	0.00	3.84	0.014	19.1	0.6	0.064	0.006	0.0125	0.0040
7405	0.17	0.00	2.86	0.012	20.2	0.6	0.062	0.004	-0.0004	0.0050
7405	0.96	0.02	18.63	0.000	20.3	0.5	0.052	0.001	0.0014	0.0009
7405	1.01	0.03	19.57	0.000	20.4	0.5	0.053	0.001	0.0025	0.0008
7405	0.41	0.02	6.67	0.019	18.9	0.5	0.068	0.003	0.0308	0.0036
7405	1.08	0.04	20.01	0.005	19.6	0.5	0.057	0.003	0.0033	0.0017
7405	1.95	0.07	36.33	0.001	19.3	0.5	0.054	0.001	0.0040	0.0012
7405	2.54	0.10	45.46	0.018	19.4	0.5	0.067	0.001	0.0386	0.0013
7405	1.11	0.03	20.43	0.006	19.4	0.5	0.058	0.001	0.0123	0.0010
7405	1.95	0.03	37.06	0.001	19.6	0.5	0.053	0.001	0.0008	0.0004
7405	2.12	0.03	41.59	0.002	19.7	0.5	0.054	0.001	0.0023	0.0006

Session No.	Pb ppm1	232Thppm1	238U ppm1	f206c	238U/ ²⁰⁶ Pb2
Correction Factor = 0.63218					
6196	0.64	0.04	12.38	0.008	30.69
6196	0.82	0.06	16.26	0.005	31.49
6196	0.33	0.01	6.22	0.007	30.76
6196	0.26	0.01	4.98	0.008	30.74
6196	0.41	0.01	7.81	0.006	31.04
6196	0.95	0.05	18.85	0.002	32.13
6196	1.03	0.02	19.44	0.002	30.71
6196	0.65	0.02	11.60	0.043	31.63
6196	0.52	0.02	9.52	0.031	31.71
6196	0.32	0.01	5.96	0.014	32.21
Correction Factor = 0.77129					
6293	1.44	0.05	28.80	0.003	25.02
6293	1.71	0.09	32.72	0.019	24.13
6293	0.46	0.04	9.47	0.006	25.85
6293	0.85	0.03	17.11	0.002	25.16
6293	0.53	0.02	10.65	0.004	25.29
6293	1.47	0.03	29.27	0.001	24.95
6293	2.38	0.05	48.80	0.000	25.79
6293	2.22	0.04	43.76	0.014	25.40
6293	1.52	0.05	29.98	0.003	25.00
6293	0.12	0.00	2.35	0.010	25.31
6293	1.56	0.05	31.23	0.005	25.53
6293	0.86	0.02	16.94	0.011	25.61
6293	1.71	0.08	35.39	0.018	24.32
6293	0.19	0.01	3.64	0.010	25.11
6293	0.26	0.01	5.17	0.005	25.48
6293	0.84	0.01	16.91	0.003	25.72
6293	0.76	0.02	15.03	0.007	25.64
6293	0.77	0.01	15.39	0.005	25.71
6293	0.31	0.01	5.91	0.011	25.23
6293	0.17	0.01	3.42	0.008	25.76

	6293	0.20	0.01	3.81	0.026	26.14
	6293	1.02	0.02	20.18	0.008	25.96
	6293	0.78	0.04	15.86	0.002	26.55
	6293	0.73	0.03	14.90	0.002	26.44
	6293	0.30	0.03	6.00	0.004	26.44
	6293	0.53	0.02	10.66	0.004	25.97
	6293	1.08	0.03	21.11	0.010	25.64
Correction Factor = 0.809275						
	6946	0.98	0.05	18.67	0.025	24.06
	6946	0.84	0.06	14.15	0.058	22.97
	6946	1.03	0.09	20.31	0.012	24.11
	6946	1.10	0.18	21.86	0.013	24.37
	6946	1.18	0.36	22.12	0.029	23.96
	6946	0.40	0.05	4.50	0.184	20.72
	6946	0.41	0.09	4.92	0.177	20.35
	6946	0.99	0.06	9.16	0.328	20.33
	6946	3.59	0.10	20.08	0.310	13.70
	6946	0.29	0.03	5.61	0.005	23.49
	6946	0.40	0.17	7.27	0.036	23.46
	6946	1.79	0.15	4.47	0.623	7.60
	6946	1.27	0.19	18.57	0.083	21.60
	6946	0.19	0.04	4.06	0.110	21.19
Correction Factor = 0.740342						
	6668	0.79	0.01	4.77	0.021	26.57
	6668	0.82	0.02	3.47	0.022	26.01
	6668	0.84	0.05	16.59	0.403	24.89
	6668	0.77	0.03	10.99	0.648	19.11
	6668	0.67	0.05	8.53	0.467	23.69
	6668	0.72	0.03	5.26	0.170	22.71
	6668	0.81	0.02	5.95	0.014	27.04
	6668	0.81	0.01	5.18	0.213	22.29
	6668	0.82	0.02	4.71	0.021	26.62
	6668	0.85	0.01	3.93	0.028	26.24
	6668	0.91	0.01	8.42	0.013	26.65
	6668	0.95	0.02	6.65	0.019	25.93
	6668	0.99	0.02	10.80	0.008	26.98

Correction Factor = 0.8092	6668	1.04	0.01	14.84	0.008	26.29
	6668	1.04	0.01	19.07	0.002	26.51
	6668	1.11	0.01	16.86	0.002	26.76
	6668	1.18	0.01	20.69	0.002	26.85
	6668	1.26	0.02	23.96	0.002	26.56
	6668	1.34	0.03	38.35	0.001	26.37
	6959	1.48	0.03	26.43	0.050	23.81
	6959	1.05	0.09	20.27	0.017	24.73
	6959	1.34	0.02	19.03	0.130	22.45
	6959	1.15	0.11	15.37	0.142	21.68
	6959	1.22	0.03	25.17	0.006	24.97
	6959	1.59	0.08	12.58	0.323	17.80
	6959	1.13	0.02	22.05	0.018	24.33
	6959	0.71	0.10	14.35	0.006	24.59
	6959	0.60	0.03	12.20	0.009	24.75
	6959	0.93	0.05	14.67	0.089	22.86
	6959	0.86	0.02	16.86	0.020	24.60
	6959	1.81	0.36	18.61	0.224	18.92
	6959	1.57	0.04	26.15	0.068	23.22
	6959	0.83	0.25	15.95	0.014	24.10
	6959	1.02	0.05	20.61	0.010	24.43
	6959	8.59	2.13	16.90	0.746	7.16
	6959	0.41	0.04	8.03	0.019	24.37
	6959	1.22	0.24	17.68	0.104	21.78
	6961	0.94	0.26	8.41	0.314	17.68
	6961	1.44	0.23	21.85	0.107	21.25
	6961	0.70	0.19	6.58	0.273	17.60
	6961	2.47	0.22	14.30	0.436	13.29
	6961	0.63	0.03	7.74	0.172	20.09
	6961	1.23	0.38	22.26	0.055	22.67
	6961	12.47	0.40	4.93	0.940	1.41
	6961	1.59	0.36	24.95	0.099	21.64

Correction Factor = 0.8320	6961	0.59	0.06	12.16	0.022	23.77
	6963	1.09	0.41	19.99	0.088	21.95
	6963	0.74	0.21	16.11	0.049	22.82
	6963	1.14	0.52	23.22	0.114	21.31
	6963	0.67	0.05	15.10	0.003	23.64
	6963	1.13	0.29	24.32	0.037	22.67
	6963	0.96	0.20	17.36	0.191	19.19
	6963	1.25	0.14	27.06	0.032	22.56
	6963	0.77	0.03	17.79	0.006	24.12
	6963	1.19	0.10	26.70	0.007	23.49
	6963	0.65	0.07	13.24	0.109	21.51
	6963	4.76	0.44	37.53	0.003	22.06
	6963	0.88	0.15	20.39	0.002	23.91
	6963	0.55	0.04	11.85	0.029	22.78
	6963	1.22	0.08	27.20	0.032	23.49
	7405	0.32	0.01	5.24	0.01	22.71
	7405	0.51	0.01	9.49	0.00	23.75
	7405	0.80	0.04	14.86	0.00	23.18
	7405	0.22	0.05	3.29	0.01	22.04
	7405	5.63	0.06	84.58	0.07	21.44
	7405	1.33	0.04	26.61	0.00	23.23
	7405	0.22	0.00	3.35	0.01	21.36
	7405	5.73	0.09	96.47	0.03	21.98
	7405	16.09	0.63	197.64	0.13	20.03
	7405	0.64	0.02	12.73	0.00	23.71
	7405	0.13	0.00	2.02	0.02	22.36
	7405	14.37	0.57	176.00	0.13	19.80
	7405	11.87	0.31	189.20	0.05	21.88
	7405	1.00	0.03	17.71	0.02	22.52
	7405	0.78	0.01	11.71	0.04	20.48
	7405	0.14	0.00	2.23	0.02	22.94
	7405	0.23	0.00	3.84	0.01	21.78

7405	0.17	0.00	2.86	0.01	23.08
7405	0.96	0.02	18.63	0.00	23.22
7405	1.01	0.03	19.57	0.00	23.28
7405	0.41	0.02	6.67	0.02	21.55
7405	1.08	0.04	20.01	0.00	22.27
7405	1.95	0.07	36.33	0.00	22.03
7405	2.54	0.10	45.46	0.02	22.03
7405	1.11	0.03	20.43	0.01	22.01
7405	1.95	0.03	37.06	0.00	22.29
7405	2.12	0.03	41.59	0.00	22.39

~~26-9~~: Analysis rejected from calculations

1: Normalised to the NIST614 reference glass.

2: Corrected for downhole fractionation

3: Normalised to the NIST614 reference glass with a $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.87 and $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.101 after Woodhead and Hergt (2001),

4: Correction factor determined from the X-intercept of the Discordia for each session divided by the X-intercept of the 'true' Discordia de

2SE	207Pb/ ²⁰⁶ Pi	2SE	208Pb/ ²⁰⁶ Pb	2SE	Session correction Factor	4
				X-int (a)	21.4005	
0.98	0.058	0.001	0.0139	0.0023 F	0.63218	
0.93	0.056	0.001	0.0080	0.0007 X-int (m)	33.852	
1.09	0.057	0.002	0.0091	0.0015		
1.07	0.058	0.002	0.0069	0.0017		
1.00	0.057	0.002	0.0127	0.0081		
0.93	0.054	0.001	0.0037	0.0006		
0.94	0.054	0.001	0.0024	0.0008		
0.97	0.082	0.004	0.0784	0.0029		
0.98	0.074	0.002	0.0575	0.0030		
1.14	0.062	0.002	0.0244	0.0030		
0.63	0.055	0.001	0.004	0.002 F	0.77129	
0.58	0.066	0.001	0.031	0.000 X-int (m)	27.7465	
0.74	0.057	0.001	0.011	0.002		
0.69	0.054	0.001	0.002	0.004		
0.75	0.055	0.001	0.004	0.004		
0.64	0.053	0.001	0.001	0.004		
0.75	0.053	0.000	0.001	0.003		
0.73	0.063	0.001	0.026	0.001		
0.65	0.055	0.001	0.007	0.001		
0.97	0.060	0.004	0.003	0.043		
0.64	0.056	0.001	0.008	0.002		
0.68	0.060	0.001	0.017	0.002		
0.62	0.065	0.002	0.013	0.002		
0.93	0.060	0.002	0.010	0.010		
0.82	0.056	0.002	0.005	0.006		
0.71	0.055	0.001	0.003	0.002		
0.70	0.057	0.001	0.010	0.005		
0.74	0.056	0.001	0.007	0.001		
0.79	0.061	0.002	0.016	0.002		
0.88	0.059	0.002	0.008	0.006		

