

Cahoon, E.B., Streck, M.J., Koppers, A.A.P., and Miggins, D.P., 2020, Reshuffling the Columbia River Basalt chronology—Picture Gorge Basalt, the earliest- and longest-erupting formation: *Geology*, v. 48, <https://doi.org/10.1130/G47122.1>

METHODS

XRF/ICPMS

Major and trace element data was acquired using a Thermo-ARL automated X-ray fluorescence spectrometer (XRF), and an Agilent inductively coupled plasma mass spectrometer (ICP-MS) at the Peter Hooper GeoAnalytical Lab at Washington State University (WSU). For sample preparation, basaltic samples were crushed into chips using the Braun Chipmunk at WSU. Then, weathered surfaces were removed from the chips so that alteration wouldn't affect the results, and then chips were further crushed into a powder in a tungsten carbide crucible. The powder was then combined with dilithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) in a ratio of 2:1, dilithium tetraborate to sample. The sample was fused into a bead in an oven at a temperature of 1000° C. The beads were re-grinded into powder, and one gram of powder was separated in order to make the ICP-MS bead. Two beads per sample were then made, again at 1000° C, one for XRF and one for ICP-MS analysis. The XRF bead was analyzed in the XRF machine, and the ICP-MS bead was dissolved for final analysis. These data provided whole-rock major and trace elemental data to confirm samples were PGB. This determination was further established using a statistical method Principal Component Analysis where each sample was compared to previously identified CRBG main-phase lavas from the dataset of Wolff and Ramos, 2008.

THIN SECTIONS

Samples selected for $^{40}\text{Ar}/^{39}\text{Ar}$ analysis first had thin sections made to reduce choosing samples with extensive interstitial alteration which was identified as glass or abundant oxides. Thin sections were prepared for petrographic study by Spectrum Petrographics in Vancouver, WA and Wagner Petrographics in Lindon, UT. Descriptions of these thin sections augment hand specimen identifications and facilitate interpretation of samples to be utilized for $^{40}\text{Ar}/^{39}\text{Ar}$ dating.

$^{40}\text{Ar}/^{39}\text{Ar}$

Sample Preparation with a focus on acid leaching

Eleven basaltic samples were selected for $^{40}\text{Ar}/^{39}\text{Ar}$ analysis, four of which were analyzed in two separate irradiations. Samples were crushed and sieved to 180-150 μm or 250-180 μm depending on the available amount of material. Samples were then run through a Frantz magnetic separator to separate feldspar. Groundmass fractions were then leached in five separate ultrasonic baths of different aqueous solutions, each for approximately one hour. Solutions, in order, included 1M hydrochloric acid, 6M hydrochloric acid, 1M nitric acid, 3M nitric acid, and milli-Q water to remove adhering glass and clay. Samples were then rinsed three times with milli-Q water and dried overnight.

During our first round of experiments, some groundmass samples displayed significant argon recoil, interpreted to be associated with highly altered material and loosely held atmospheric argon based on alteration of glass to clays (Baksi, 1973). Samples affected by recoil do not overlap in error at their lower and higher temperature steps, preventing an age plateau from being resolved. The lower temperature steps on an inverse isochron are discordant and lie to the left of the isochron, which results in a curved isochron, a trademark of recoil. The higher temperature steps affected by recoil often are highly radiogenic making inverse isochrons

difficult to determine. The potential for recoil is challenging to identify during sample preparation and experiments result in age data that is not geologically meaningful when considered alone. This issue was addressed during the second round of sample preparation by adding a mild (5%) hydrofluoric acid (HF) bath for approximately three minutes to groundmass samples following the full suite of a standard groundmass leach. This additional step removed the altered material responsible for the argon recoil but potentially introduced atmospheric argon. Data resulting from these samples leached in hydrofluoric acid are meaningful, as their age plateaus overlapped with the non-hydrofluoric treated fraction at their intermediate temperature heating steps. And, inverse isochrons of the hydrofluoric leached samples, cut through the apex of the ellipsoids on inverse isochron plots from samples that were plagued by argon recoil. All sample ages included in the manuscript text and associated figures are the dates acquired from sample fractions that underwent this additional leaching step during sample preparation. By combining the most useful temperature steps from both sample experiments, our data is then spaced out along an inverse isochron, increasing the spreading factor. Some, but not all samples, exhibited a decrease in their K/Ca ratios from the non-hydrofluoric leached sample to the hydrofluoric leached sample.

