Extreme isotopic heterogeneity in impact melt rocks: implications for Martian Meteorites

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ABSTRACT

Pb isotope ratios have been determined in multiple feldspar grains from individual hand samples of impact melt rock at the Manicouagan and Sudbury impact structures. The results reveal an extreme range of isotope values. This indicates that melt sheets are not homogeneous with respect to Pb at the mm scale. Such heterogeneity is significantly larger than what is seen in non-impact-generated igneous rocks. Individual Pb isotope ratios of feldspars from martian shergottites show a large range in ^{206}Pb/^{204}Pb values within one sample, more similar to the terrestrial impact melt sheets than to non-impact igneous rocks. We suggest crystallization from

an impact melt sheet rather than volcanic source as a petrogenetic model for some of the martian shergottites.

INTRODUCTION

Impact Melts

Impact cratering is a dominant geologic process in the Solar System. This process can generate igneous rocks in the form of impact melt products (Dressler and Reimold, 2001; Osinski et al., 2018). During an impact event, target materials can undergo wholescale melting as the result of immense transfer of kinetic energy and pressure-volume work done by the impact (Dence 1971). The resulting products of this melt can be glass (e.g., tektites), and crystallized melt rocks. Crystalline melt-bearing rocks include those dominated by discrete melt blebs in a lithic matrix (suevites), clast-bearing breccias, and coherent clast-free melt rocks (Osinski et al., 2018). Here we focus specifically on the clast-free melt rocks that are pure melt products without remnant inclusions or clasts.

Because clast-free melt rocks crystallize after the passage of the shock wave, they are difficult to distinguish from other igneous rocks. Typically, they are identified by context and with association to known impact structures. For example, the Sudbury impact melt sheet was debated for decades before its impact origin was resolved (Lightfoot, 2017). Additionally, identification by context is challenging for extraterrestrial samples, which are represented by small meteorite samples that lack spatial context.

Mars: Impacts and Meteorites

Surprisingly, despite a heavily cratered surface, large melt sheets are not interpreted on Mars (Pope et al., 2006) or as sources for the martian meteorites. Even though rovers have explored large craters, no igneous rock has been unambiguously identified as impact melt. On the Moon, however, igneous bodies are commonly interpreted as melt sheets. It is likely that impact melt rocks are important on Mars, with their recognition being hindered by sedimentary cover materials (Hamilton, 2016).

Currently, the only samples available for laboratory geochemical study from Mars are meteorites. This suite consists of 262 samples representing 150 pairing groups. These include: shergottites (basalts and gabbros), nakhlites (clinopyroxenites), chassignites (dunites), regolith breccia, and orthopyroxenite ALH 84001 (Udry et al. 2020). Shergottites represent the largest proportion of martian meteorites. There are different geochemical and textural groups within shergottites, but they all are interpreted as being igneous in origin, emplaced as either shallow intrusions or thick flows.

The report of ancient Pb-Pb ages (Bouvier et al., 2009) in shergottites sparked debate over age interpretation of shergottites, particularly in light of robust, younger Ar-Ar ages ranging between 150 and 346 Ma (Udry et al., 2020). Currently, most meteoriticists do not consider shergottites to have ancient ages and their ages are commonly interpreted as crystallization ages (Udry et al. 2020; McFarlane and Spray 2022). However, the Pb data cannot be entirely ignored and required explanation. Bouvier et al. (2009) argued that the ancient Pb represents the original age and the young Ar values result from disturbances during shock. Shock resetting of Ar however is complex (e.g., Walton et al., 2007). Shock experiments show no evidence of Ar resetting (Jessberger and Ostertag 1982) but Jaret et al. (2016) showed partial resetting of naturally shocked plagioclase.

