

THE ISOTOPE GEOCHEMISTRY OF Zn and Cr IN UREILITES. Frederic Moynier^{1, 2}, Qing-zhu Yin¹, Philippe Gillet³, Pierre Beck⁴, Tristan Ferroir³, Jean-Alix Barrat⁵ and Francis Albarede³. ¹Department of Geology, University of California Davis ²(present address) Department of Earth and Planetary Sciences, Washington University in St Louis ³Laboratoire de Sciences de la Terre, Ecole normale supérieure de Lyon, France ⁴Laboratoire de Planetologie, Université Joseph Fourier, Grenoble, France ⁵Institut d'étude de la mer, Université de Bretagne occidentale, Brest, France. (moynier@geology.ucdavis.edu).

Introduction: The advent of the high precision, multiple-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) has opened the door for the precise measurement of “non-traditional” stable isotopes of alkali earth and transition metals [1]. The ‘new’ stable isotope systems, notably Mg [2], Fe [3-5], Cu [6], Zn [7], Ni [8] and Cr [9] are providing new insights for the early solar nebular and planetary differentiation processes. Ureilites are differentiated meteorites which consist of olivines and pyroxenes plus minor carbons, metals and sulphides. The ureilites have an igneous origin, either by partial melting or they are cumulate from magma. However ureilites are unique in that they are the only achondrites to plot on a mass-independent fractionation line with a slope 1 in the 3 oxygen isotope plot [10], similar to carbonaceous chondrites and their refractory components. This suggests a very strong genetic link between ureilites and carbonaceous chondrites; i.e. ureilites must have been differentiated from a carbonaceous chondrite parent body, and so some nebular signature remains in ureilites. This contrast between nebular and igneous origins is still not well understood. Zn is a moderately volatile element, its isotopes are strongly fractionated during volatilization from impact processes [11, 12] but are hardly fractionated during igneous processes [13]; in addition Zn has unique isotopic compositions in chondrites which can be used as a tracer for genetic links between meteorites [7]. Cr isotopes are not fractionated by igneous processes, either [14], but is probably fractionated during metal/silicate fractionation [15] and nebular processes [9]. Here we report Zn and Cr stable isotopes in 9 ureilites recently discovered in the Sahara desert, North West Africa.

Samples and analytical methods: We analyzed the Zn isotopic composition in the whole-rock samples of 9 ureilites at both ENS-Lyon and UC-Davis and the Cr isotopic composition of 5 ureilites at UC-Davis. These samples have been recently discovered in the Sahara desert, North West Africa. Roughly 150 mg of powders have been dissolved in a mixture of HNO₃/HF under pressure. Cr and Zn have been purified on different aliquots from the same dissolution. The chemical purification of the Cr is an adapted from [16-20]. First, Cr was separated from the major elements with 1N HCl by elution through cationic-exchange resin. This step was repeated two

times to completely eliminate any traces of major elements. Cr was further purified of other elements, in particular Ti and V, on cation-exchange resin with HNO₃/HF/HCl. The Cr yield was checked and found to be better than 90%. The total blank of the chemistry procedure is <1ng, which is negligible, given the size of the samples and Cr concentration in the samples. The absence of isotopic fractionation induced by the chemical purification has been double checked by 1) processing the standard through the column and 2) running one sample several times through the columns. In both cases, no difference in the measured isotopic ratio has been observed.

Zn was purified by anion-exchange chromatography using a procedure adapted from Moynier et al. [11]. Briefly, samples were loaded in 1.5N HBr on a 0.25 ml AG-1x8 (200-400 mesh) chromatographic columns and Zn was extracted in 0.5N HNO₃. The process was repeated on a 100 µl column to further purify Zn.

Cr and Zn isotopic composition were measured on a Nu plasma HR MC-ICP-MS at the University of California Davis (both Cr and Zn) and the Ecole normale supérieure de Lyon (Zn). The Zn isotopic composition is analyzed as described in [11]. For Cr, the samples were introduced to the mass spectrometer via a DSN-100 desolvating nebulizer. The mass spectrometer was operated in pseudo-high-resolution mode, which allows interferences, notably ⁴⁰Ar¹²C at mass 52 and ⁴⁰Ar¹³C at mass 53, to be resolved. A total of 40 ratios in 2 blocks of 20 ratios each with an integration time of 10 sec/scan, were measured for each sample. The instrumental mass bias has been controlled by bracketing each sample with standard. Isobaric interferences with Ti and V were below the detection limit of the mass spectrometer. The elemental abundances of Zn have been measured by ICP-MS and the abundance of Cr by ICP-AES in Brest.

Results and discussions: Isotope ratios are expressed in δ permil units with respect to the standard SRM 979 for Cr and the standard JMC 0749 L for Zn. The full range is about 0.6 permil for δ^{66/64}Zn and 0.3 permil for δ^{50/52}Cr/(-2) (Fig. 1, 2, 3). δ^{66/64}Zn is strongly correlated with Zn concentration (Fig. 2). The samples with low Zn concentrations are isotopically more fractionated than samples with high Zn concentrations and show excess of heavy isotopes of up to 1 permil for ⁶⁶Zn/⁶⁴Zn, which is a rather

large of fractionation for Zn in comparison to terrestrial as well as meteorite samples.