Analytical Methods

Eleven new $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Appendix C) obtained by incremental heating methods using the ARGUS-VI mass spectrometer. Groundmass samples were irradiated for 6 hours (Irradiation 15-OSU-07) in the TRIGA CLICIT nuclear reactor at Oregon State University, along with the FCT sanidine (28.201 ± 0.023 Ma, 1σ) flux monitor (Kuiper et al. 2008). Individual J-values for each sample were calculated by parabolic extrapolation of the measured flux gradient against irradiation height and typically give 0.2-0.3% uncertainties (1σ). The $^{40}\text{Ar}/^{39}\text{Ar}$ incremental

heating age determinations were performed on a multi-collector ARGUS-VI mass spectrometer at Oregon State University that has 5 Faraday collectors (all fitted with 10^{12} Ohm resistors) and 1 ion-counting CuBe electron multiplier (located in a position next to the lowest mass Faraday collector). This allows us to measure simultaneously all argon isotopes, with mass 36 on the multiplier and masses 37 through 40 on the four adjacent Faradays. This configuration provides the advantages of running in a full multi-collector mode while measuring the lowest peak (on mass 36) on the highly sensitive electron multiplier (which has an extremely low dark-noise and a very high peak/noise ratio). Irradiated samples were loaded into Cu-planchettes in an ultra-high vacuum sample chamber and incrementally heated by scanning a defocused 25 W CO₂ laser beam in preset patterns across the sample, in order to release the argon evenly. After heating, reactive gases were cleaned up using an SAES Zr-Al ST101 getter operated at 400°C for ~10 minutes and two SAES Fe-V-Zr ST172 getters operated at 200°C and room temperature, respectively. All ages were calculated using the corrected Steiger and Jäger (1977) decay constant of $5.530 \pm 0.097 \times 10^{-10}$ 1/yr (2 σ) as reported by Min et al. (2000). For all other constants used in the age calculations we refer to Table 2 in Koppers et al. (2003). Incremental heating plateau ages and isochron ages were calculated as weighted means with $1/\sigma^2$ as weighting factor (Taylor 1997) and as YORK2 least-square fits with correlated errors (York 1968) using the ArArCALC v2.6.2 software from Koppers (2002) available from the <http://earthref.org/ArArCALC/> website. ArArCALC is a data reduction program that includes utilities that are executed within Microsoft Excel 2000-XP-2003-2007-2011: curved or linear data regression, blank evolution analysis, age calculation, J-value calculation, air shot calculation, and age recalibration.

Data are reduced for age calculations using the ArArCALC software using the currently accepted ^{40}K decay constant (Steiger and Jäger, 1977). ArArCALC software (Koppers, 2002) was used to reduce the isotopic data and make age calculations. Further details of analytical procedures were described in Duncan and Keller (2004; see also the OSU laboratory website, [http:// www.coas.oregonstate.edu/research /mgg/chronology .html](http://www.coas.oregonstate.edu/research/mgg/chronology.html)).

ArAr Methodology References

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PGB-like chemistry at Dug Bar References