0.86	0.071	0.002	0.042	0.002	
0.71	0.059	0.001	0.013	0.001	
0.72	0.054	0.001	0.003	0.003	
0.73	0.054	0.001	0.001	0.005	
0.79	0.056	0.002	0.009	0.003	
0.80	0.055	0.001	0.004	0.003	
0.69	0.060	0.001	0.019	0.002	
0.31	0.070	0.004	0.027	0.000 F	0.80928
0.22	0.093	0.002	0.106	0.001 X-int (m)	26.5043
0.19	0.061	0.001	0.025	0.000	
0.20	0.062	0.001	0.025	0.000	
0.20	0.073	0.001	0.059	0.000	
0.42	0.179	0.011	0.271	0.002	
0.34	0.174	0.004	0.318	0.002	
0.21	0.278	0.004	0.608	0.004	
1.58	0.266	0.037	0.095	0.001	
0.25	0.057	0.001	0.013	0.000	
0.25	0.078	0.002	0.071	0.000	
0.08	0.481	0.004	1.162	0.009	
0.70	0.110	0.013	0.098	0.001	
0.54	0.128	0.016	0.039	0.000	
0.59	0.067	0.002	0.023	0.002 F	0.74034
0.57	0.068	0.002	0.027	0.003 X-int (m)	28.9063
0.37	0.330	0.005	0.741	0.011	
0.33	0.498	0.004	1.186	0.009	
0.44	0.374	0.006	0.861	0.013	
0.48	0.170	0.003	0.315	0.007	
0.57	0.062	0.002	0.019	0.003	
0.49	0.199	0.003	0.382	0.008	
0.61	0.067	0.002	0.023	0.002	
0.56	0.072	0.002	0.036	0.004	
0.52	0.062	0.001	0.015	0.001	
0.54	0.066	0.002	0.021	0.003	
0.54	0.058	0.001	0.009	0.001	

0.50	0.059	0.001	0.010	0.002	
0.50	0.054	0.001	0.002	0.000	
0.51	0.054	0.001	0.005	0.003	
0.50	0.054	0.001	0.002	0.001	
0.50	0.054	0.001	0.007	0.008	
0.51	0.053	0.001	0.001	0.000	
0.29	0.087	0.001	0.083	0.003 F	0.8092
0.28	0.065	0.003	0.010	0.001 X-int (m)	26.4475
0.20	0.142	0.001	0.231	0.003	
0.34	0.151	0.006	0.226	0.013	
0.24	0.057	0.001	0.007	0.001	
0.61	0.275	0.017	0.476	0.027	
0.19	0.065	0.001	0.025	0.002	
0.19	0.057	0.001	0.010	0.001	
0.21	0.059	0.001	0.012	0.002	
0.19	0.114	0.001	0.157	0.003	
0.27	0.067	0.001	0.033	0.001	
0.25	0.207	0.005	0.387	0.013	
0.18	0.100	0.001	0.118	0.003	
0.25	0.063	0.001	0.027	0.001	
0.16	0.059	0.001	0.015	0.001	
0.28	0.565	0.008	1.311	0.021	
0.20	0.066	0.002	0.022	0.002	
0.18	0.124	0.002	0.184	0.005	
0.22	0.269	0.005	0.56	0.012	
0.16	0.127	0.001	0.19	0.003	
0.26	0.241	0.007	0.46	0.017	
0.14	0.352	0.003	0.77	0.008	
0.28	0.171	0.007	0.27	0.015	
0.21	0.091	0.001	0.10	0.003	
0.04	0.699	0.002	1.67	0.006	
0.11	0.121	0.002	0.18	0.005	

0.17	0.068	0.001	0.036	0.001	
0.15	0.113	0.002	0.170	0.004 F	0.8320
0.20	0.086	0.002	0.089	0.003 X-int (m)	25.721
0.27	0.131	0.005	0.197	0.011	
0.23	0.055	0.001	0.007	0.001	
0.13	0.078	0.002	0.065	0.004	
0.88	0.184	0.024	0.093	0.009	
0.20	0.075	0.004	0.034	0.003	
0.22	0.057	0.001	0.011	0.002	
0.24	0.058	0.001	0.014	0.001	
0.60	0.127	0.007	0.176	0.008	
0.33	0.055	0.000	0.007	0.000	
0.21	0.054	0.001	0.006	0.001	
0.17	0.073	0.001	0.054	0.002	
0.18	0.075	0.001	0.056	0.003	
0.42	0.057	0.002	0.039	0.036	
0.21	0.056	0.002	0.005	0.001	
0.19	0.055	0.001	0.007	0.001	
0.53	0.060	0.004	0.029	0.009	
0.16	0.105	0.002	0.141	0.003	
0.21	0.055	0.001	0.004	0.001	
0.64	0.063	0.005	0.011	0.005	
0.16	0.078	0.001	0.072	0.001	
0.10	0.157	0.002	0.282	0.001	
0.30	0.055	0.002	0.008	0.012	
0.43	0.066	0.006	0.007	0.007	
0.12	0.155	0.003	0.276	0.006	
0.13	0.096	0.002	0.118	0.001	
0.15	0.071	0.002	0.047	0.002	
0.19	0.083	0.003	0.081	0.006	
0.48	0.067	0.004	0.022	0.007	
0.33	0.064	0.006	0.013	0.004	

0.35	0.062	0.004	0.000	0.005
0.16	0.052	0.001	0.001	0.001
0.17	0.053	0.001	0.002	0.001
0.32	0.068	0.003	0.031	0.004
0.17	0.057	0.003	0.003	0.002
0.13	0.054	0.001	0.004	0.001
0.12	0.067	0.001	0.039	0.001
0.16	0.058	0.001	0.012	0.001
0.13	0.053	0.001	0.001	0.0004
0.15	0.054	0.001	0.002	0.001

)
defined by a $^{207}\text{Pb}/^{206}\text{Pb}(i)$ of 0.74 and an age of 316.47 Ma. Full description of the method is described in Li et al. (2016).

Session No.	Pb ppm	1 232Th	ppm	238U ppm	f206c	238U/ ²⁰⁶ P 2SE	207Pb/ ²⁰⁶ P 2SE	208Pb/ ²⁰⁶ P 2SE		
"MTM" in thin section										
Primary										
6946	0.15	0.01	2.90	0.011	19.37	0.42	0.060	0.0020	16.639	0.554
6946	0.58	0.01	10.63	0.031	18.88	0.36	0.074	0.0012	13.514	0.219
6946	1.60	0.06	26.99	0.066	18.47	0.36	0.098	0.0017	10.173	0.176
6946	0.24	0.01	4.19	0.027	18.30	0.45	0.072	0.0016	13.966	0.312
6946	6.10	1.80	42.99	0.356	13.46	0.40	0.298	0.0099	3.359	0.112
6946	3.15	0.16	63.02	0.005	19.38	0.38	0.056	0.0004	17.737	0.120
6946	1.03	0.07	21.25	0.003	19.69	0.36	0.055	0.0006	18.275	0.207
6946	2.91	0.17	56.67	0.018	19.20	0.38	0.065	0.0008	15.344	0.188
6946	2.88	0.35	53.13	0.024	18.72	0.36	0.070	0.0005	14.382	0.101
6946	3.77	0.15	60.94	0.074	18.12	0.38	0.103	0.0036	9.671	0.337
6946	2.99	0.12	59.35	0.012	19.46	0.37	0.061	0.0005	16.305	0.133
6946	2.92	0.15	57.28	0.009	18.96	0.35	0.059	0.0005	17.039	0.151
6946	3.12	1.27	57.77	0.021	18.50	0.34	0.067	0.0006	14.863	0.130
6946	3.35	0.23	66.44	0.008	19.21	0.37	0.058	0.0004	17.100	0.123
6946	2.34	0.20	44.58	0.022	19.10	0.36	0.068	0.0008	14.797	0.173
6946	1.80	0.09	35.42	0.010	19.20	0.33	0.060	0.0006	16.736	0.174
6946	0.98	0.03	19.42	0.009	19.35	0.36	0.059	0.0008	17.010	0.237
6946	3.34	0.31	9.90	0.617	7.09	0.13	0.477	0.0046	2.099	0.020
6946	2.58	0.09	52.76	0.002	19.55	0.38	0.054	0.0004	18.519	0.151
6946	1.33	0.20	27.11	0.001	19.58	0.35	0.053	0.0005	18.748	0.158
6946	9.28	0.34	98.31	0.213	15.18	0.29	0.199	0.0019	5.028	0.048
6946	2.03	0.11	33.59	0.068	18.42	0.32	0.099	0.0009	10.078	0.095
6946	13.80	0.35	139.23	0.242	15.09	0.26	0.219	0.0018	4.558	0.037
6946	11.77	0.34	116.75	0.252	15.01	0.29	0.226	0.0008	4.426	0.015
6946	10.60	0.24	112.11	0.231	15.56	0.27	0.211	0.0011	4.733	0.025
6946	8.45	0.25	100.27	0.178	15.90	0.33	0.175	0.0020	5.711	0.065
6946	16.54	0.33	97.21	0.367	13.19	0.88	0.305	0.0250	3.279	0.269
6946	5.74	0.30	51.42	0.273	14.16	0.28	0.240	0.0021	4.163	0.036
6946	11.39	0.33	111.87	0.246	15.02	0.31	0.222	0.0022	4.513	0.045
6946	3.32	0.15	16.37	0.463	9.91	0.20	0.371	0.0048	2.694	0.035
6946	7.22	0.22	88.05	0.176	16.31	0.32	0.174	0.0009	5.759	0.030
6946	11.10	0.23	107.59	0.230	15.04	0.50	0.211	0.0110	4.739	0.247
6946	5.52	0.18	99.29	0.041	18.58	0.36	0.081	0.0010	12.390	0.146
6946	2.74	0.10	42.62	0.081	17.65	0.36	0.109	0.0014	9.200	0.118
6946	9.00	0.22	111.63	0.166	16.55	0.57	0.167	0.0100	5.988	0.359
6946	7.19	0.21	108.08	0.098	17.44	0.35	0.120	0.0008	8.347	0.052

6946	3.70	0.13	69.49	0.023	18.66	0.38	0.069	0.0004	14.522	0.089
6946	5.39	0.15	91.72	0.056	18.17	0.36	0.091	0.0004	10.939	0.051
6946	2.72	0.10	53.86	0.007	19.25	0.40	0.058	0.0004	17.385	0.118
6946	2.55	0.15	35.42	0.113	16.85	0.31	0.130	0.0010	7.668	0.056
6946	3.77	0.19	55.57	0.091	17.97	0.49	0.115	0.0065	8.673	0.489
6946	2.02	0.10	25.77	0.152	16.08	0.50	0.157	0.0077	6.365	0.312
6946	6.24	0.24	99.90	0.063	17.18	0.36	0.096	0.0027	10.373	0.291
6946	1.29	0.08	5.85	0.518	9.87	0.33	0.409	0.0120	2.445	0.072
6946	1.06	0.03	5.57	0.463	10.74	0.26	0.371	0.0043	2.696	0.031
6946	1.21	0.06	4.30	0.621	8.80	0.31	0.480	0.0057	2.084	0.025
6946	2.09	0.18	4.20	0.774	5.76	0.29	0.584	0.0060	1.711	0.018
6946	2.88	0.16	56.79	0.006	19.03	0.39	0.057	0.0005	17.513	0.153
6946	0.17	0.02	3.32	0.008	19.31	0.43	0.059	0.0021	17.065	0.612
6946	10.36	0.79	5.55	0.937	1.78	0.09	0.697	0.0024	1.435	0.005
6946	0.36	0.04	4.27	0.150	16.75	0.60	0.156	0.0190	6.410	0.781
6946	0.29	0.01	5.61	0.010	19.31	0.36	0.060	0.0014	16.694	0.390
6946	0.39	0.02	7.62	0.016	19.63	0.39	0.064	0.0013	15.601	0.316