Another challenge is the ‘martian meteorite age paradox’ (Nyquist et al. 1998), the discrepancy between the young shergottite ages with the old surface age for most of Mars. Based on morphology and crater-count retention ages on Mars, few young endogenic igneous terrains exist that could source the meteorites. When only a few shergottites where known, this could be explained by a unique launch from one unusually young source (such as Tharsis). However, we now recognize at least 11 ejection events, separated in time by nearly 2 million years. Given this, it is hard to envision a scenario where only young terrains are sampled. To explain this, Chen and Wasserburg (1986) posed the possibility that some of the shergottites might represent impact melts and not require a crater-free terrane source. This has been expounded by Hamilton (2016, 2019) who advocates that Mars has been essentially inactive in terms of endogenic igneous activity since ~4 Ga and that younger igneous rocks are the products of impact melting.

Pb isotopes in Feldspar

Feldspars are unique capsules of the isotope composition of Pb incorporated at the time of their formation because they strongly exclude U and Th. Virtually no radiogenic Pb ingrowth occurs after formation (Hemming and Rasbury, 2000). In the case of feldspars, the Pb isotopic signature is not a measure of time and Pb evolution since crystallization, but rather a reflection of the Pb evolution until melting. Thus, Pb isotopes in feldspars represent a snapshot of the composition of the source melt. If a melt has a homogeneous composition, then the Pb isotopes in the feldspars will be homogeneous. Conversely, any heterogeneity in the melt will be captured by feldspars.

SAMPLES

We present Pb isotope measurements from individual feldspars of the melt sheet of the ~85-km diameter Manicouagan impact structure within Canadian Shield Precambrian rocks that experienced regional 0.8–1.0 Ga Grenville orogenesis (Spray and Thompson 2011). The structure has a well-developed, crystalline, impact melt sheet (O’Connell-Cooper and Spray, 2011) and a well-exposed melt sheet-target rock contact. The thickness of the melt sheet at

Manicouagan varies from 200 m to over 1000 m, with the thicker portions having undergone chemical differentiation (O'Connell Cooper and Spray 2011). U-Pb zircon ages and plagioclase ^{40}Ar/^{39}Ar ages from the melt sheet agree and indicate a time of impact of 215.4 +/- 0.6 Ma (Jaret et al., 2018; Ramazani et al., 2005).

Individual grains were separated from a single hand sample of the medium-grained quartz monzodiorite collected at Observation Lake (Jaret et al. 2016). This is from an undifferentiated section of the impact melt sheet. This sample is clast-free and contains subhedral to euhdedral (1-3 mm) plagioclase, quartz, clinopyroxene, and locally altered amphibole and orthopyroxene. In some cases, plagioclase has K-feldspar overgrowths (Fig. S6-S7). Pb isotopes values reported here are from the fused beads of samples that were previously measured for ^{40}Ar/^{39}Ar analyses.

Individual plagioclase grains were separated from the Footwall Norite unit along the North Range of the Sudbury Igneous Complex. The norite comprises plagioclase (50-60 vol%) – orthopyroxene (25-30 vol. %) cumulus phases and intercumulus augite + phlogopite (10-25 vol.%) with 1% pyrrhotite and other sulfides in trace quantities.

The sample from the Duluth Complex is from part of the anorthositic suite of the shallow intrusions. This sample is a medium grained gabbroic anorthosite consisting primarily of plagioclase cumulate phases (82-95%). Other phases include granular poikilitic olivine and rare poikilitic clinopyroxene. This sample has been widely used as a zircon standard for high precision U-Pb geochronology and is known to have well behaved U-Pb systematics (Paces and Miller, 1993).

RESULTS

Pb isotope Analyses

Plagioclase from the Manicouagan sheet have a wide range of Pb isotope values: ^{207}Pb/^{204}Pb ranges from 15.305 to 15.667 and ^{206}Pb/^{204}Pb ranges from 16.716 to 19.163 (Fig.1; Table 1). Sudbury norite samples also have a wide range of isotopic values: ^{207}Pb/^{204}Pb ratios are 15.002 to 15.317 and ^{206}Pb/^{204}Pb ratios are 15.863 to 18.082. The Duluth anorthosite, on the other hand, has considerably lower variability: ^{207}Pb/^{204}Pb ratios are 15.429 to 15.556 and ^{206}Pb/^{204}Pb ratios are 17.01 to 17.10 (Table 1).