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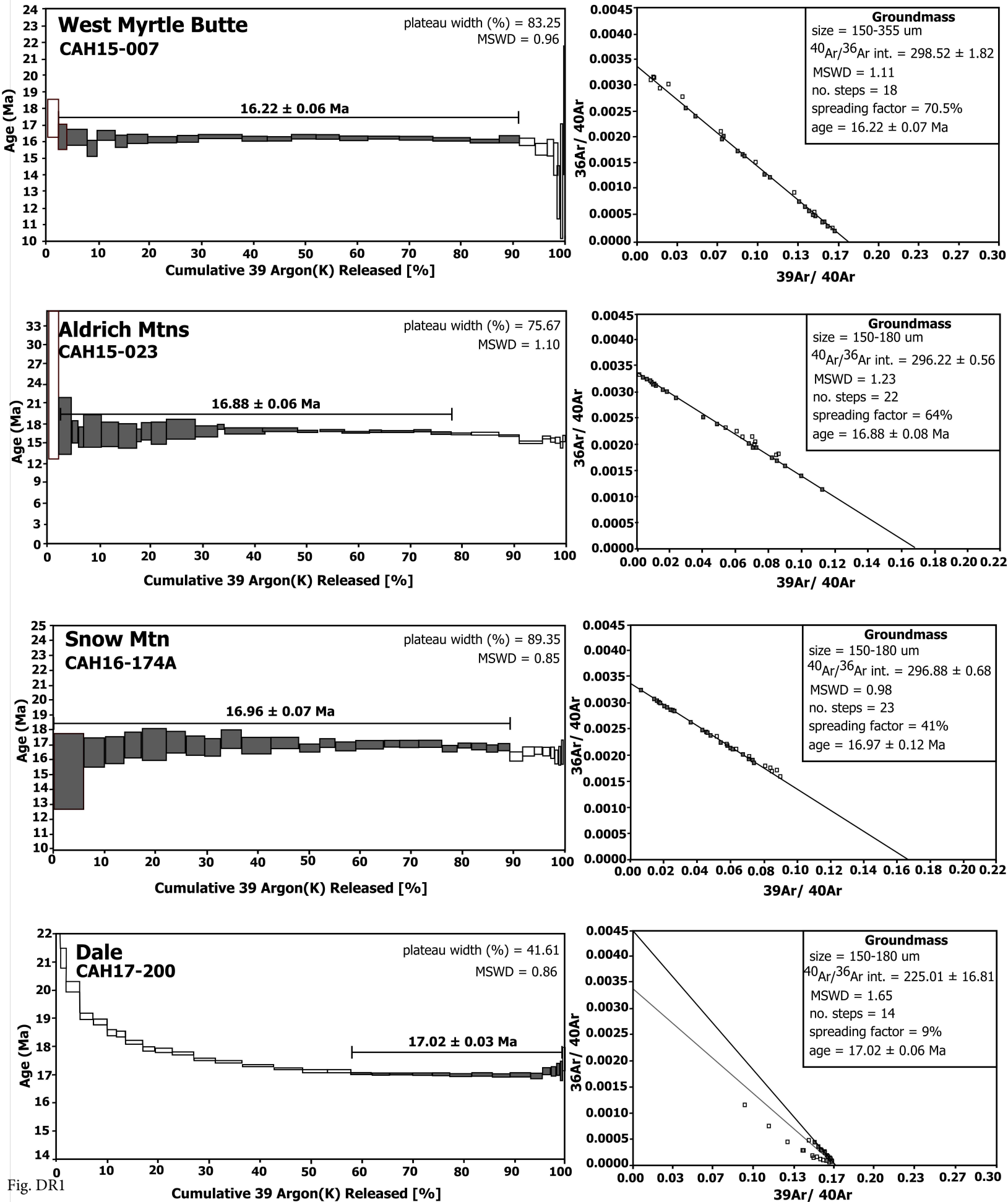
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Supplementary Tables