Alteration

6946	0.53	0.07	10.83	0.003	20.30	0.41	0.055	0.0009	0.007	0.001
6946	1.26	0.09	10.57	0.288	13.77	0.43	0.251	0.0071	0.521	0.018
6946	1.11	0.49	7.72	0.306	14.28	0.88	0.263	0.0200	0.326	0.032
6946	1.30	0.22	22.75	0.053	19.03	0.33	0.089	0.0012	0.096	0.003
6946	0.60	0.10	10.63	0.046	19.37	0.46	0.085	0.0037	0.058	0.004
6946	1.17	0.19	12.93	0.200	16.06	0.29	0.191	0.0046	0.377	0.012
6946	1.84	0.16	11.40	0.397	11.65	0.31	0.326	0.0046	0.730	0.012
6946	0.86	0.05	17.67	0.005	19.84	0.38	0.056	0.0006	0.007	0.001
6946	0.90	0.08	18.28	0.005	19.71	0.38	0.056	0.0006	0.009	0.001
6946	1.05	0.08	15.79	0.096	17.52	0.36	0.119	0.0018	0.176	0.004
6946	0.83	0.08	16.89	0.004	19.80	0.37	0.056	0.0007	0.008	0.001
6946	0.74	0.03	14.24	0.015	19.29	0.38	0.063	0.0009	0.029	0.001
6946	0.71	0.04	14.79	0.002	19.87	0.39	0.054	0.0007	0.003	0.001
6946	0.61	0.01	12.45	0.004	19.82	0.39	0.055	0.0008	0.003	0.001
6946	0.48	0.02	9.67	0.002	19.58	0.41	0.054	0.0009	0.005	0.002
6946	0.77	0.02	16.13	0.001	20.01	0.39	0.053	0.0006	0.003	0.001
6946	0.73	0.06	14.74	0.006	19.65	0.37	0.057	0.0007	0.009	0.001
6946	0.65	0.01	12.59	0.021	19.38	0.38	0.067	0.0009	0.036	0.001
6946	0.52	0.01	10.51	0.005	19.69	0.39	0.056	0.0009	0.008	0.001
6946	0.76	0.01	10.94	0.115	17.44	0.35	0.132	0.0015	0.205	0.004
6946	0.37	0.01	7.18	0.016	19.54	0.46	0.064	0.0011	0.023	0.002
6946	0.42	0.01	8.05	0.020	19.19	0.56	0.067	0.0011	0.032	0.002

6946	2.50	0.21	14.24	0.444	11.61	0.27	0.358	0.0040	0.805	0.010
6946	1.57	0.04	33.05	0.001	20.14	0.36	0.054	0.0005	0.002	0.000
6946	0.86	0.01	17.56	0.003	19.75	0.41	0.055	0.0006	0.005	0.001
6946	0.73	0.09	14.83	0.010	19.97	0.39	0.060	0.0007	0.017	0.001
6946	0.85	0.03	17.95	0.001	20.01	0.38	0.054	0.0007	0.003	0.001
6946	1.14	0.14	24.07	0.001	20.23	0.38	0.054	0.0005	0.003	0.000
6946	1.03	0.02	21.87	0.000	20.15	0.37	0.053	0.0006	0.002	0.001
6946	0.57	0.02	11.72	0.007	20.09	0.39	0.057	0.0010	0.007	0.002
6946	0.85	0.04	12.53	0.106	17.46	0.43	0.126	0.0026	0.188	0.005
6946	1.31	0.12	15.24	0.207	16.67	0.32	0.195	0.0049	0.376	0.014
6946	0.72	0.10	15.08	0.003	20.17	0.36	0.055	0.0008	0.005	0.001
6946	0.81	0.12	16.83	0.005	20.14	0.39	0.056	0.0007	0.009	0.001
6946	3.25	0.45	21.05	0.318	14.32	0.91	0.271	0.0250	0.278	0.036
6946	1.25	0.04	13.92	0.191	15.65	0.34	0.184	0.0031	0.345	0.008
6946	2.11	0.04	12.63	0.416	11.39	0.22	0.338	0.0038	0.755	0.010
6946	0.55	0.01	11.12	0.011	19.72	0.38	0.060	0.0009	0.019	0.001
6946	0.97	0.06	13.89	0.124	18.22	0.48	0.138	0.0071	0.194	0.015
6946	0.76	0.03	12.30	0.083	18.43	0.35	0.110	0.0015	0.149	0.004
6946	1.67	0.28	11.19	0.439	13.16	0.27	0.354	0.0041	0.803	0.010
6946	0.90	0.04	18.55	0.004	19.86	0.37	0.056	0.0006	0.007	0.000
6946	0.87	0.04	18.00	0.006	19.89	0.37	0.057	0.0007	0.007	0.001
6946	0.92	0.26	12.25	0.143	17.17	0.34	0.151	0.0033	0.249	0.007
6946	0.79	0.17	16.19	0.007	19.77	0.39	0.058	0.0007	0.017	0.001
6946	0.94	0.10	19.74	0.003	20.17	0.36	0.055	0.0006	0.005	0.001
6946	0.18	0.03	3.62	0.007	19.71	0.42	0.058	0.0016	0.022	0.008
6946	1.41	0.24	9.61	0.371	13.59	0.46	0.308	0.0160	0.619	0.038
6946	1.61	0.32	26.90	0.061	18.68	0.36	0.095	0.0023	0.102	0.003
6946	0.37	0.05	5.11	0.121	17.36	0.35	0.136	0.0027	0.218	0.007
6946	0.99	0.11	11.92	0.178	17.16	0.53	0.175	0.0100	0.245	0.013
6946	1.11	0.32	13.82	0.171	16.94	0.33	0.170	0.0019	0.315	0.004
6946	0.70	0.21	10.61	0.100	17.99	0.36	0.121	0.0014	0.186	0.003
6946	0.61	0.11	11.69	0.017	19.32	0.38	0.064	0.0008	0.032	0.001
6946	2.63	0.29	4.12	0.790	4.36	0.10	0.596	0.0041	1.420	0.010
6946	2.41	0.35	7.55	0.654	7.86	0.15	0.502	0.0039	1.180	0.009
6946	0.88	0.05	17.31	0.005	19.46	0.39	0.056	0.0008	0.007	0.002
6946	0.84	0.06	16.53	0.006	19.20	0.38	0.057	0.0007	0.008	0.001
6946	1.55	0.29	22.46	0.102	17.29	0.38	0.123	0.0026	0.184	0.006
6946	0.97	0.05	13.98	0.127	18.16	0.36	0.140	0.0034	0.233	0.009

Echassières
Wolframite B

ECH20-1

6963	0.42	0.01	10.45	0.003	19.89	0.36	0.055	0.0009	0.006	0.002
6963	0.41	0.00	9.94	0.001	19.44	0.36	0.054	0.0008	0.037	0.103
6963	0.99	0.02	25.59	0.003	20.71	0.36	0.055	0.0006	0.005	0.001
6963	0.64	0.02	16.07	0.011	19.93	0.34	0.061	0.0008	0.020	0.001
6963	0.20	0.02	4.95	0.007	19.87	0.39	0.059	0.0013	0.017	0.005
6963	0.15	0.01	3.70	0.015	19.39	0.40	0.065	0.0018	0.025	0.006
6963	0.19	0.00	4.65	0.004	19.59	0.38	0.056	0.0014	0.005	0.002
6963	0.24	0.00	5.95	0.005	19.88	0.37	0.057	0.0013	0.028	0.019
6963	0.43	0.01	10.78	0.003	19.93	0.35	0.055	0.0011	0.043	0.112
6963	0.41	0.01	9.94	0.024	19.22	0.34	0.072	0.0011	0.046	0.002
6963	0.12	0.02	2.83	0.025	19.50	0.39	0.073	0.0025	0.044	0.009
6963	2.18	0.03	48.21	0.000	18.03	0.33	0.053	0.0004	-0.005	0.012
6963	1.31	0.02	29.29	0.000	18.05	0.39	0.053	0.0005	0.005	0.005
6963	1.76	0.03	40.49	0.001	18.85	0.31	0.053	0.0005	0.002	0.001
6963	0.76	0.01	18.35	0.002	19.26	0.35	0.054	0.0007	0.004	0.001
6963	0.73	0.03	18.06	0.009	19.82	0.34	0.060	0.0007	0.016	0.001
6963	0.81	0.03	19.90	0.005	19.86	0.33	0.057	0.0006	0.009	0.000
6963	0.29	0.03	6.85	0.003	18.85	0.34	0.055	0.0011	0.014	0.006
6963	0.72	0.02	16.63	0.002	18.71	0.37	0.054	0.0006	0.000	0.000
6963	0.10	0.01	2.50	0.006	19.76	0.43	0.058	0.0019	0.004	0.002
6963	0.12	0.03	3.01	0.017	19.63	0.38	0.067	0.0019	0.032	0.008
6963	0.16	0.01	3.94	0.006	19.73	0.36	0.057	0.0016	0.026	0.009
6963	0.13	0.01	3.20	0.007	19.85	0.38	0.059	0.0019	0.071	0.087
6963	0.12	0.01	2.82	0.010	19.67	0.38	0.061	0.0020	0.077	0.077
6963	0.13	0.01	3.16	0.014	19.59	0.38	0.064	0.0019	0.036	0.013
6963	0.22	0.07	5.31	0.020	19.42	0.36	0.069	0.0013	0.039	0.002
6963	0.16	0.04	3.86	0.018	19.18	0.37	0.067	0.0018	0.027	0.003
6963	0.22	0.03	5.24	0.015	19.51	0.36	0.065	0.0015	0.023	0.002
6963	0.19	0.04	4.60	0.013	19.26	0.36	0.063	0.0013	0.020	0.003
6963	0.27	0.11	5.87	0.085	17.73	0.34	0.121	0.0031	0.177	0.007

ECH20-3

6963	1.58	0.03	37.40	0.026	19.25	0.32	0.073	0.0025	0.035	0.003
6964	2.42	0.05	54.25	0.006	18.31	0.33	0.058	0.0004	0.013	0.000
6965	1.13	0.02	28.15	0.010	20.04	0.33	0.061	0.0006	0.022	0.001
6966	0.43	0.03	10.21	0.059	18.97	0.33	0.100	0.0016	0.120	0.003
6967	0.80	0.02	19.36	0.025	19.51	0.34	0.073	0.0009	0.050	0.002
6968	1.57	0.04	36.99	0.019	19.03	0.31	0.068	0.0008	0.039	0.002
6969	0.77	0.05	18.80	0.033	19.57	0.33	0.080	0.0011	0.070	0.002
6970	1.41	0.03	30.75	0.027	17.56	0.34	0.074	0.0009	0.055	0.002