Pb diffusion modeling

We use the integrated products of time and self-diffusivities in a basaltic melt for a thick, differentiated melt sheet to predict fractional equilibration of isotopic heterogeneities with wavelengths of 3 and 10 cm (Fig. 2, and Supplementary Information). Differences in composition between our quartz-normative melt sheet and the basaltic melt do not contribute significant uncertainty to our model, particularly for Pb in feldspar. Our model predicts that significant fractions of the melt sheet will retain a few percent of Pb isotopic heterogeneity over 1-3 cm. This analysis suggests that at least 1-10% of pre-impact isotopic heterogeneity will persist over centimeter scales for large parts of the melt sheet. The first-principle diffusion model predicts the behavior of isotopic heterogeneity for a bulk composition of Grenville target rocks at Manicouagan cooling asymmetrically over time from high, impact melt-sheet temperatures (>2000 ºC) as expected for a thick melt sheet.

Discussion

The extreme level of Pb heterogeneity has not previously been reported for any igneous rock – impact or endogenic. One possible explanation could be that this represents some mixing with modern Pb. Based on the work by Hemming and Rasbury, 2000 who analyzed Pb in fused monitor standards, we see little evidence of Pb contamination in fused feldspars. Furthermore, our analytical methods used a cleaning and leaching procedure (see supplement) to minimize Pb contamination. A second possible explanation for the range of Pb values could be that U or Th-rich inclusions might introduce radiogenic Pb since the time of crystallization. With a conservative estimate of Pb concentration feldspars (1ppm) the range of thorogenic and uranogenic Pb represented in our data would require a concentration of Th and U in the feldspars near equal to the Th and U in the bulk rock (O'Connell Cooper et al., 2012). Although we cannot entirely rule out the presence of nanoinclusions, we find it unlikely that the majority of Th and U in the whole rock reside as nanoinclusions in the feldspars. We therefore interpret the range of Pb values to be reflecting heterogeneity within the impact melt itself.

There is an assumption in the literature that magmatic rocks are homogeneous with respect to their radiogenic isotopes, (Grieve 1975; Koeberl et al., 2012; Palme et al., 1979). For most planetary studies of impact melts on other planets it has been assumed that a compositionally diverse target will produce homogenous melt sheets (Greenberger et al., 2020; Ryder and Wood, 1977). This is likely a scale issue because individual single grain analyses are uncommon for Pb in feldspars of igneous rocks, especially for plagioclase which generally has low concentrations of Pb (Davidson, 2007). Pb isotope analyses in igneous rocks are typically either whole rock or feldspar separates, and measurements of separates often combine multiple grains. Modern analytical techniques now allow for single grain analysis and there is a growing recognition that some grain-to-grain variability is common even in igneous rocks (Baltybaev et al., 2016). Nevertheless, the measured heterogeneity seen for Pb in feldspars is extremely small.

In addition to Manicouagan, we also considered a second sample from the large, differentiated Sudbury meltsheet. Although the range of values in plagioclase grains is consistent with evolution of Pb in the parent Archean and Paleproterozoic rocks at the time of impact (1.8

Ga), this does not define an isochron nor imply an age or genetic relationship prior to the impact. This data array is similar to the spread of Pb isotope values of detrital feldspars from the Proterozoic Chelmsford Formation in the Sudbury Basin (Hemming et al., 1996). Sudbury is clearly more complex than Manicouagan, likely owing to the larger variation in target rocks represented. Importantly, the range of ^{207}Pb/^{204}Pb values that require an ancient heritage and heterogeneity must reflect incomplete resetting in the melt sheet.

