CHROMIUM ISOTOPE SYSTEMATICS OF THE CHROMITE-BEARING UREILITES LAPAZ ICEFIELD 03587 AND CUMULUS HILLS 04048.

P. M. Kruttasch[1], A. Anand[1] and K. Mezger[1], [1]Institut für Geologie, Universität Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland (pascal.kruttasch@geo.unibe.ch).

Introduction: Ureilites are the second largest group of achondrites with currently more than 600 members, and are primarily characterized as highly depleted mantle restites (having lost a S-rich metal melt and a feldspar-rich magma) with a relatively high carbon content of ~3 wt.%. Their mineral composition is dominantly olivine and pyroxene with interstitial carbon phases, sulfide and metal. A characteristic feature of all ureilites are the reduction rims with tiny Fe-metal inclusions around olivine cores. These rims exhibit reverse zonation to high Mg# and are attributed to a smelting process [e.g. 1, 2]. Within a ureilite sample olivine cores have homogeneous Fo contents, but cover a large range of Fo contents from Fo75 to nearly pure Fo in all known ureilites. Heterogeneities exist in the bulk chemical composition (e.g. FeO/MnO, FeO/MgO) and also in O isotopes that correlate with Mg# [e.g. 3, 4]. The heterogeneities remain enigmatic and are unexpected since all ureilites are thought to represent mantle restites from the same parent body. The similar cooling history and the same statistical Mg# abundances in monomict and polymict ureilites may suggest that all known ureilites formed on a single parent body - the ureilite parent body (UPB) [e.g. 4, 5], with a size of up to 690 km [6] or a Mars-sized body [7]. The presence of isotope heterogeneities in ^{13}C, ^{54}Cr and variable REE patterns of ureilites led to the suggestion that the UPB formed by accretion of distinct precursor materials from at least two reservoirs that were not fully homogenized on the final UPB [8, 9, 10].

The timing of the UPB evolution within their reservoir is still subject of ongoing debate and is discussed in context of new Cr isotope data of acid-leachates from ureilites (LAP 03587 and CMS 04048) with chromite + Ca-rich pyroxene, formed in symplectic inclusions in olivine by subsolidus exsolution [11, 12]. Chromite grains in LAP 03587 occur also in veins along with metal and sulfide that were ascribed to areas of secondary reduction [12].

Chromium isotopes were analyzed in acid-leachates of these samples to (1) constrain the ^{54}Cr isotopic composition to characterize the isotopic reservoir, since ^{54}Cr was heterogeneously distributed in the early solar system and to (2) determine the timing of the last isotopic closure of the short-lived ^{53}Mn-^{53}Cr system in different mineral phases.

Methods: Whole rock fragments of LAP 03587 and CMS 04048 were crushed in an agate mortar and separated into two fractions for sequential digestion and WR analyses, respectively. For sequential digestion (slightly modified after [13]), WR powders were treated with acids of increasing strengths: (1) 0.5 M acetic acid for 30 min, (2) 0.2 M HNO$_3$ for 30 min, (3) 1 M HCl for 1 h, (4) 6 M HCl for 48 h, and (5) conc. HNO$_3$+HF for 42 h on a hotplate at 140 °C. Step 1 to 4 were ultrasonicated at room temperature. Residual chromite grains in step 5 were separated and were digested along with WR powders in conc. HNO$_3$+HF for ca. 60 h using Parr® bombs at 190°C. Each analyte was split into two aliquots to determine (1) element concentrations of Cr, Mn and Fe, and (2) Cr isotope ratios. The second aliquot was purified by three-step cation-anion exchange chromatography as described in [14, 15] and were loaded onto outgassed Re-filaments with activators. Chromium isotopes in all samples were measured by sample-standard bracketing along with the terrestrial standard NIST SRM 979 on a Thermal Ionization Mass Spectrometer (TIMS) at the University of Bern. The ^{53}Cr/^{52}Cr and ^{54}Cr/^{52}Cr ratios were corrected for instrumental mass fractionation and are reported in ε-values.

Results: The Fe/Cr ratios in all analytes are relatively low and do not correlate with ε^{53}Cr and ε^{54}Cr. Hence, spallogenic effects on Cr are negligible and thus the measured isotope compositions do not require a correction for cosmogenic contributions [16]. Leachates L6 in LAP 03587 and CMS 04048 are almost pure chromite with Mn/Cr ratios of 0.010±0.001 and 0.017±0.001, respectively, while earlier leachates are essentially silicates, metal and sulfides. All leachates of each sample have a nearly homogeneous ε^{54}Cr composition, except for L6, which has a more negative ε^{54}Cr that, in case of LAP 03587, is clearly distinct from all other leachates. The ^{54}Cr analyses confirm that LAP 03587 and CMS 04048 are ureilites and plot in the non-carbonaceous chondrite (NC) reservoir [e.g. 17, 18]. Individual leachates from both samples are heterogeneous in ε^{53}Cr and correlate with Mn/Cr ratios. The WR analyses show a good agreement of ε^{54}Cr and ε^{53}Cr with weighted means of leachates from the same sample.