	6971	1.15	0.04	28.22	0.007	19.89	0.34	0.059	0.0005	0.015	0.001
	6972	1.60	0.03	36.82	0.044	18.80	0.30	0.089	0.0010	0.095	0.003
	6973	1.27	0.03	30.19	0.037	19.03	0.32	0.083	0.0010	0.077	0.002
	6974	2.07	0.02	46.36	0.002	18.15	0.31	0.055	0.0004	0.003	0.000
	6975	0.65	0.02	15.28	0.037	18.96	0.32	0.082	0.0019	0.068	0.005
	6976	0.68	0.04	15.51	0.042	18.68	0.33	0.087	0.0010	0.090	0.002
	6977	1.33	0.05	32.52	0.019	19.61	0.33	0.068	0.0008	0.041	0.002
	6978	0.29	0.20	6.65	0.074	18.80	0.35	0.113	0.0017	0.155	0.003
	6979	2.18	0.03	48.76	0.010	18.20	0.33	0.061	0.0004	0.020	0.001
	6980	1.68	0.06	38.31	0.037	18.60	0.30	0.082	0.0008	0.077	0.002
	6981	1.01	0.02	23.57	0.052	18.81	0.33	0.095	0.0043	0.082	0.008
	6982	0.97	0.02	22.80	0.039	18.98	0.33	0.084	0.0014	0.081	0.003
	6983	0.62	0.06	13.26	0.133	17.21	0.29	0.161	0.0023	0.281	0.005
	6984	0.29	0.01	6.98	0.017	19.58	0.35	0.067	0.0011	0.032	0.002
	6985	0.31	0.02	5.67	0.239	15.04	0.30	0.245	0.0096	0.469	0.021
	6986	0.28	0.01	6.88	0.022	19.59	0.36	0.070	0.0016	0.039	0.003
	6987	0.27	0.02	6.43	0.031	19.08	0.35	0.078	0.0014	0.064	0.002
	6988	1.55	0.11	27.59	0.277	14.42	0.30	0.276	0.0092	0.578	0.022
ECH20-4 -Fe	6959	0.07	0.00	1.11	0.051	18.43	0.44	0.094	0.0048	1.126	0.015
	6959	0.06	0.00	0.87	0.043	19.12	0.48	0.087	0.0050	1.406	0.012
	6959	0.07	0.00	1.03	0.040	18.40	0.43	0.085	0.0040	0.009	0.001
	6959	0.12	0.00	1.55	0.119	16.82	0.36	0.149	0.0043	0.022	0.015
	6959	0.11	0.00	1.87	0.040	18.73	0.38	0.085	0.0028	1.701	0.007
	6959	0.11	0.01	1.67	0.074	17.91	0.37	0.112	0.0035	0.041	0.008
	6959	0.10	0.01	1.64	0.044	18.54	0.41	0.089	0.0034	0.013	0.002
	6959	0.12	0.00	2.07	0.037	18.51	0.38	0.083	0.0032	0.020	0.002
	6959	0.07	0.01	1.02	0.096	17.18	0.44	0.130	0.0091	0.128	0.030
	6959	0.16	0.01	2.30	0.093	17.76	0.36	0.128	0.0046	0.166	0.007
	6959	0.06	0.00	1.01	0.030	18.88	0.42	0.077	0.0042	0.116	0.095
	6959	0.05	0.00	0.87	0.032	18.72	0.46	0.078	0.0046	0.137	0.092
	6959	0.08	0.00	1.45	0.036	19.06	0.42	0.082	0.0032	0.061	0.017
	6959	0.08	0.00	1.42	0.030	18.77	0.43	0.077	0.0038	0.072	0.028
	6959	0.08	0.00	1.37	0.030	19.05	0.42	0.077	0.0033	0.120	0.078
	6959	0.03	0.02	0.39	0.080	17.75	0.60	0.117	0.0089	0.286	0.147
	6959	0.04	0.03	0.48	0.111	18.04	0.54	0.143	0.0090	0.154	0.022
	6959	0.46	0.39	2.74	0.376	12.07	0.41	0.356	0.0130	0.758	0.034
	6959	0.13	0.06	2.57	0.015	19.55	0.38	0.065	0.0021	0.040	0.015
	6959	0.11	0.02	2.05	0.020	19.13	0.42	0.069	0.0023	0.045	0.015
	6959	0.03	0.00	0.42	0.061	18.40	0.62	0.102	0.0078	0.179	0.102

	6959	0.22	0.03	3.16	0.101	17.34	0.32	0.134	0.0035	0.204	0.008
	6959	0.08	0.05	1.45	0.031	19.27	0.43	0.078	0.0031	0.049	0.008
	6959	0.15	0.02	2.94	0.010	19.10	0.37	0.061	0.0018	0.020	0.005
	6959	1.35	0.05	2.47	0.736	5.36	0.11	0.647	0.0065	1.518	0.016
	6959	0.29	0.01	5.82	0.008	19.53	0.37	0.059	0.0016	0.008	0.002
	6959	0.35	0.01	7.04	0.005	19.40	0.37	0.057	0.0011	0.007	0.002
	6959	0.27	0.05	4.88	0.018	18.44	0.33	0.067	0.0033	0.024	0.005
	6959	1.13	0.02	23.55	0.002	19.75	0.32	0.054	0.0006	0.004	0.001
	6959	0.65	0.02	13.29	0.006	19.61	0.35	0.058	0.0011	0.007	0.002
	6959	0.54	0.02	10.43	0.009	18.85	0.33	0.060	0.0012	0.011	0.002
	6959	0.60	0.01	12.37	0.002	19.47	0.35	0.055	0.0007	0.005	0.001
	6959	0.34	0.01	6.78	0.005	19.31	0.36	0.057	0.0012	0.016	0.008
	6959	0.13	0.00	2.41	0.018	19.44	0.40	0.067	0.0023	0.033	0.011
	6959	0.18	0.04	2.60	0.083	17.53	0.36	0.120	0.0033	0.163	0.006
	6959	0.17	0.03	2.58	0.094	18.05	0.36	0.129	0.0042	0.172	0.008
	6959	0.36	0.03	7.37	0.014	20.11	0.35	0.064	0.0014	0.022	0.002
	6959	0.31	0.02	5.83	0.022	19.33	0.35	0.070	0.0029	0.021	0.002
	6959	0.61	0.01	12.17	0.010	19.41	0.33	0.061	0.0010	0.016	0.001
	6959	0.12	0.01	2.18	0.028	19.52	0.42	0.075	0.0033	0.057	0.023
ECH20-4 -Mn	6959	0.67	0.03	13.65	0.003	19.92	0.35	0.055	0.0007	0.007	0.002
	6959	0.28	0.02	5.45	0.009	19.84	0.37	0.060	0.0014	0.013	0.002
	6959	0.27	0.02	5.45	0.003	19.79	0.36	0.055	0.0011	0.050	0.123
	6959	0.55	0.02	11.21	0.003	20.09	0.36	0.055	0.0009	0.010	0.007
	6959	0.63	0.02	12.91	0.002	20.01	0.36	0.055	0.0008		
	6959	0.26	0.02	5.19	0.004	19.58	0.35	0.056	0.0012		
	6959	0.22	0.01	4.43	0.003	19.76	0.36	0.056	0.0012		
	6959	0.27	0.01	5.37	0.004	20.00	0.37	0.056	0.0014	0.011	0.007
	6959	0.27	0.01	5.32	0.005	19.95	0.36	0.057	0.0015	0.026	0.030
	6959	0.23	0.01	4.62	0.004	20.02	0.36	0.056	0.0014		
	6959	0.23	0.02	4.52	0.006	19.83	0.36	0.058	0.0017	0.014	0.005
	6959	0.28	0.02	5.54	0.003	19.55	0.35	0.056	0.0012	0.012	0.004
	6959	0.74	0.03	14.71	0.001	19.59	0.35	0.054	0.0007	0.005	0.002
	6959	0.16	0.01	3.20	0.006	19.73	0.39	0.058	0.0016	0.020	0.009
	6959	0.29	0.02	5.64	0.005	19.63	0.37	0.057	0.0012	0.015	0.007
	6959	0.10	0.02	1.79	0.018	19.53	0.42	0.067	0.0029	0.032	0.008
	6959	0.10	0.01	1.90	0.016	19.14	0.42	0.066	0.0029		
	6959	0.08	0.00	1.46	0.020	19.34	0.44	0.069	0.0033	0.074	0.042
	6959	0.08	0.00	1.41	0.032	19.20	0.41	0.079	0.0031	0.040	0.007
	6959	0.25	0.01	4.83	0.010	19.37	0.36	0.061	0.0014	0.016	0.004

6959	0.11	0.00	1.99	0.024	19.38	0.42	0.072	0.0028	0.035	0.008
6959	0.14	0.01	2.83	0.011	19.92	0.41	0.062	0.0018		
6959	0.11	0.01	2.20	0.012	19.93	0.40	0.063	0.0027	0.010	0.007
6959	0.13	0.01	2.62	0.011	20.11	0.40	0.062	0.0020	0.034	0.013
6959	1.04	0.04	21.59	0.003	20.39	0.35	0.055	0.0006	0.003	0.001
6959	0.99	0.04	20.43	0.001	20.35	0.34	0.054	0.0005	0.005	0.005
6959	0.12	0.01	2.37	0.006	20.61	0.42	0.058	0.0021	0.015	0.010
6959	0.15	0.01	3.04	0.006	20.46	0.38	0.058	0.0017	0.037	0.041
6959	0.15	0.01	3.10	0.006	20.16	0.37	0.058	0.0014		
6959	0.23	0.01	4.64	0.003	20.27	0.38	0.056	0.0011	0.003	0.001

ECH20-5 - Mazet vein

6959	0.11	0.02	1.26	0.196	17.72	0.44	0.211	0.0067	2.450	0.100
6959	0.05	0.03	0.39	0.300	16.26	0.58	0.295	0.0170	1.818	0.099
6959	0.06	0.01	0.62	0.226	17.30	0.48	0.235	0.0092	2.460	0.130
6959	15.32	0.01	0.88	0.696	6.95	0.96	0.615	0.0320	0.762	0.047
6959	0.84	0.01	0.69	0.858	2.89	0.11	0.745	0.0160	0.640	0.120
6959	0.11	0.00	1.52	0.103	19.78	0.50	0.136	0.0088	6.680	0.610
6959	0.08	0.00	0.51	0.449	14.87	0.50	0.415	0.0680	1.580	0.100
6959	0.38	0.02	1.02	0.640	7.99	0.44	0.569	0.0190	0.751	0.029
6959	0.04	0.00	0.43	0.218	17.60	0.65	0.229	0.0130	2.780	0.250
6959	0.08	0.02	0.50	0.403	13.46	0.40	0.378	0.0120	1.192	0.043
6959	0.01	0.00	0.11	0.286	20.53	1.95	0.284	0.0440	1.980	0.990
6959	3.38	0.01	2.54	0.949	2.76	0.07	0.819	0.0047	0.493	0.003
6959	0.02	0.00	0.14	0.446	13.64	0.73	0.413	0.0280	1.740	0.190
6959	9.48	0.01	4.74	0.922	1.84	0.08	0.797	0.0033	0.508	0.002
6959	9.06	0.01	4.04	0.931	1.59	0.06	0.804	0.0038	0.505	0.003
6959	0.05	0.00	0.11	0.813	8.09	0.62	0.709	0.0430	0.880	0.059
6959	3.59	0.00	0.98	0.957	1.00	0.04	0.825	0.0041	0.492	0.003
6959	86.66	0.01	3.09	0.808	0.21	0.03	0.705	0.0190	0.514	0.009
6959	6.62	0.00	0.71	0.554	4.71	0.83	0.500	0.0720	0.679	0.055
6959	0.05	0.01	0.36	0.103	15.62	0.63	0.136	0.0710	2.150	0.270
6959	0.53	0.00	0.14	0.944	1.18	0.07	0.815	0.0130	0.492	0.008
6959	1.52	0.00	0.30	0.958	0.73	0.02	0.826	0.0060	0.491	0.004
6959	0.02	0.00	0.08	0.508	15.71	1.34	0.463	0.0580	1.650	0.380
6959	0.03	0.00	0.41	0.093	20.57	0.69	0.128	0.0100	8.000	1.500
6959	0.06	0.00	0.37	0.436	14.62	0.72	0.405	0.0210	1.183	0.065
6959	0.05	0.00	0.36	0.343	15.29	0.59	0.330	0.0180	1.650	0.100
6959	0.03	0.00	0.18	0.419	15.72	0.73	0.391	0.0300	2.030	0.360
6959	0.04	0.00	0.09	0.705	6.94	0.38	0.622	0.0320	0.721	0.042