The range of ^{206}Pb/^{204}Pb values for the Duluth gabbro plagioclase is much smaller than the range seen in impact melts (Fig. 3). Similarly, Pb isotope values in granites and migmatites from the Ladoga Region, Finland (Baltybaev et al., 2016) show a narrow range: 0.067 and 0.058. In contrast, the Pb isotope range from Manicouagan impact melt is 2.89, and the range at Sudbury is 2.67. Marian shergottites LAR 12011, RBT04261, and Zagami, show a range of Pb isotope values between 0.94 and 2.0 (Bellucci et al., 2015), more similar to terrestrial melt sheets than to endogenic rocks. Furthermore, our impact melt heterogeneity hypothesis would remove the need for the mixing with a high-μ martian crustal component, as proposed by Bellucci et al. (2015).

The samples measured here are structurally plagioclase and structurally different from shocked plagioclase glass common in martian meteorites. However, this is an appropriate material for comparison of Pb isotopes for the following reasons: i) Pb isotope data from unshocked target rocks and maskelynite from Manicouagan show no evidence of Pb-loss in the maskelynite. ii) data from shock experiments suggest that shock metamorphism does not lead to disturbances in the Pb system (Gaffney et al., 2011); ii) total fusion experiments on plagioclase (Hemming and Rasbury, 2000) indicate that purely thermal melting processes do not affect Pb isotopes.

Our modelling also explains the difference in isotopic resetting across multiple systems. The diffusion modeling indicates that Pb is the least homogenized of all isotope systems and the different degrees of heterogeneity between isotopic systems are consistent with expectations based on the relative self-diffusivities of these elements in the melt sheet (Fig. 2). This explains heterogeneity of Pb isotopes in our samples yet uniform ^{40}Ar/^{39}Ar.

CONCLUSIONS

Individual feldspar grains from single hand samples of impact melt rocks at Manicouagan and Sudbury show a dramatically large range of ^{206}Pb/^{204}Pb values indicating that the melt sheet is not homogeneous with respect to Pb at the mm scale. Individual Pb isotope analyses of feldspars from three martian shergottites (Bellucci et al., 2015) show a large range in ^{206}Pb/^{204}Pb values within one sample, comparable to impact melt rocks rather than endogenic products. Chen and Wasserburg (1986) posed the possibility that some of the shergottites might represent impact melts and so do not require an endogenic igneous source. Our new data Pb isotope data in feldspars from terrestrial impact melt sheets and our Pb diffusion modeling support an impact melt origin for the shergottites.

Such an origin would also resolve the longstanding ‘martian meteorite age paradox.’ If most of martian endogenic igneous activity occurred early in the evolution of the planet (e.g., Hamilton, 2019), subsequent and especially younger igneous rock production is probably due to impact melting. Impact melt sheets should be considered a viable and significant source of rocks with igneous textures on Mars.

Fig 1. Pb isotope values of Manicouagan melt sheet feldspar crystals (error ellipses). Shown for context are single-stage U-Pb growth curves (using Canyon Diablo Pb isotope as an initial) for μ=8 (^{238}U/^{204}Pb) and κ=4 (^{232}Th/^{238}U) and whole-rock values of the regional geologic units including the Paleoproterozoic to Mesoproterozoic Manicouagan Imbricate Zone (MIZ) and the Archean Gagnon Terrane (O’Connell-Cooper et al. 2012). The feldspar data lie along a line that can be explained by Pb evolution from 1.6 Ga to the time of impact at 214 Ma, with target source of MIZ. The feldspar data extend beyond the whole rock MIZ field consistent with a heterogeneous mix of minerals with variable μ within the MIZ.

Fig. 2. % homogenization of isotopic ratios over <10 cm (A) and <3 cm (B) length scales for a melt sheet. Pb,w denotes diffusivity in rhyolite with 1 wt.% water. Current diffusion parameters for Ar does not allow modeling at this scale, but we expect Ar to be even more readily homogenized than Sr. The dashed grey line represents 50% heterogeneity.

