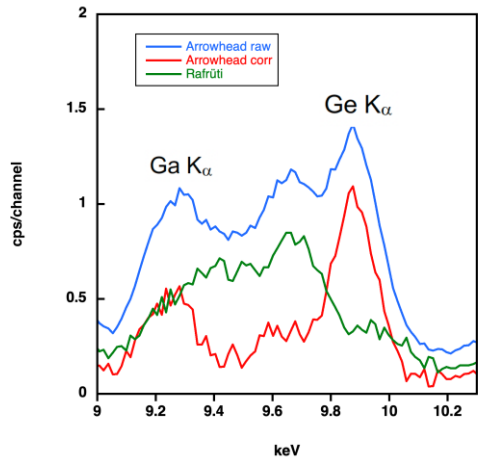
Supporting information S3: Analytical methods

S3.1: X-ray fluorescence (XRF)

Gallium and Germanium were analyzed using the GaKα peak at 9.25 keV and the Ge Kα peak at 9.89 keV. Energy dispersive XRF-spectra of the area of interest are shown in Fig. S3-1 and S3-2. Note a general relatively high intensity between the two peaks of interest for the raw spectrum, possibly due to contribution from ZnKβ (9.57 keV), Au Lα (9.71 keV) and other elements present within the instrument. A spectrum of the Rafrüti meteorite with an almost identical matrix (bulk composition) as the other analyzed iron meteorites, but lacking XRF-detectable Ga and Ge (both < 1 ppm) shows the same high irregular background in the area of interest in the absence of Ga and Ge. A corrected spectrum (corr, Fig. S3-1) of the arrowhead is obtained by subtracting the Rafrüti spectrum from the arrowhead spectrum. In the corrected spectrum, the GaKα and GeKα peaks are much better resolved. This procedure eliminates the high background in the area of interest for samples of metallic Fe-Ni (iron meteorites) and was applied to all spectra used for calibration and quantification of the elements Ga and Ge. Fig S3-2 shows corrected spectra of the Mörigen arrowhead and of several of the iron meteorites used for calibration of Ga and Ge. The relatively high background of the arrowhead sample most likely is due to the presence of contaminating elements including the surficial oxidation.



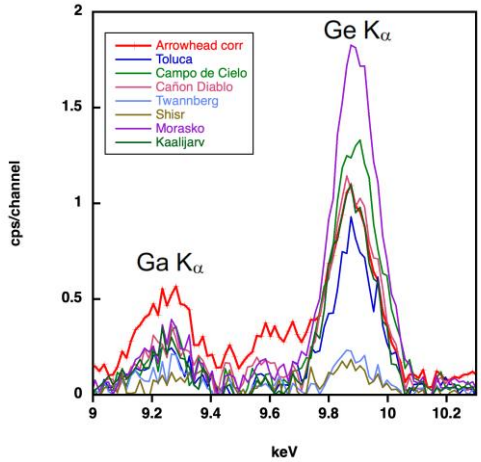


Fig. S3-1 (left) shows X-ray fluorescence spectra for the Mörigen arrowhead (raw and corr, see text) and for the Rafrüti meteorite (Ga and Ge both < 1ppm).
Fig. S3-2 (right) shows X-ray fluorescence spectra (all corrected) of the Mörigen arrowhead and of the iron meteorites used for Ga-Ge-calibration.

For all samples, background measurements for Ga and Ge were taken at 9.04/9.40 keV for Ga and 9.71/10.07 keV for Ge, peak measurements were the background-corrected sums of 15 channels for Ga (9.16 – 9.37 keV) and 21 channels for Ge (9.74 – 10.04 keV). The summed background-corrected cps (counts per second) for Ga and Ge for the meteorites used for calibration are shown in Table S3-T1.

Table S3-T1: XRF calibration data for Ga and Ge

	Ga ppm	Ga cps	Ga calc*	deviation (ppm)	deviation rel%	Ge ppm	Ge cps	Ge calc*	deviation (ppm)	deviation rel%
Toluca	69	1.024	51	-18	-26.5	245	9.150	245	-0.2	-0.1
Campo de Cielo	78	1.768	74	-4	-5.1	392	13.179	359	-33	-8.4
Cañon Diablo	90	2.314	91	1	1.3	330	12.606	343	13	3.9
Shisr 043	19	0.179	24	5	27.1	37	1.718	34	-3	-8.3
Twannberg1	35	0.961	49	14	39.1	49	2.322	51	2	4.2
Morasko	103	2.242	89	-14	-13.7	500	18.127	499	-1	-0.1
Kaalijarv	80	2.479	96	16	20.4	293	11.719	318	25	8.4
	Average difference calc-lit is 19 %					Average error calc-lit is 4.8 %				
Arrowhead		3.711	136±42				9.778	263±78		