Sample locations and XRF and ICP-MS data
2020093_Table DR2.xlsx

Summary Table
2020093_Table DR3.xlsx



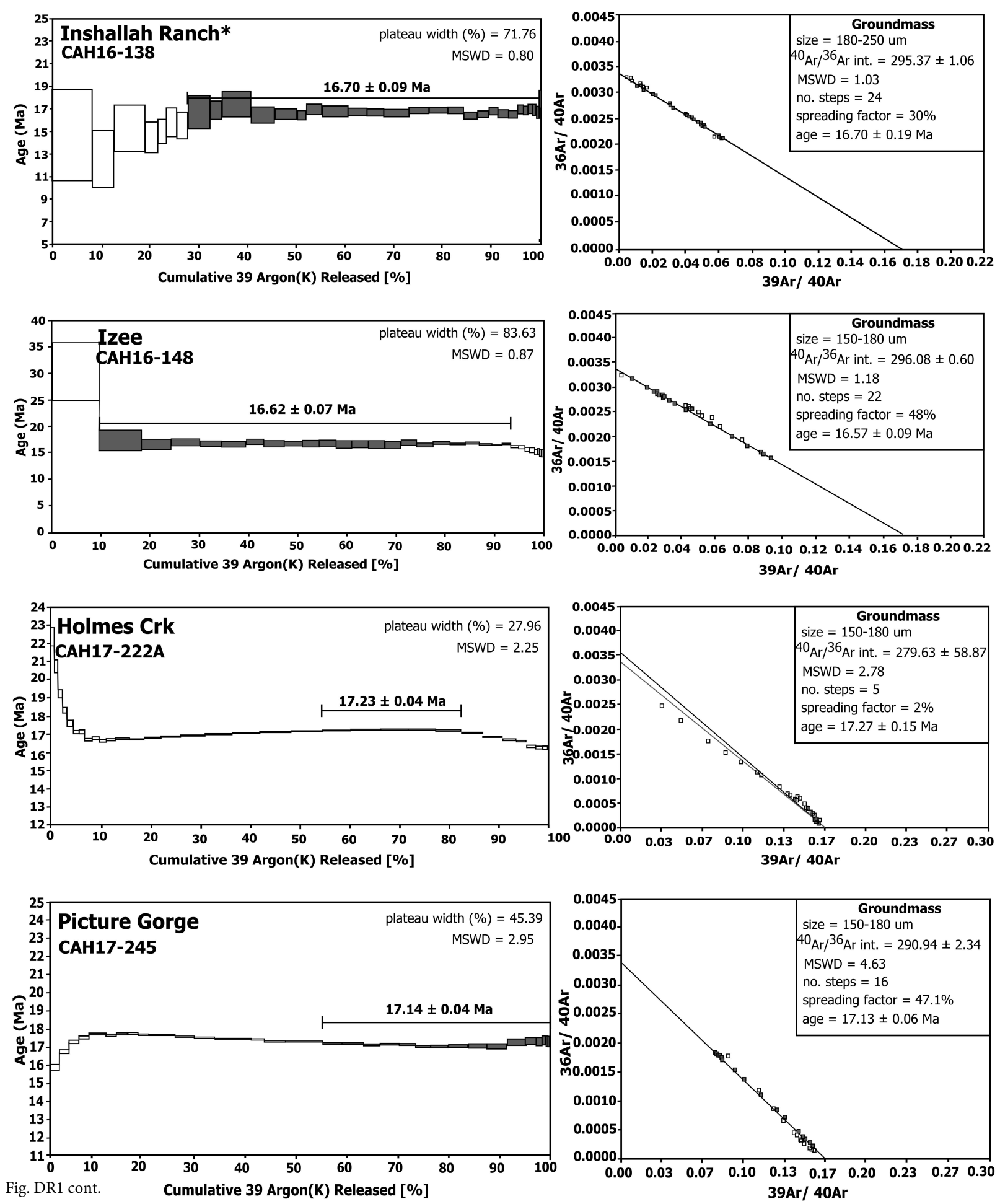


Fig. DR1 cont.