Fig. 3: ^{206}Pb/^{204}Pb values from individual feldspar grains in impact melt sheets, martian meteorites, and endogenic terrestrial igneous rocks. The absolute values for each sample depends upon initial ratio, age, and μ, thus the important element here is the range of values rather than absolute ratio. Impact melt sheets show an extreme range within one sample compared to both the felsic and mafic endogenic melts. Three shergottites show a similar heterogeneity within one sample to the melt sheets and are distinct from the endogenic melts.

ACKNOWLEDGMENTS

JGS and LMS acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian Space Agency. We thank Joshua Snape and J.N. Connelly for thoughtful reviews, and Marc Norman for editorial handling.

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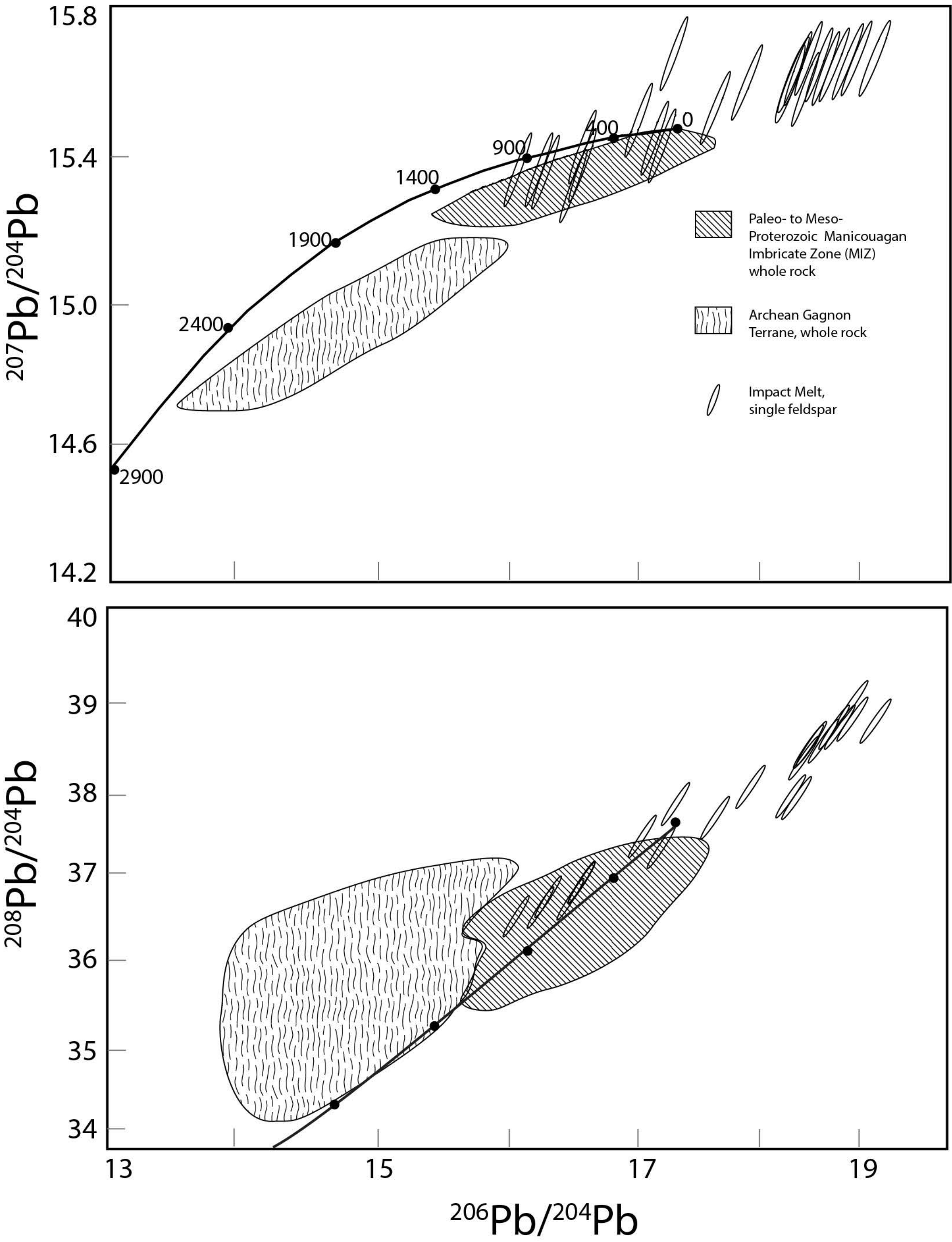
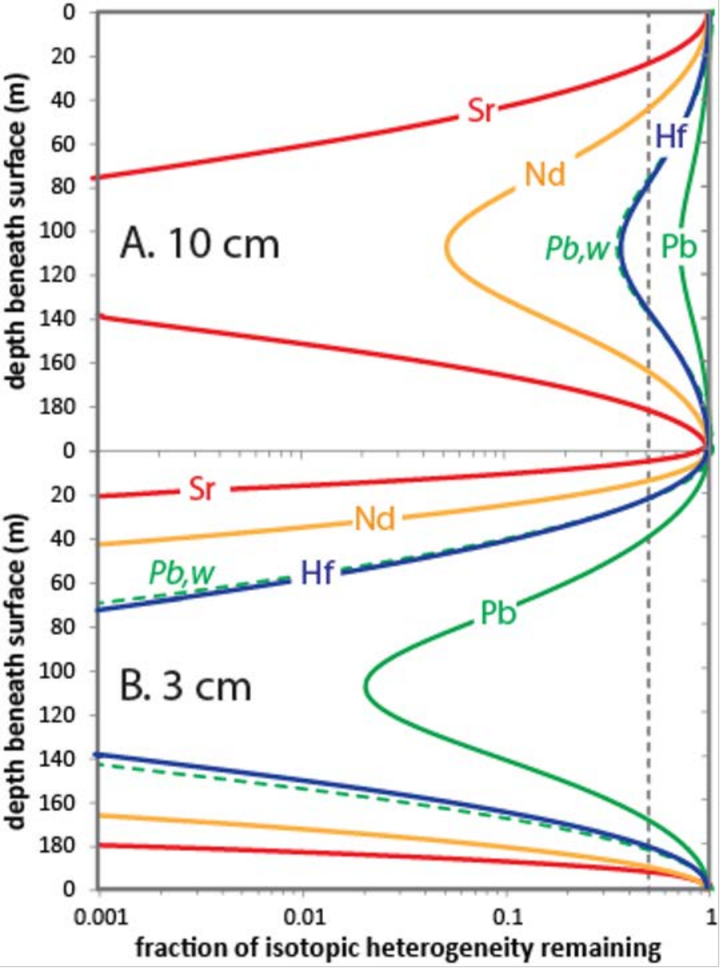
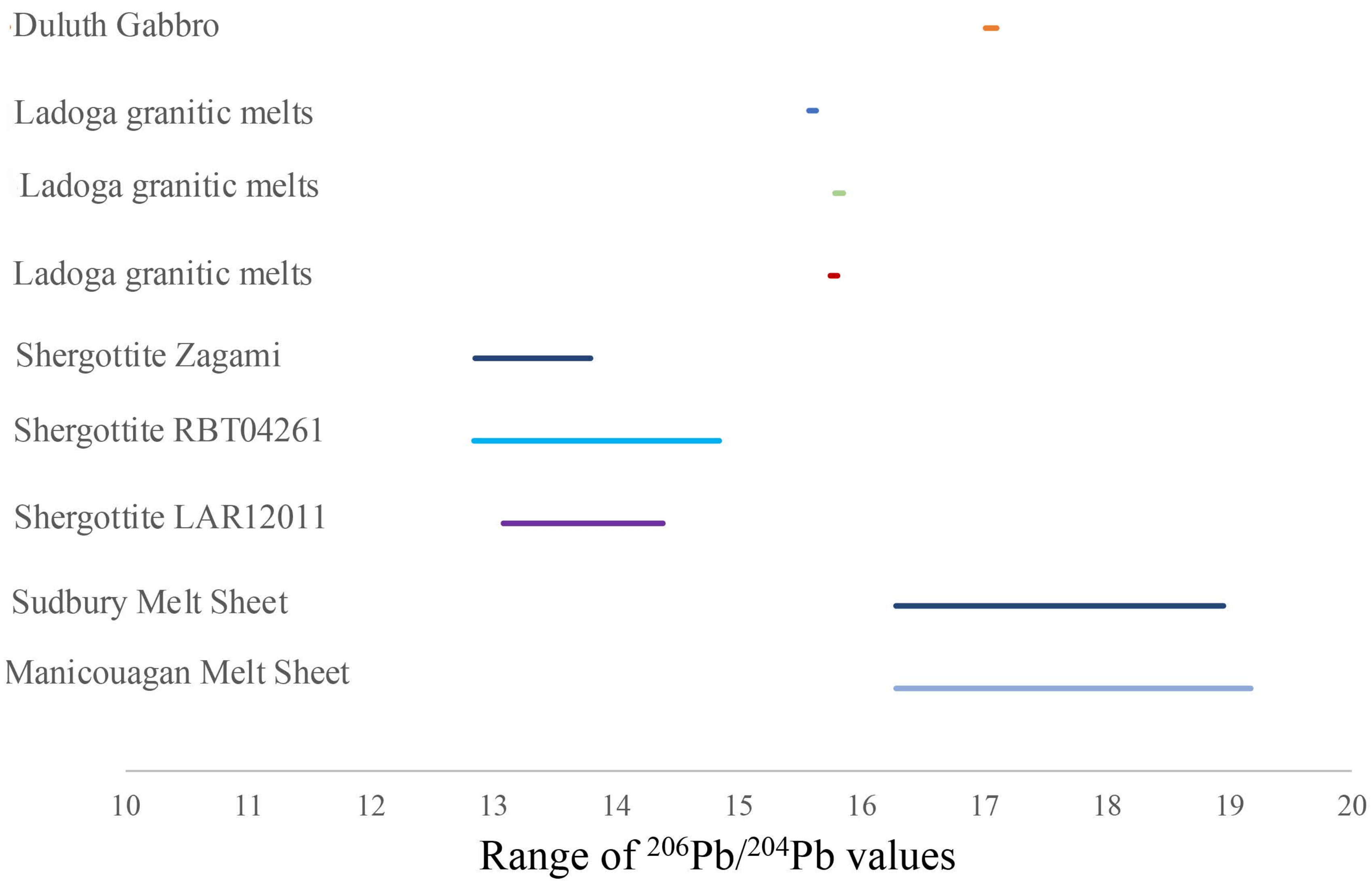

15.8
15.4
15.0
14.6
14.2
^{207}Pb/^{204}Pb
2900
2400
1900
1400
900
400
0
Paleo- to Meso-Proterozoic Manicouagan Imbricate Zone (MIZ) whole rock
Archean Gagnon Terrane, whole rock
Impact Melt, single feldspar
40
39
38
37
36
35
34
^{208}Pb/^{204}Pb
13
15
17
19
^{206}Pb/^{204}Pb



depth beneath surface (m)
0
20
40
60
80
100
120
140
160
180
0
A. 10 cm
Sr
Nd
Hf
Pb,w
Pb
20
40
60
80
100
120
140
160
180
0
B. 3 cm
Sr
Nd
Pb,w
Hf
Pb
0.001
0.01
0.1
1
fraction of isotopic heterogeneity remaining


Duluth Gabbro
Ladoga granitic melts
Ladoga granitic melts
Ladoga granitic melts
Shergottite Zagami
Shergottite RBT04261
Shergottite LAR12011
Sudbury Melt Sheet
Manicouagan Melt Sheet
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Range of ^{206}Pb/^{204}Pb values