6959	0.32	0.01	0.09	0.952	0.98	0.03	0.821	0.0130	0.502	0.009
6959	0.37	0.03	0.42	0.821	3.69	0.09	0.716	0.0092	0.574	0.008
6959	0.33	0.01	0.15	0.928	1.63	0.04	0.802	0.0110	0.506	0.007
6959	0.57	0.01	0.10	0.955	0.66	0.02	0.824	0.0093	0.487	0.006
6959	1.23	0.03	0.07	0.978	0.43	0.02	0.842	0.0120	0.479	0.007
6959	0.16	0.01	0.09	0.877	2.82	0.16	0.761	0.0250	0.566	0.023
6959	0.17	0.04	0.07	0.937	1.54	0.05	0.809	0.0180	0.506	0.012
6959	0.21	0.02	0.31	0.788	4.79	0.10	0.689	0.0120	0.593	0.011
6959	0.01	0.00	0.09	0.285	19.61	2.17	0.283	0.0490	2.880	0.960
6959	0.03	0.01	0.25	0.343	15.61	0.68	0.330	0.0180	1.850	0.160

Session No.
CFM
Session 1

Pb ppm1 232Th ppr238U pprf206c

6196	0.1	0.05	0.6	0.184
6196	0.2	0.23	2.4	0.131
6196	0.2	0.06	3.9	0.022
6196	0.2	0.11	3.5	0.086
6196	0.3	0.19	4.8	0.065
6196	0.2	0.05	3.0	0.058
6196	0.1	0.03	1.3	0.144
6196	0.1	0.04	2.3	0.074
6196	0.1	0.01	0.5	0.289
6196	0.1	0.16	0.9	0.174
6196	0.1	0.27	0.8	0.316
6196	0.9	0.25	16.9	0.006
6196	0.1	0.17	2.0	0.094
6196	0.2	0.04	3.6	0.045
6196	0.2	0.15	1.1	0.407
6196	0.3	0.06	2.5	0.235
6196	0.1	0.01	0.9	0.164
6196	0.2	0.08	2.5	0.068

Session 4

6923	0.4	0.31	2.6	0.352
6923	0.2	0.14	3.1	0.054
6923	0.2	0.21	3.2	0.100
6923	0.2	0.11	2.8	0.098
6923	0.3	0.79	2.5	0.227
6923	0.5	2.93	4.8	0.316
6923	0.1	0.04	2.1	0.031
6923	0.2	0.09	3.8	0.038
6923	0.2	0.14	4.3	0.309
6923	0.1	0.10	1.7	0.030
6923	0.2	0.11	3.3	0.052

6923	0.2	0.06	3.1	0.037
6923	0.5	2.78	7.2	0.232
6923	0.5	0.48	6.1	0.116
6923	0.3	0.08	6.4	0.004
6923	0.6	0.15	9.3	0.066
6923	0.4	0.14	6.0	0.065
6923	0.6	1.18	7.6	0.126
6923	0.2	0.14	2.1	0.234
6923	0.4	3.27	6.4	0.429
6923	0.3	0.08	3.3	0.120
6923	0.2	0.09	3.6	0.050

Common lead for CFM: $^{207}\text{Pb}/^{206}\text{Pb} = 0.86 \pm 0.02$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$

ENG

Session 4

6923	0.7	0.03	2.5	0.617
6923	0.4	0.01	1.8	0.509
6923	0.1	0.02	2.0	0.087
6923	0.1	0.02	1.3	0.166
6923	0.1	0.01	1.6	0.024
6923	0.1	0.02	2.1	0.067
6923	0.4	0.03	4.2	0.126
6923	0.1	0.00	1.1	0.068
6923	0.0	0.03	0.8	0.077
6923	0.5	0.01	0.8	0.730
6923	0.0	0.00	0.5	0.121
6923	0.1	0.00	0.6	0.435
6923	0.2	0.00	0.9	0.492
6923	0.1	0.01	0.6	0.499
6923	0.2	0.00	0.5	0.594
6923	0.1	0.00	0.9	0.292
6923	0.2	0.00	0.4	0.616
6923	0.4	0.01	1.8	0.491
6923	0.1	0.00	0.4	0.271

6923	0.8	0.02	2.0	0.592
6923	1.9	0.03	3.4	0.767
6923	0.1	0.01	2.3	0.056
6923	0.2	0.02	2.8	0.136
6923	0.3	0.01	2.0	0.240
6923	0.1	0.00	0.6	0.171
6923	0.3	0.01	2.0	0.366
6923	0.1	0.01	2.0	0.073
6923	0.2	0.02	1.7	0.319
6923	0.2	0.01	2.7	0.147
6923	0.3	0.02	1.4	0.550
6923	0.3	0.02	1.8	0.329
6923	0.1	0.01	1.8	0.034
6923	0.3	0.01	1.3	0.370
6923	6.6	0.10	6.5	0.870
6923	0.1	0.01	1.9	0.006
6923	0.3	0.01	1.4	0.370
6923	0.3	0.02	3.0	0.245
6923	0.3	0.02	4.2	0.080
6923	0.1	0.01	1.9	0.012
6923	0.1	0.01	1.9	0.029
6923	0.1	0.01	1.9	0.016
6923	2.9	0.14	5.3	0.625

Common lead for CFM: $^{207}\text{Pb}/^{206}\text{Pb} = 0.86 \pm 0.02$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$

LCP

Session 1

6196	0.1	0.00	1.7	0.035
6196	0.1	0.00	0.5	0.252
6196	0.1	0.00	1.5	0.050
6196	3.0	0.00	2.3	0.093
6196	0.0	0.02	0.2	0.964
6196	0.3	0.00	0.9	0.610
6196	0.2	0.02	0.2	0.815

Session 4

6196	0.2	0.00	0.5	0.542
6196	0.1	0.00	1.4	0.085
6196	0.1	0.00	1.1	0.283
6196	0.1	0.00	0.9	0.033
6196	0.1	0.00	1.0	0.153
6196	0.1	0.00	1.1	0.315
6196	0.5	0.00	4.8	0.186
6196	0.3	0.00	5.3	0.054
6196	0.4	0.00	0.5	0.337
6196	0.0	0.00	0.4	0.594
6196	0.2	0.01	0.2	0.852
6196	0.3	0.01	0.4	0.801
6196	0.1	0.00	0.9	0.211
6196	0.1	0.00	1.0	0.064
6196	5.6	0.00	1.1	0.926
6196	0.1	0.00	1.8	0.066
6923	0.1	0.00	0.3	0.661
6923	0.0	0.00	0.3	0.235
6923	0.2	0.01	0.6	0.595
6923	0.1	0.00	0.8	0.077
6923	0.1	0.00	0.3	0.677
6923	0.0	0.00	0.2	0.486
6923	0.1	0.01	1.2	0.050
6923	0.2	0.01	0.3	0.720
6923	0.1	0.00	1.3	0.065
6923	0.1	0.00	1.0	0.134
6923	0.1	0.00	1.0	0.045
6923	0.0	0.00	0.6	0.078
6923	0.1	0.00	1.0	0.039
6923	0.3	0.00	0.8	0.608
6923	0.2	0.00	1.9	0.272
6923	0.2	0.00	1.2	0.375
6923	0.3	0.00	1.3	0.499

6923	0.1	0.00	1.3	0.072
6923	0.5	0.24	2.4	0.680
6923	0.6	0.00	1.2	0.652
6923	1.0	0.00	0.9	0.842
6923	0.8	0.00	2.4	0.591
6923	0.4	0.00	1.5	0.406

Common lead for CFM: $^{207}\text{Pb}/^{206}\text{Pb} = 0.86 \pm 0.02$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$
ML

Session 1

6196	0.3	0.05	4.8	0.094
6196	0.5	0.08	5.6	0.167
6196	0.4	0.63	5.0	0.153
6196	0.3	0.24	3.8	0.117
6196	0.4	0.39	5.8	0.089
6196	0.5	0.11	6.7	0.137
6196	1.1	0.48	5.1	0.452
6196	0.2	0.03	2.1	0.179
6196	1.1	2.36	10.6	0.234
6196	0.2	0.13	3.0	0.069
6196	2.9	23.01	12.3	0.535

Session 4

6923	1.6	1.04	7.2	0.535
6923	0.3	0.07	2.4	0.235
6923	0.3	0.26	3.2	0.219
6923	0.3	0.32	4.1	0.151
6923	2.4	0.41	7.4	0.713
6923	0.7	0.55	4.2	0.415
6923	0.2	0.08	3.1	0.095
6923	0.3	0.13	4.8	0.086
6923	0.3	0.15	5.7	0.048
6923	0.6	0.16	5.8	0.235
6923	0.5	0.18	4.5	0.252
6923	0.5	0.25	6.2	0.173

Session 4

6923	0.7	0.49	8.6	0.156
6923	0.4	0.10	7.7	0.041
7405	0.5	0.06	8.7	0.044
7405	0.5	0.11	7.5	0.058
7405	1.5	0.62	6.7	0.510
7405	1.3	0.23	5.8	0.481
7405	0.5	0.18	5.9	0.156
7405	0.8	0.17	3.0	0.531
7405	0.2	0.04	3.6	0.067
7405	0.7	0.15	10.2	0.075
7405	0.7	0.43	10.9	0.073
7405	11.8	2.20	21.3	0.808
7405	1.9	0.37	9.5	0.474
7405	0.7	0.13	8.8	0.094
7405	1.2	0.23	8.0	0.382
7405	0.3	0.11	3.0	0.159
7405	0.9	0.33	11.4	0.247

Common lead for CFM: $^{207}\text{Pb}/^{206}\text{Pb} = 0.86 \pm 0.02$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$

SM

Session 4

6923	1.6	0.06	14.1	0.226
6923	0.6	0.07	8.5	0.118
6923	0.5	0.02	4.1	0.267
6923	1.2	0.09	17.8	0.091
6923	0.8	0.06	12.3	0.064
6923	0.1	0.01	1.5	0.119
6923	2.7	0.01	1.3	0.889
6923	0.1	0.00	0.7	0.169
6923	0.5	0.02	2.1	0.489
6923	0.5	0.01	1.2	0.662

6923	0.2	0.01	1.2	0.318
6923	0.2	0.00	0.5	0.688
6923	0.2	0.01	1.5	0.315
6923	0.6	0.03	7.0	0.130
6923	1.0	0.07	17.2	0.049
6923	1.2	0.09	20.0	0.056
6923	0.3	0.03	4.6	0.017
6923	0.3	0.04	5.2	0.017
6923	0.3	0.04	5.9	0.010
6923	0.8	0.04	7.0	0.272
6923	14.4	0.07	8.4	0.728
6923	0.2	0.03	3.3	0.032
6923	1.5	0.04	6.5	0.486
6923	0.1	0.01	0.8	0.094
6923	0.2	0.02	2.4	0.222
6923	0.1	0.01	2.0	0.078
6923	0.1	0.00	0.7	0.123
6923	0.1	0.01	1.5	0.047
6923	0.2	0.04	1.4	0.176
6923	2.9	0.06	7.0	0.470
6923	1.4	0.06	8.8	0.352
6923	0.5	0.09	9.0	0.022
6923	0.5	0.08	9.8	0.019
6923	0.4	0.06	8.1	0.017
6923	0.5	0.06	8.8	0.022
6923	0.6	0.08	11.6	0.022
6923	1.0	0.07	8.2	0.243
6923	0.6	0.08	7.7	0.122
6923	0.5	0.06	9.7	0.027
6923	0.6	0.06	9.4	0.085
6923	1.9	0.16	18.3	0.220

Common lead for CFM: $^{207}\text{Pb}/^{206}\text{Pb} = 0.60 \pm 0.02$, $^{208}\text{Pb}/^{206}\text{Pb} = 2.090$
BOS3c

Session 1

6196	0.2	0.25	3.2	0.087
6196	0.2	0.15	3.5	0.074
6196	0.1	0.02	2.2	0.023
6196	0.1	0.13	0.7	0.180
6196	0.9	0.29	3.1	0.378
6196	0.4	0.05	0.9	0.452
6196	0.4	0.25	3.1	0.173
6196	4.0	0.49	9.2	0.365
6196	1.2	0.18	5.0	0.363
6196	0.7	0.17	7.3	0.154
6196	0.4	0.08	7.1	0.024
6196	0.3	0.10	5.4	0.044
6196	0.3	0.16	3.8	0.087
6196	0.3	0.18	3.1	0.125
6196	0.5	0.09	0.8	0.364
6196	0.2	0.11	0.8	0.385

Session 4

6923	0.3	0.35	4.1	0.078
6923	0.1	0.06	0.7	0.201
6923	0.4	0.16	4.3	0.123
6923	0.7	0.22	6.6	0.158
6923	1.0	0.89	5.8	0.280
6923	0.5	0.38	3.8	0.159
6923	0.5	0.29	3.9	0.204
6923	7.2	0.44	22.7	0.497
6923	0.9	0.39	10.6	0.143
6923	3.4	0.49	9.5	0.519
6923	10.9	0.29	9.6	0.680
6923	1.9	0.52	12.6	0.269
6923	0.8	0.27	9.3	0.103
6923	3.5	0.73	13.0	0.390
6923	2.6	0.51	11.3	0.303
6923	3.4	0.83	15.5	0.336

6923	2.7	1.31	14.3	0.313
6923	1.4	0.80	8.8	0.272

~~26.9~~: Analysis rejected from calculations

1: Normalised to the NIST614 reference glass.