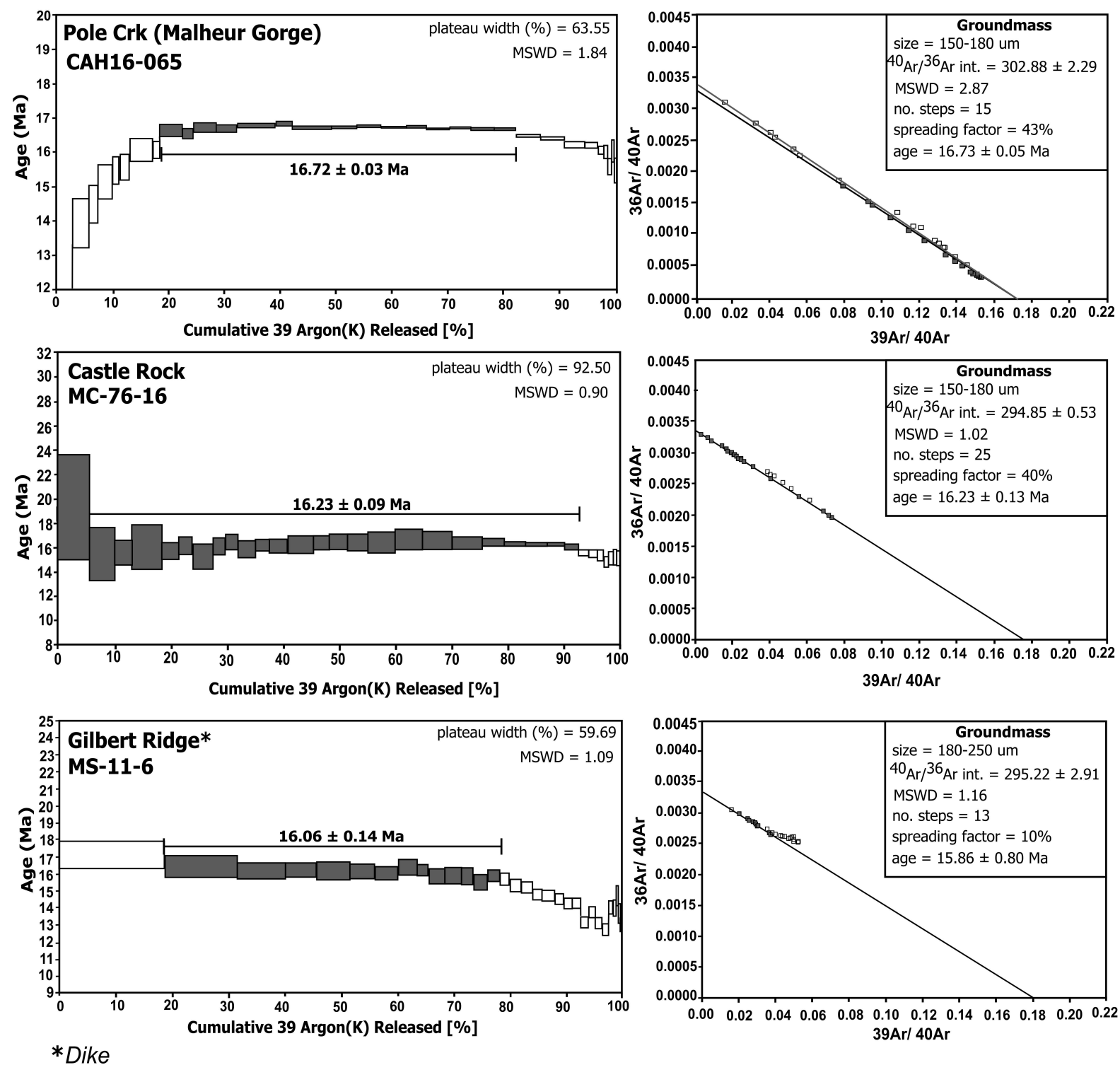
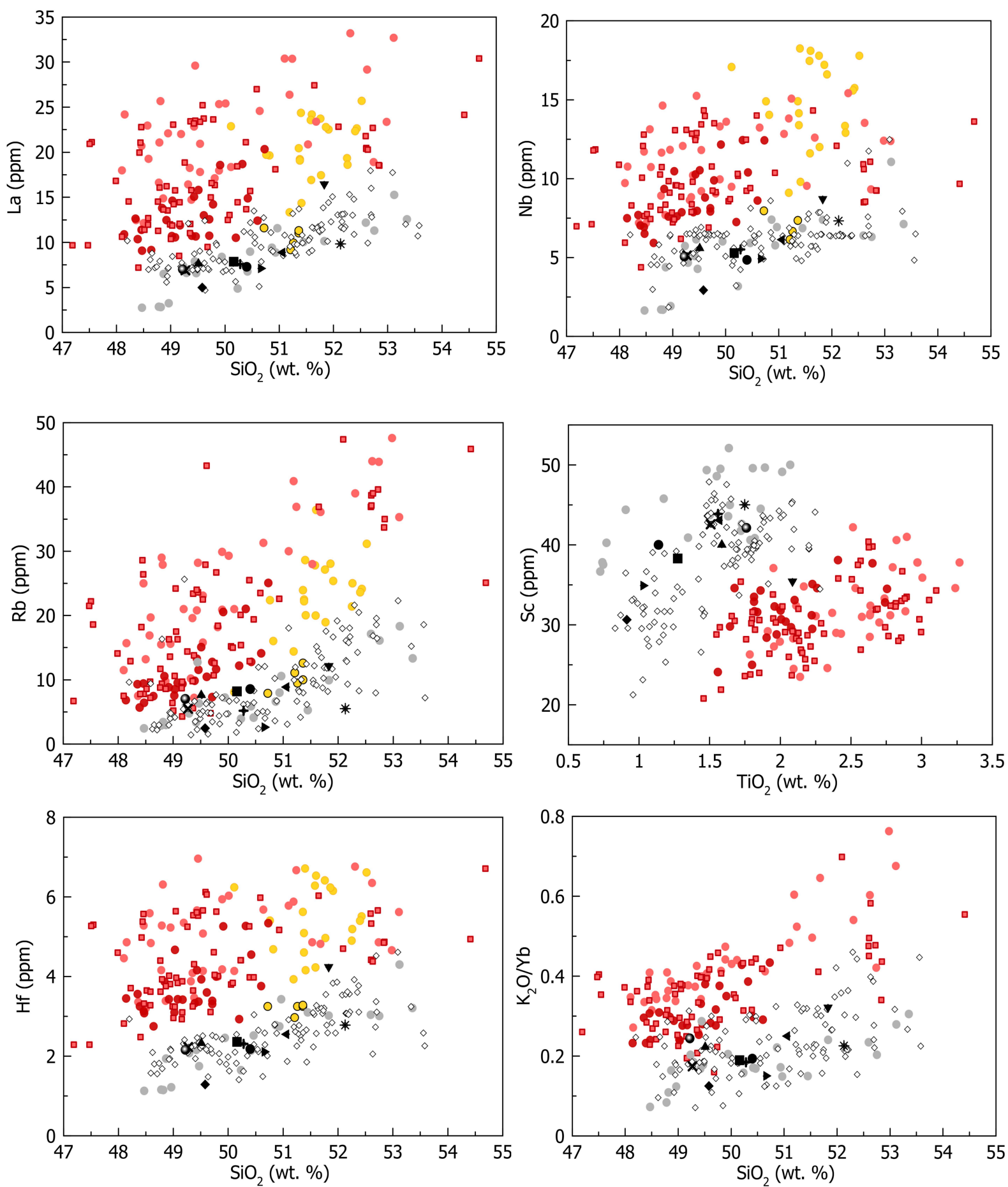


Fig. DR1 cont.



Our dated samples

- GR (MS-11-6)
- ◆ WMB (CAH15-007)
- AM (CAH15-023)
- ✦ SM (CAH16-174A)
- ✖ D (CAH17-200)
- ✱ PG (CAH17-245)
- ▲ CR (MC-76-16)
- ▼ PC (CAH16-065)
- ▶ IR (CAH16-138)
- ◀ I (CAH16-148)
- HC (CAH17-222A)

- Dug Bar samples, Innaha
- Innaha, American Bar (Wolff et al., 2008)
- Upper Steens (Wolff et al., 2008)
- Lower Steens (Wolff et al., 2008)
- Steens, undifferentiated (Moore et al., 2018)
- previous PGB (Wolff et al., 2008)
- ◇ PGB (this study, all samples)

Fig. DR4