Discussion: As documented in [11, 12], symplectic chromites + Ca-rich pyroxene inclusions in olivine in LAP 03587 and CMS 04048 formed by subsolidus exsolution, while chromite grains in veins in LAP

03587 were associated with areas of secondary reduction. Leachate 6 of LAP 03587 and CMS 04048 represent the Cr isotopic signature of chromites in these samples and have lower values in $\varepsilon^{54}Cr$ relative to other leachates (more extreme in LAP 03587 than in CMS 04048), suggesting isotopic disequilibrium between chromite and other mineral phases. This is unexpected since chromites were formed by subsolidus exsolution from olivine. Since the chromite grains in LAP 03587 also occur in veins, the Cr isotopic signature could be a mixture of the two observed chromite species, possibly indicating that the chromites in veins reflect an even more negative $\varepsilon^{54}Cr$ signature. Because chromite grains in veins are associated with secondary reduction, the $\varepsilon^{54}Cr$ signature may have been inherited from a different source that triggered impact-related reduction on the parent body. The $\varepsilon^{54}Cr$ signature in LAP 03587 L6 is the lowest determined in all known ureilites and is linked, along with all analytes from LAP 03587 and CMS 04048, to the NC reservoir and is potentially a spatial endmember that formed in an extreme position in the early solar system.
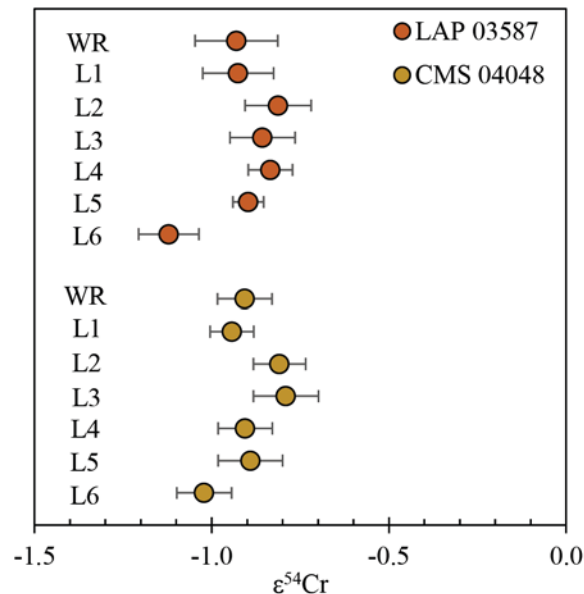

Fig. 1. $\varepsilon^{54}Cr$ isotopic composition of individual leachates of LAP 03587 and CMS 04048. L1-L6 refers to leachates with increasing strength (see Method).

Disequilibrium of Cr in mineral phases, as indicated by isotope heterogeneities in ^{54}Cr, must be considered when interpreting isochrons, not only for ureilite leachates, but also for WR. Mn-Cr model ages of chromites date the last isotopic close of the ^{53}Mn-^{53}Cr system and are modeled for LAP 03587 L6, CMS 04048 L6 and chromite in NWA 766 from [13] in Fig. 2. Mn-Cr model ages of chromite in NWA 766 possibly date the Cr isotopic closure of primary chromites

[11, 12], whereas chromites in LAP 03587 and CMS 04048, which have slightly younger model ages, are secondary and formed in the aftermath of a catastrophic disruption of the parent body. The Mn-Cr model ages of LAP 03587 L6 and CMS 04048 L6 are consistent with a proposed age of ~5 Ma after CAI for the breakup of the UPB [19, 20].
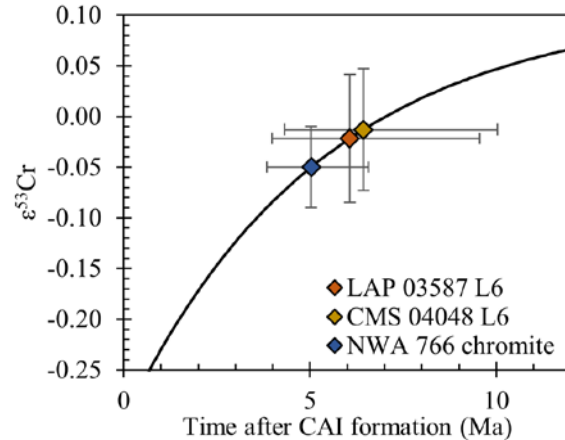

Fig. 2. Mn-Cr model ages of chromite fractions from LAP 03587, CMS 04048 and NWA 766 from [13] on a $\varepsilon^{53}Cr$ evolution curve modeled using solar system initials and Eq. 1 reported in [15].

References: [1] Warren P. H. and Rubin A. E. (2010) *GCA, 74,* 5109-5133. [2] Goodrich C. A. et al. (2007) *GCA, 71,* 2876-2895. [3] Sanders I. S. et al. (2017) *Meteorit. Planet. Sci., 52(4),* 690-708. [4] Downes H. et al. (2008) *GCA, 72,* 4825-4844. [5] Herrin J. S. et al. (2010) *Meteorit. Planet. Sci., 45(10-11),* 1789-1803. [6] Warren P. H. (2012) *Meteorit. Planet. Sci., 47(2),* 209-227. [7] Nabiei F. et al. (2018) *Nat. Comm., 9,* 1327. [8] Barrat J.-A. et al. (2016) *GCA, 294,* 163-178. [9] Zhu K. et al. (2020) *ApJ, 888,* 126. [10] Barrat J.-A. et al. (2017) *EPSL, 478,* 143-149. [11] Goodrich C. A. et al. (2013) *GCA, 122,* 280-305. [12] Goodrich C. A. et al. (2014) *GCA, 135,* 126-169. [13] Yamakawa A. et al. (2010) *ApJ, 720,* 150-154. [14] Anand A. et al. (2021a) *GCA, 307,* 281-301. [15] Anand A. et al. (2021b) *Geochem. Persp. Let. 20,* 6–10. [16] Liu J. et al. (2019) *GCA, 251,* 73-86. [17] Warren P. H. (2011) *GCA, 75,* 6912-6926. [18] Warren P. H. (2011) *EPSL, 311,* 93-100. [19] Goodrich C. A. et al. (2010) *EPSL, 295,* 531-540. [20] Goodrich C. A. et al. (2015) *Meteorit. Planet. Sci., 50(4),* 782-809.