2: Corrected for downhole fractionation and multiplied by the session correction factor shown in Table 1

3: Normalised to the NIST614 reference glass with a $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.87 and $^{208}\text{Pb}/^{206}\text{Pb}$ of 2.10 after Woodhead and Hergt (2001)

4: Corrected for downhole fractionation and normalised to the MTM wolframite

$^{238}\text{U}/^{206}\text{Pb}_2$	2SE	$^{207}\text{Pb}/^{206}\text{Pb}_3$	2SE	$^{208}\text{Pb}/^{206}\text{Pb}_2$		
16.1		0.8	0.201	0.016	0.376	0.103
18.3		0.4	0.159	0.005	0.284	0.038
20.6		0.4	0.070	0.003	0.041	0.117
19.1		0.4	0.122	0.004	0.186	0.057
18.9		0.4	0.105	0.003	0.143	0.056
19.1		0.5	0.100	0.005	0.118	0.084
16.8		0.5	0.169	0.011	0.274	0.114
18.4		0.4	0.112	0.004	0.153	0.052
14.7		0.5	0.286	0.016	0.546	0.056
15.9		0.5	0.193	0.009	0.357	0.054
14.0		0.5	0.308	0.013	0.659	0.054
19.8		0.3	0.057	0.001	0.014	0.079
17.2		0.4	0.128	0.004	0.211	0.046
18.7		0.4	0.089	0.003	0.085	0.056
11.4		0.3	0.381	0.009	0.855	0.036
14.6		0.3	0.242	0.008	0.497	0.033
16.5		0.5	0.185	0.011	0.280	0.080
18.6		0.4	0.107	0.006	0.111	0.113
13.3		0.3	0.337	0.007	0.762	0.016
19.4		0.5	0.096	0.004	0.115	0.007
17.6		0.4	0.133	0.004	0.217	0.009
17.9		0.4	0.132	0.004	0.206	0.008
15.9		0.4	0.236	0.006	0.486	0.015
20.5		0.5	0.308	0.006	0.727	0.013
19.7		0.5	0.078	0.004	0.080	0.044
19.7		0.5	0.084	0.004	0.066	0.009
11.7		0.5	0.302	0.018	0.578	0.041
19.8		0.5	0.077	0.005	0.052	0.010
19.1		0.4	0.095	0.003	0.100	0.005

19.5	0.4	0.082	0.003	0.064	0.005
22.7	0.5	0.240	0.006	0.545	0.014
17.0	0.4	0.147	0.003	0.264	0.007
20.4	0.4	0.056	0.002	0.011	0.003
19.1	0.4	0.106	0.002	0.133	0.004
19.0	0.4	0.105	0.004	0.131	0.007
18.7	0.4	0.154	0.003	0.287	0.007
15.8	0.4	0.242	0.008	0.495	0.018
27.0	1.7	0.399	0.010	0.964	0.025
17.4	0.4	0.150	0.005	0.238	0.010
19.8	0.4	0.093	0.003	0.102	0.005

9.21	0.38	0.550	0.012	1.301	0.029
10.11	0.31	0.464	0.011	1.074	0.028
17.68	0.71	0.123	0.013	0.099	0.028
16.39	0.66	0.186	0.016	0.182	0.032
18.96	0.48	0.072	0.004	0.091	0.058
18.45	0.44	0.107	0.005	0.129	0.007
49.12	0.54	0.155	0.007	0.249	0.015
18.67	0.61	0.108	0.007	0.116	0.038
20.74	0.91	0.115	0.009	0.143	0.044
4.79	0.32	0.642	0.016	1.474	0.040
18.09	0.69	0.151	0.012	0.162	0.035
10.94	0.53	0.404	0.018	0.882	0.039
10.00	0.45	0.450	0.016	0.975	0.038
10.38	0.36	0.455	0.015	1.037	0.037
7.80	0.33	0.532	0.018	1.227	0.043
14.28	0.51	0.289	0.014	0.572	0.030
7.70	0.39	0.550	0.021	1.253	0.052
10.35	0.55	0.449	0.019	0.957	0.043
14.19	0.71	0.271	0.018	0.473	0.036

7.18	0.68	0.531	0.021	1.202	0.050
5.54	0.29	0.672	0.011	1.625	0.026
19.04	0.43	0.098	0.005	0.080	0.012
17.37	0.65	0.162	0.016	0.156	0.019
14.15	1.10	0.246	0.010	0.452	0.018
16.45	0.57	0.191	0.011	0.253	0.029
12.38	0.63	0.348	0.014	0.717	0.030
18.32	0.43	0.112	0.005	0.139	0.010
13.39	0.53	0.310	0.015	0.610	0.029
16.88	0.48	0.172	0.008	0.295	0.017
10.20	0.28	0.497	0.012	1.139	0.030
13.29	0.53	0.318	0.017	0.588	0.045
19.59	0.50	0.080	0.005	0.050	0.010
10.64	1.82	0.351	0.024	0.671	0.038
3.59	0.11	0.755	0.005	1.855	0.015
20.47	0.51	0.057	0.003	0.099	0.148
11.89	0.83	0.351	0.029	0.482	0.054
15.91	0.34	0.251	0.005	0.505	0.011
18.79	0.47	0.117	0.008	0.116	0.010
19.89	0.49	0.062	0.003	0.055	0.043
19.60	0.51	0.076	0.004	0.057	0.014
19.71	0.52	0.065	0.004	0.030	0.010
5.08	0.11	0.557	0.005	1.334	0.012

19.2	0.6	0.081	0.005	0.093	0.381
14.1	1.1	0.256	0.026	0.503	0.255
18.9	0.5	0.093	0.006	0.095	0.305
18.4	0.4	0.128	0.005	0.176	0.061
0.2	0.01	0.831	0.008	2.077	0.039
7.8	0.3	0.545	0.018	1.299	0.069
3.6	0.2	0.711	0.024	1.745	0.071

9.1	0.6	0.490	0.025	1.171	0.151
18.8	0.5	0.121	0.008	0.157	0.133
14.2	0.9	0.281	0.043	0.600	0.239
18.0	0.6	0.079	0.006	0.050	0.187
17.2	0.8	0.176	0.028	0.169	0.150
13.9	0.6	0.307	0.027	0.569	0.108
16.3	0.4	0.203	0.008	0.377	0.053
18.9	0.4	0.096	0.003	0.108	0.046
14.0	0.6	0.324	0.018	0.685	0.103
11.5	1.2	0.533	0.102	0.944	0.160
3.0	0.1	0.741	0.022	1.739	0.055
4.2	0.2	0.700	0.021	1.655	0.057
15.8	0.5	0.223	0.009	0.402	0.065
18.4	0.5	0.105	0.007	0.114	0.108
0.7	0.1	0.801	0.009	2.001	0.127
19.5	0.6	0.106	0.005	0.123	0.101
6.5	0.3	0.586	0.020	1.347	0.053
15.4	0.8	0.242	0.020	0.364	0.066
8.2	0.3	0.533	0.017	1.257	0.034
19.6	0.7	0.115	0.008	0.119	0.026
7.8	0.4	0.599	0.025	1.346	0.057
10.3	0.6	0.445	0.032	0.737	0.077
20.1	0.6	0.093	0.006	0.120	0.043
5.5	0.3	0.634	0.020	1.487	0.045
19.3	0.6	0.105	0.006	0.097	0.019
18.1	0.6	0.160	0.010	0.181	0.021
19.9	0.6	0.089	0.007	0.078	0.027
19.5	0.8	0.115	0.012	0.159	0.049
20.2	0.6	0.084	0.006	0.073	0.028
7.4	0.3	0.544	0.016	1.227	0.037
15.2	0.4	0.272	0.010	0.533	0.021
12.6	0.6	0.356	0.020	0.673	0.043
10.5	0.5	0.456	0.016	0.994	0.037

18.6	0.5	0.111	0.005	0.109	0.014
13.2	0.6	0.602	0.013	1.436	0.033
6.8	0.3	0.579	0.017	1.349	0.044
3.3	0.1	0.732	0.010	1.782	0.023
5.9	0.8	0.529	0.027	1.167	0.063
10.3	0.9	0.380	0.026	0.721	0.058

18.25	0.389	0.129	0.005	0.187	0.045
17.70	0.352	0.187	0.004	0.358	0.032
19.03	0.399	0.177	0.008	0.326	0.028
18.08	0.409	0.147	0.004	0.260	0.041
18.99	0.362	0.124	0.003	0.196	0.033
17.78	0.462	0.163	0.009	0.291	0.071
10.98	0.477	0.417	0.015	0.940	0.065
16.74	0.482	0.197	0.008	0.358	0.055
16.62	0.401	0.241	0.007	0.532	0.054
19.39	0.416	0.108	0.003	0.141	0.049
12.40	0.321	0.485	0.012	1.364	0.053

11.56	0.22	0.485	0.006	1.162	0.013
15.72	0.40	0.243	0.008	0.499	0.017
16.60	0.38	0.229	0.006	0.472	0.013
18.29	0.41	0.175	0.005	0.333	0.010
9.59	0.21	0.628	0.006	1.513	0.014
12.76	0.27	0.388	0.006	0.874	0.015
18.96	0.45	0.129	0.004	0.187	0.008
19.39	0.44	0.122	0.003	0.181	0.007
21.00	0.44	0.092	0.002	0.112	0.004
16.42	0.34	0.243	0.004	0.493	0.010
16.00	0.37	0.256	0.005	0.526	0.011
18.10	0.35	0.193	0.003	0.375	0.008

17.86	0.35	0.179	0.003	0.336	0.006
20.44	0.41	0.086	0.002	0.085	0.003
20.05	0.84	0.088	0.006	0.073	0.004
19.96	0.77	0.098	0.011	0.105	0.006
12.92	0.72	0.462	0.014	1.109	0.035
11.99	0.62	0.440	0.013	1.049	0.030
17.47	0.65	0.177	0.005	0.326	0.010
9.53	0.42	0.486	0.011	1.147	0.022
19.52	0.89	0.105	0.011	0.109	0.007
19.30	0.81	0.112	0.005	0.157	0.013
19.20	0.75	0.111	0.003	0.167	0.008
6.37	0.27	0.724	0.011	1.795	0.009
12.03	0.52	0.434	0.009	1.016	0.018
18.86	0.83	0.128	0.004	0.197	0.008
14.56	0.61	0.358	0.008	0.808	0.016
16.97	0.74	0.180	0.007	0.342	0.015
21.58	0.89	0.246	0.007	0.514	0.011