$\delta^{50/52}\text{Cr}/(-2)$ is weakly correlated with Cr concentration (Fig.3) as well as with $\delta^{66/64}\text{Zn}$ (Fig. 1). However the three samples with the lowest concentrations are isotopically heavier than the two samples with the highest concentrations.

These negative correlations may reflect isotopic fractionations during volatile loss on the ureilites parent bodies.

Shocks from impacts are known to fractionated Zn isotopes on the Moon and on Earth [11, 12]. Ureilites are one of the achondrite groups the most shocked by impact processes, therefore, heating and vaporization due to shocks is a probable mechanism for the origin of the loss of Zn and Cr among the samples investigated. The shock grades for our samples still need to be determined, thus we can not conclude with certainty on the origin of the vaporization.

The magnitude of the observed fractionation is much smaller than that predicted by a simple Rayleigh distillation. A more realistic dynamic model of isotopic fractionation during shocks from impacts needs to be developed to explain the data.

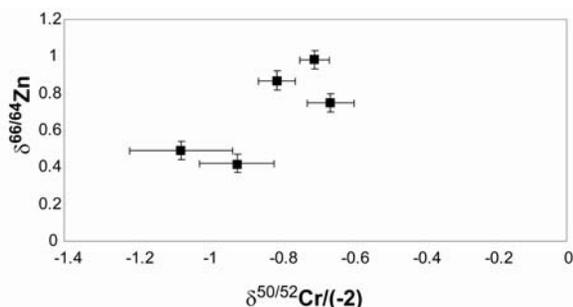


Fig.1: $\delta^{66/64}\text{Zn}$ vs $\delta^{50/52}\text{Cr}/(-2)$ in ureilites. The error bar is $2\sigma_{\text{mean}}$ based on repeated measurements.

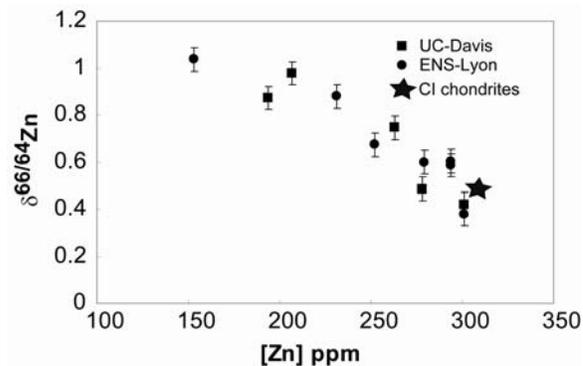


Fig.2: $\delta^{66/64}\text{Zn}$ vs $[\text{Zn}]$ in ureilites. The negative correlation indicates that the isotopic fractionation may be due to vaporization. The values for CI are from Luck, et al. [7] for the isotope composition and Anders & Grevesse [21] for the elemental abundance.

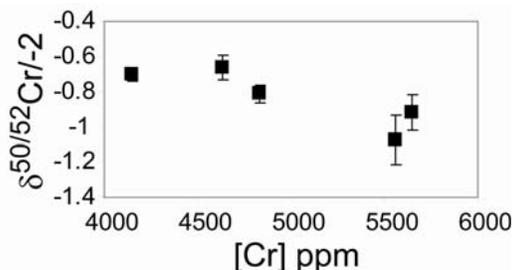


Fig.3: $\delta^{50/52}\text{Cr}/(-2)$ vs $[\text{Cr}]$ in ureilites.

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References:[1] C.M. Johnson et al. (2004) Rev.Min.Geo. 55. [2] M. Norman et al, (2004) LPSC A1447. [3] F. Poitrasson et al. (2004) EPSL 223 253-266. [4] S. Weyer et al. (2005) EPSL 240 251-264. [5] X.K. Zhu et al. (2001) Nature 412 311-313. [6] J.M. Luck et al. (2003) GCA 67 143-151. [7] J.M. Luck et al. (2005) GCA 69 5351-5363. [8] F. Moynier et al (2007) GCA 71 4365-4379. [9] F. Moynier et al. (2007) LPSC 38 A1406. [10] R.N. Clayton et al. (1996) GCA 60 1999-2017. [11] F. Moynier et al. (2006) GCA 70 6103-6117 [12] F. Albarede et al. (2007) MAPS 42 A11. [13] D. Ben Othman et al. (2006) GCA 70 A46. [14] R. Schoenberg et al. (submitted) CG. [15] F. Moynier et al. (in prep). [16] J.L. Birck et al. (1984) GRL 12 745-748. [17] G.W. Lugmair and A. Shokulyukov. (1998) GCA 62 2863-2886. [18] D.P. Glavin, et al. (2004) MAPS 39 693-700. [19] L. Nyquist et al. (2001) MAPS 36 911-938. [20] A. Trinquier et al. (2006) ApJ 655 1179-1185 [21] E. Anders and N. Grevesse (1989) GCA 53 197-214.