*ppm calculated from regression displayed in Fig. S3-2

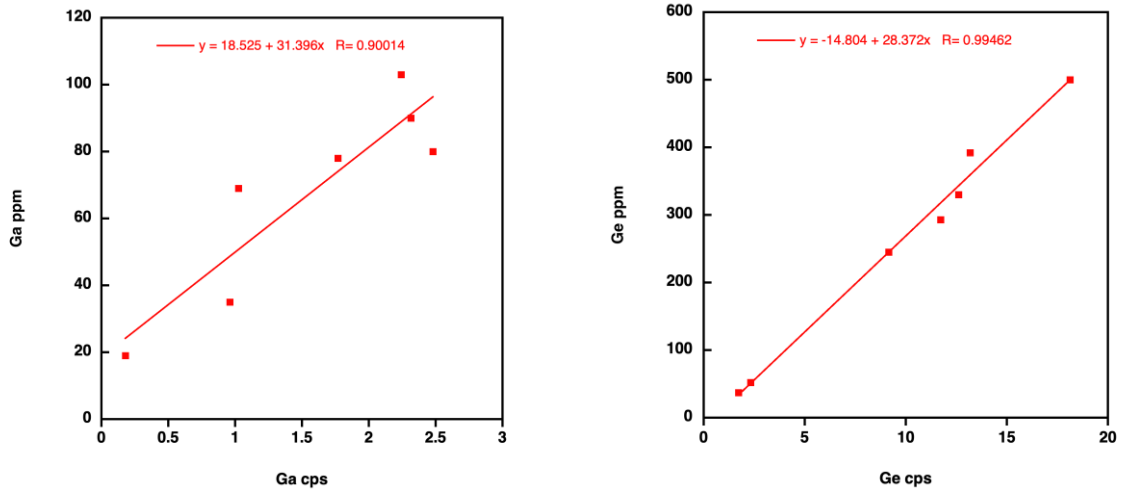


Fig. S3-3 (left) and S3-4 (right) show the correlation of cps with known Ga and Ge concentrations for the iron meteorites used for calibration, resulting in a good correlation for Ga (R=0.90) and a very good correlation for Ge (R= 0.995). The lower precision for Ga is mainly caused by the generally lower concentration range of this element (20-100 ppm), as compared with Ge (37-500 ppm).

The Ga calc and Ge calc values in Table S3-T1 are concentrations calculated from the correlations shown in Figures S3-3 and S3-4, with corresponding deviations from literature values in ppm and relative %. The errors for Ga and Ge reported for the arrowhead corresponds to the standard deviation of individual analyses (table S4). Lower errors (Ga: 136±26 ppm, Ge: 263±13 ppm) would result from the correlation alone. We conservatively use the larger errors because the source of the variations of Ga and Ge in the individual analyses may be due to sample heterogeneity (also present in all the meteorites analyzed as standards), but could also result from oxide coverage and local remobilization of Ga and Ge.

S3.2 : Muon Induced X-ray emission (MIXE)

The MIXE technique, which was developed in the 1980's, has found a recent resurgence in the field of applied physics with increased muon intensities in different large-scale accelerator facilities worldwide. This technique is a non-destructive technique using which the elemental composition of an object can be determined.

Some of its advantages over other non-destructive techniques are: (i) it is equally sensitive to all the elements in the periodic table with atomic number, Z > 1; (ii) the isotopic ratios of the heavier elements (Z > 20) can be determined; (iii) determination of elemental composition from deep inside the sample (up to a few centimeters); (iv) it is a depth-sensitive technique with depth resolutions ranging from 50 to 1000 μm and hence the depth-selective elemental composition can be determined; and (v) there is no detectable radiation damage to the sample.

The MIXE technique utilizes a μ^- beam. This is achieved at PSI using a proton beam of energy 590 MeV at a current of up to 2.4 mA, produced in the High Intensity Proton Accelerator (HIPA) complex (Grillenberger et al., 2021). These high-energy protons upon colliding with a carbon production target leads to the subsequent production of a continuous beam of μ^-, which are then transported to the πE1 beamline. By a proper tuning of a series of electric dipoles, magnetic quadrupoles and slits, along the πE1 beamline, the μ^- at a given muon momentum (p) and momentum distribution/spread (Δp/p) can be selected, with the maximum μ^- rates hitting the meteorite/arrowhead sample. The μ- rates ranged from ~10 kHz at p = 25 MeV/c (Δp/p = 2%) to ~60 kHz at p = 45 MeV/c (Δp/p = 2%). Once the μ^- is captured by the different elements present inside the sample, at a particular penetration depth, a cascade of μ-X rays and γ-rays are produced, which are then detected by the GIANT setup.

The GIANT setup, placed around the sample, consisted of 10 High Purity Germanium (HPGe) detectors. The energy and efficiency calibrations for this setup was done using the standard radioactive sources of ^{60}Co, ^{152}Eu, ^{133}Ba, ^{88}Y , ^{109}Cd, ^{228}Th, ^{57}Co, ^{241}Am, ^{22}Na, ^{210}Pb, and natural background radiation spanning the energy range from ~20 to 2500 keV. In addition, the μ-X rays of natural Pb at ~6000 keV were also used for calibration purposes. Besides the HPGe detectors, there were two scintillator detectors made of polyvinyltoluene (BC-400), which were placed in vacuum, at the end of the πE1 beamline: (i) a muon entrance detector of thickness 200 μm, to count the number of μ^- and measure the arrival time of the μ^- and (ii) a 5 mm thick muon veto detector with a 18 mm (diameter) hole. The vacuum inside the πE1 beamline is separated from the air (as the sample is placed in air) by a 10 μm thick Ti window. The typical μ^- beam spot diameter is ~2cm. Analyses of the two Twannberg meteorites were performed using collimators made of polyethylene (PE), so that a cross-section of ~2.6-2.8 cm was illuminated with the beam. However, the analyses of the Mörigen arrowhead were performed without collimators. All the three samples were placed in an INCA plastic holder, which was mounted on the target frame.

The K_α ($K_{\alpha1}$ and $K_{\alpha2}$) peaks of μ-X rays for (i) Fe (1257 and 1253 keV), (ii) Ni (1432 and 1426 keV), and (iii) Co (1341 and 1336 keV) were identified in all the three samples. The areas under the above-mentioned peaks normalized to the e^-/e^+ annihilation peak (511 keV) were used for the estimation of concentrations (in at.%), assuming pure Fe-Ni-Co-systems. The resulting at.% were converted to wt.%. This approach ignores the poorly known μ-X ray attenuation factors inside the sample environment, but analysis of the unoxidized Twannberg TW1 meteorite (see Table 1) shows that our analyses are very close to the results obtained by other methods.