14.26	0.30	0.235	0.003	0.477	0.006
17.31	0.34	0.148	0.006	0.228	0.012
14.00	0.44	0.268	0.009	0.541	0.021
17.97	0.31	0.126	0.004	0.180	0.006
18.23	0.35	0.104	0.002	0.133	0.005
17.25	0.51	0.149	0.007	0.210	0.014
1.58	0.16	0.770	0.009	1.887	0.022
16.39	0.57	0.189	0.011	0.266	0.028
9.57	0.28	0.447	0.008	1.016	0.020
6.84	0.17	0.587	0.010	1.381	0.021

13.88	0.40	0.309	0.010	0.630	0.024
5.93	0.17	0.608	0.016	1.415	0.034
13.96	0.36	0.307	0.008	0.668	0.019
16.84	0.35	0.157	0.003	0.270	0.005
18.21	0.39	0.092	0.003	0.089	0.008
18.27	0.37	0.098	0.003	0.108	0.004
18.55	0.45	0.067	0.002	0.029	0.004
19.86	0.41	0.066	0.002	0.031	0.003
19.42	0.42	0.061	0.002	0.018	0.002
14.47	0.36	0.272	0.007	0.574	0.016
4.94	0.33	0.644	0.034	1.399	0.143
19.51	0.45	0.079	0.003	0.044	0.008
10.21	0.39	0.445	0.012	0.994	0.026
18.43	0.60	0.128	0.008	0.139	0.024
15.80	0.39	0.232	0.007	0.450	0.015
18.03	0.49	0.115	0.005	0.144	0.009
16.77	0.60	0.152	0.009	0.204	0.019
19.62	0.56	0.091	0.005	0.075	0.013
14.11	1.47	0.195	0.033	0.105	0.023
6.51	1.10	0.432	0.034	0.778	0.086
12.48	0.26	0.337	0.004	0.744	0.009
19.58	0.39	0.070	0.002	0.034	0.003
19.57	0.38	0.068	0.001	0.037	0.002
19.81	0.40	0.066	0.002	0.032	0.002
19.96	0.38	0.070	0.002	0.031	0.005
19.52	0.39	0.070	0.001	0.041	0.002
14.35	0.88	0.249	0.024	0.345	0.029
15.97	1.40	0.151	0.028	0.067	0.006
19.38	0.41	0.074	0.003	0.041	0.004
18.30	0.47	0.122	0.009	0.100	0.013
15.52	0.28	0.230	0.006	0.460	0.015

16.82	0.46	0.123	0.004	0.203	0.055
18.35	0.48	0.112	0.003	0.156	0.060
19.98	0.48	0.072	0.003	0.035	0.130
13.65	0.56	0.198	0.009	0.391	0.070
7.10	0.27	0.358	0.007	0.830	0.046
6.35	0.30	0.418	0.014	1.015	0.126
11.12	0.23	0.192	0.004	0.382	0.031
6.73	0.51	0.347	0.018	0.983	0.194
9.16	0.23	0.345	0.007	0.773	0.043
15.39	0.39	0.177	0.004	0.326	0.044
19.28	0.39	0.072	0.002	0.045	0.058
18.41	0.36	0.088	0.002	0.092	0.068
17.57	0.35	0.123	0.004	0.183	0.048
15.08	0.31	0.154	0.004	0.267	0.032
3.37	0.08	0.347	0.006	0.787	0.053
9.56	0.24	0.363	0.011	0.784	0.034
0.00					
16.27	0.36	0.116	0.003	0.195	0.005
8.65	0.28	0.215	0.008	0.419	0.017
13.47	0.29	0.152	0.003	0.281	0.007
13.13	0.38	0.180	0.006	0.336	0.014
10.62	0.24	0.279	0.004	0.621	0.007
11.73	0.46	0.181	0.005	0.353	0.011
12.69	0.53	0.217	0.008	0.413	0.021
7.58	0.19	0.454	0.003	1.068	0.007
16.41	0.29	0.168	0.003	0.310	0.006
7.07	0.15	0.471	0.004	1.108	0.010
2.61	0.09	0.601	0.004	1.445	0.009
12.30	0.38	0.270	0.008	0.580	0.023
15.49	0.29	0.135	0.002	0.229	0.005
7.83	0.15	0.367	0.004	0.843	0.009
8.27	0.17	0.298	0.003	0.671	0.006
9.03	0.18	0.324	0.002	0.738	0.005

9.93	0.17	0.305	0.002	0.689	0.005
11.46	0.21	0.272	0.004	0.606	0.010

EMPA compositions of Echassieres wolframite

	MTM-1-mn-1	MTM-1-mn-2	MTM-1-mn-3	MTM-1-mn-4	MTM-1-mn-5	MTM-1-mn-6	MTM-1-mn-7	MTM-1-mn-8	MTM-1-mn-9
WO3	75.72	76.51	76.67	76.72	76.76	76.42	76.55	76	76.3
FeO	17.78	18.26	17.5	17.95	18.83	18.48	18.45	18.8	18.26
MnO	6.59	6.56	6.75	6.52	5.95	5.94	6.54	5.33	6.35
Nb2O5	0.51	0.38	0.43	0.33	0.4	0.87	0.11	0.68	0.19
TaO5	0	0	0	0	0	0.01	0	0	0
Sc	0	0	0	0	0	0.01	0	0	0
TiO2	0.04	0.05	0.03	0.03	0.02	0.05	0.01	0.03	0.02
	0	0	0	0	0	0	0	0	0
Total	100.67	101.81	101.42	101.58	102	101.83	101.7	100.89	101.17
		78.14							
ΣO	1.33	1.35	1.34	1.34	1.35	1.35	1.34	1.33	1.34
Nb O	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
W	0.98	0.98	0.99	0.99	0.98	0.98	0.98	0.98	0.99
Fe	0.74	0.76	0.73	0.74	0.78	0.76	0.77	0.78	0.76
Mn	0.28	0.28	0.28	0.27	0.25	0.25	0.27	0.23	0.27
Nb	0.01	0.01	0.01	0.01	0.01	0.02	0.00	0.02	0.00
Ta	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sc	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe/(Fe+Mn)	0.73	0.73	0.72	0.73	0.76	0.75	0.74	0.78	0.74

Analytical conditions, reference standards and limits of detection are given in the text. bdl: below detection limit

MTM-1-mn-10	MTM-1-mn-11	MTM-1-mn-12	MTM-1-mn-13	MTM-1-mn-14	MTM-1-mn-15	MTM-1-mn-16	MTM-1-mn-17	MTM-1-mn-18	MTM-1-mn-19
76.52	77.25	74.86	76.7	76.86	77.6	75.8	76.23	76.46	75.38
17.58	18.68	18.61	18.21	18.26	17.59	9.91	19.05	18.26	18.2
7.07	5.96	5.98	6.09	6.58	6.42	14.63	5.28	5.77	6.27
0.15	0.15	0.65	0.6	0.5	0.24	0.56	0.39	0.55	0.47
0	0	0.01	0.01	0	0	0	0	0	0
0	0	0	0	0	0	0.05	0	0	0
0	0	0.05	0.04	0.04	0.02	0.09	0.02	0.03	0.02
0	0	0	0	0	0	0	0	0	0
101.36	102.09	100.2	101.7	102.29	101.92	101.08	101.01	101.1	100.38
1.34	1.35	1.33	1.34	1.35	1.34	1.34	1.33	1.34	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.99	0.97	0.98	0.98	1.00	0.98	0.99	0.99	0.98
0.73	0.77	0.78	0.75	0.75	0.73	0.41	0.80	0.76	0.76
0.30	0.25	0.25	0.26	0.27	0.27	0.62	0.22	0.24	0.27
0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.71	0.76	0.75	0.75	0.73	0.73	0.40	0.78	0.76	0.74

[illegible]

MTM-1-fe-30	MTM-1-fe-32	MTM-1-fe-33	MTM-1-fe-34	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35
76.55	75.43	76.65	75.6	77.2	76.92	77.07	75.79	75.89	77.19
19.17	18.9	15.02	12.46	17.88	17.67	17.64	18.16	17.69	18.34
4.61	5.41	9.05	11.49	6.28	6.18	6.04	5.84	6.11	5.78
0.63	1.04	0.14	0.79	0.2	0.47	0.43	0.36	0.49	0.55
0	0	0	0	0	0	0	0	0	0
0.02	0.04	0	0.08	0	0	0	0	0	0
0.31	0.05	0.02	0.16	0	0.01	0.02	0.02	0.03	0.03
0	0	0	0	0	0	0	0	0	0
101.35	100.91	100.93	100.62	101.62	101.28	101.29	100.21	100.27	101.92
1.34	1.34	1.33	1.33	1.34	1.34	1.34	1.32	1.32	1.35
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.98	0.97	0.99	0.98	0.99	0.99	0.99	0.99	0.99	0.99
0.80	0.79	0.63	0.52	0.74	0.74	0.73	0.76	0.74	0.76
0.19	0.23	0.38	0.49	0.26	0.26	0.25	0.25	0.26	0.24
0.01	0.02	0.00	0.02	0.00	0.01	0.01	0.01	0.01	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.80	0.78	0.62	0.52	0.74	0.74	0.74	0.75	0.74	0.76

MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35
76.07	77.39	76.28	76.73	76.81	77.58	77.85	75.41	77.26	76.71
18.2	17.94	18.5	18.55	18.59	18.9	19.14	19.07	19.65	19.57
5.72	5.71	5.58	5.67	5.37	5.07	5.14	4.43	4.56	4.46
0.47	0.44	0.42	0.21	0.23	0.25	0.04	0.07	0.03	0.11
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0.04	0.03	0.03	0.01	0.01	0.01	0.08	0.04	0.06	0.09
0	0	0	0	0	0	0	0	0	0
100.55	101.56	100.84	101.23	101.06	101.87	102.32	99.07	101.61	100.96
1.33	1.34	1.33	1.34	1.33	1.34	1.35	1.31	1.34	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	1.00	0.99	0.99	0.99	1.00	1.00	1.00	1.00	0.99
0.76	0.75	0.77	0.77	0.78	0.78	0.79	0.81	0.82	0.82
0.24	0.24	0.24	0.24	0.23	0.21	0.21	0.19	0.19	0.19
0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.76	0.76	0.77	0.76	0.77	0.79	0.79	0.81	0.81	0.81

MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35
76.76	76.78	76.74	77.42	77.61	77.51	77.97	77.17	76.73	78.14
19.51	19.2	19.76	19.48	19.51	19.76	19.63	19.27	19.58	19.58
4.71	4.58	4.58	4.62	4.28	4.39	4.46	4.39	4.5	4.51
0.1	0.12	0.05	0.05	0.15	0.15	0.09	0.13	0.07	0.09
0	0	0	0	0	0	0	0	0	0
0	0	0.01	0	0	0	0	0	0	0
0.09	0.08	0.1	0.09	0.11	0.1	0.1	0.1	0.12	0.09
0	0	0	0	0	0	0	0	0	0
101.21	100.8	101.27	101.7	101.7	101.96	102.3	101.11	101.09	102.45
1.34	1.33	1.34	1.34	1.34	1.35	1.35	1.33	1.33	1.35
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	1.00	0.99	1.00	1.00	0.99	1.00	1.00	0.99	1.00
0.81	0.80	0.82	0.81	0.81	0.82	0.81	0.80	0.82	0.81
0.20	0.19	0.19	0.19	0.18	0.18	0.19	0.19	0.19	0.19
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.80	0.81	0.81	0.81	0.82	0.82	0.81	0.81	0.81	0.81

MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-35	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36
74.88	77.2	76.79	77.13	76.52	76.95	76.59	77.63	75.78	77.45
18.69	19.46	19.67	20.02	19.15	18.59	18.03	18.11	18.5	18.66
4.39	4.4	4.67	4.53	5.06	5.67	5.92	5.83	5.96	5.77
0.07	0.16	0.16	0.1	0.4	0.11	0.17	0.14	0.14	0.31
0	0	0	0	0.01	0	0	0	0	0
0	0	0	0	0	0.01	0	0	0	0
0.1	0.09	0.1	0.09	0.03	0	0.01	0	0.01	0.01
0	0	0	0	0	0	0	0	0	0
98.17	101.36	101.43	101.91	101.21	101.34	100.76	101.75	100.44	102.25
1.29	1.34	1.34	1.34	1.34	1.34	1.33	1.34	1.32	1.35
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
1.00	1.00	0.99	0.99	0.99	0.99	0.99	1.00	0.99	0.99
0.80	0.81	0.82	0.83	0.80	0.77	0.76	0.75	0.78	0.77
0.19	0.19	0.20	0.19	0.21	0.24	0.25	0.25	0.25	0.24
0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.81	0.81	0.81	0.81	0.79	0.76	0.75	0.75	0.75	0.76

MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36
76.9	76.4	78.14	77.71	76.28	77.99	76.2	76.52	75.99	77.05
18.77	19.28	19.1	19.08	19.54	19.17	19.59	19.65	19.61	19.42
5.61	5.54	5.16	5.07	4.96	4.78	4.69	4.74	4.6	4.66
0.35	0.31	0.18	0.13	0.36	0.06	0.24	0.27	0.33	0.01
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0.01	0	0.01	0	0.02	0.01	0.19	0.27	0.12	0.01
0	0	0	0	0	0	0	0	0	0
101.68	101.57	102.63	102.04	101.2	102.05	100.95	101.51	100.7	101.2
1.34	1.34	1.35	1.34	1.34	1.34	1.33	1.34	1.33	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.98	1.00	1.00	0.98	1.00	0.99	0.98	0.99	1.00
0.78	0.80	0.79	0.79	0.81	0.79	0.82	0.82	0.82	0.81
0.24	0.23	0.21	0.21	0.21	0.20	0.20	0.20	0.19	0.20
0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.77	0.77	0.79	0.79	0.80	0.80	0.80	0.80	0.81	0.80

MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36
76.75	76.16	76.6	74.62	77.35	68.24	76.13	77.57	76.99	76.88
19.46	19.32	19.49	18.17	19.13	23.74	19.06	18.9	18.51	18.18
4.63	4.72	4.76	4.82	4.86	4.29	5.59	5.47	5.89	6.19
0.12	0.33	0.31	0.33	0.35	0.23	0.35	0.18	0.12	0.18
0	0	0	0.01	0	0	0	0	0	0
0	0	0	0.01	0	0	0	0	0	0
0.01	0	0.01	0.03	0.01	0.03	0.01	0	0	0.01
0	0	0	0	0	0	0	0	0	0
101.02	100.59	101.19	98.06	101.72	96.61	101.19	102.15	101.57	101.48
1.33	1.33	1.34	1.29	1.34	1.28	1.34	1.35	1.34	1.34
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.99	0.99	1.00	0.99	0.92	0.98	0.99	0.99	0.99
0.81	0.81	0.81	0.78	0.79	1.03	0.79	0.78	0.77	0.76
0.20	0.20	0.20	0.21	0.20	0.19	0.24	0.23	0.25	0.26
0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.81	0.80	0.80	0.79	0.80	0.85	0.77	0.77	0.76	0.74

MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	MTM-1-fe-36	ECH3-1	ECH3-2	ECH3-3	ECH3-4	ECH3-5	ECH3-6
77.24	76.93	76.34	76.72	76.62	76.41	76.47	76.52	76.35	76.05
17.97	18.57	18.65	18.87	20.1	19.67	19.44	19.56	19.37	19.33
6.02	5.75	5.7	5.56	4.53	4.79	4.85	4.79	4.76	4.74
0.13	0.6	0.76	0.57	0.2	0.33	0.07	0.33	0.36	0.27
0	0	0.02	0	0	0	0	0	0	0
0	0	0	0.01	0	0	0	0	0	0
0.02	0.01	0.02	0.03	0	0.01	0	0.01	0	0.02
0	0	0	0						
101.42	101.9	101.54	101.79	101.49	101.27	100.88	101.27	100.87	100.44
1.34	1.35	1.34	1.35	1.34	1.34	1.33	1.34	1.33	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
1.00	0.99	0.98	0.98	0.99	0.99	0.99	0.99	0.99	0.99
0.75	0.77	0.77	0.78	0.84	0.82	0.81	0.81	0.81	0.81
0.25	0.24	0.24	0.23	0.19	0.20	0.21	0.20	0.20	0.20
0.00	0.01	0.02	0.01	0.00	0.01	0.00	0.01	0.01	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.75	0.76	0.76	0.77	0.81	0.80	0.80	0.80	0.80	0.80

ECH3-7	ECH3-8	ECH3-9	ECH3-10	ECH3-11	ECH3-12	ECH3-13	ECH3-14	ECH3-15	ECH1-1
76.44	75.64	76.58	76.97	75.52	76.26	76.21	76.22	75.86	76.6
19.66	19.54	19.78	19.07	19.85	20.04	19.74	19.93	19.34	19.97
4.81	4.62	4.64	4.85	4.74	4.55	4.35	4.6	4.71	3.57
0.39	0.11	0.43	0	0.18	0.2	0.1	0.27	0.32	0.4
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0.02	0.01	0	0.01	0.02
101.35	99.96	101.48	100.94	100.34	101.11	100.48	101.07	100.28	100.61
1.34	1.32	1.34	1.33	1.32	1.33	1.32	1.33	1.32	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.99	0.99	1.00	0.98	0.99	0.99	0.99	0.99	1.00
0.82	0.83	0.82	0.80	0.83	0.84	0.83	0.83	0.81	0.84
0.20	0.20	0.20	0.21	0.20	0.19	0.19	0.19	0.20	0.15
0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.80	0.81	0.81	0.80	0.81	0.81	0.82	0.81	0.80	0.85

ECH1-2	ECH1-3	ECH1-4	ECH1-5	ECH1-6	ECH1-7	ECH1-8	ECH1-9	ECH1-10	ECH1-11
75.63	76.62	75.45	76.06	75.73	76.92	76.54	75.41	73.46	76.97
19.35	19.42	19.4	19.33	20.06	19.4	19.6	20.07	21.53	19.01
4.58	4.82	4.47	4.36	4.11	4.58	4.02	3.53	3.78	4.73
0.51	0.27	0.32	0.48	1.06	0.8	0.68	1	0.22	0.32
0	0	0	0	0.38	0	0.07	0.21	0	0
0	0	0	0	0	0	0	0	0	0
0.01	0.11	0	0.06	0.08	0.03	0.06	0.07	0	0
100.12	101.3	99.7	100.33	101.52	101.78	101.03	100.35	99.05	101.06
1.32	1.34	1.32	1.33	1.34	1.35	1.33	1.33	1.31	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.99	0.99	0.99	0.97	0.99	0.99	0.98	0.97	1.00
0.81	0.81	0.82	0.81	0.83	0.80	0.82	0.84	0.92	0.79
0.20	0.20	0.19	0.19	0.17	0.19	0.17	0.15	0.16	0.20
0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01
0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.81	0.80	0.81	0.81	0.83	0.81	0.83	0.85	0.85	0.80

ECH1-12	ECH1-13	ECH1-14	ECH1-15	ECH4-1	ECH4-2	ECH4-3	ECH4-4	ECH4-5	ECH4-6
76.26	75.46	76.23	74.97	75.49	76.19	75.17	75.48	76.33	76.03
19.3	19.26	18.82	19.82	20.34	20.25	21.44	17.56	17.71	17.71
4.63	4.66	4.83	4.1	2.7	3.39	2.6	6.22	6.06	6.08
0.66	0.79	0.42	1.44	0.34	0.4	0.17	0.29	0.14	0.44
0	0	0	0.03	0	0	0	0	0	0.01
0	0	0	0	0	0.01	0	0	0	0.02
0.01	0	0	0.06	0	0	0	0.01	0.03	0.02
100.91	100.23	100.37	100.51	98.93	100.28	99.44	99.59	100.32	100.36
1.33	1.33	1.32	1.33	1.30	1.32	1.31	1.31	1.32	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
0.99	0.98	0.99	0.97	1.00	0.99	0.99	0.99	1.00	0.99
0.81	0.81	0.79	0.83	0.87	0.85	0.91	0.74	0.75	0.74
0.20	0.20	0.21	0.17	0.12	0.14	0.11	0.27	0.26	0.26
0.01	0.02	0.01	0.03	0.01	0.01	0.00	0.01	0.00	0.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.80	0.80	0.79	0.83	0.88	0.86	0.89	0.74	0.74	0.74

ECH4-7	ECH4-8	ECH4-9	ECH4-10	ECH4-11	ECH4-12	ECH5-1	ECH5-2	ECH5-3	ECH5-4
77.13	76.39	76.38	75.79	75.47	76.65	77.13	77.12	77.34	77.29
18.09	19.55	20.03	17.96	18.19	18.3	5.53	2.86	3.91	5.58
5.8	4.3	4.2	6.23	6.21	5.82	18.07	21.23	19.65	18.25
0.06	0.05	0.05	0.11	0.05	0.08	0.13	0.16	0.21	0.2
0	0	0	0	0	0	0	0	0	0
0	0	0	0.01	0	0	0	0	0	0
0	0	0.01	0	0	0.02	0	0.02	0	0.06
101.1	100.32	100.72	100.14	99.97	100.93	100.87	101.4	101.13	101.4
1.33	1.32	1.33	1.32	1.32	1.33	1.33	1.34	1.34	1.34
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
1.00	1.00	0.99	0.99	0.99	0.99	1.00	0.99	1.00	0.99
0.76	0.82	0.84	0.76	0.77	0.77	0.23	0.12	0.16	0.23
0.25	0.18	0.18	0.27	0.27	0.25	0.76	0.89	0.83	0.77
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.75	0.82	0.82	0.74	0.74	0.76	0.23	0.12	0.16	0.23

ECH5-5	ECH5-6	ECH5-7	ECH5-8	ECH5-9	ECH5-10	ECH5-11	ECH5-12	ECH5-13	ECH5-14
76.79	77.26	76.87	77.37	78.02	77.04	78.05	76.88	77.51	76.93
3.38	5.05	9.8	6.52	10.91	2.29	2.33	3.28	2.57	8.63
19.87	19.03	14.04	17.86	12.98	20.95	21.4	20.38	21.05	14.87
0.16	0.22	0.09	0.13	0.12	0.17	0.19	0.15	0.15	0.11
0	0	0	0	0	0	0	0	0	0
0	0	0	0.01	0	0	0	0	0	0
0.06	0	0	0	0	0	0	0	0	0
100.26	101.57	100.83	101.91	102.05	100.46	101.97	100.7	101.28	100.55
1.33	1.34	1.33	1.35	1.35	1.33	1.35	1.33	1.34	1.33
4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
1.00	0.99	1.00	0.99	1.00	1.00	1.00	1.00	1.00	1.00
0.14	0.21	0.41	0.27	0.45	0.10	0.10	0.14	0.11	0.36
0.85	0.80	0.59	0.75	0.54	0.89	0.90	0.86	0.89	0.63
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.14	0.21	0.41	0.26	0.45	0.10	0.10	0.14	0.11	0.36

[illegible]

Click here to access/download
Supplementary file
Appendix_XRFmaps.pptx

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: