

**HIGH-PRECISION OXYGEN THREE-ISOTOPE SIMS ANALYSES OF ORDOVICIAN EXTRATERRESTRIAL CHROMITE GRAINS FROM SWEDEN AND CHINA: DEBRIS OF THE L CHONDRITE PARENT ASTEROID BREAKUP** P. R. Heck<sup>1</sup>, T. Ushikubo<sup>1</sup>, B. Schmitz<sup>2</sup>, N. T. Kita<sup>1</sup>, M. J. Spicuzza<sup>1</sup> and J. W. Valley<sup>1</sup>, <sup>1</sup>Wisc-SIMS, Department of Geology and Geophysics, University of Wisconsin, 1215 W. Dayton St., Madison, WI 53706, USA, prheck@gmail.com, <sup>2</sup>Department of Geology, University of Lund, Sölvegatan 12, SE-22362 Lund, Sweden.

**Introduction:** The L chondrite parent body breakup event manifests itself in present-day meteorites more distinctly than any other asteroid breakup event in younger solar system history. Its most distinctive features are recorded in most modern L chondrite falls, and include a highly prominent Ar gas-retention age cluster at ~0.5 Ga and extensive signs of shock [1-3]. Fossil meteorites and sediment-dispersed extraterrestrial chromite (SEC) grains were found in mid-Ordovician sediments at different locations in Sweden by B. Schmitz and coworkers in high abundances (~100× higher than the background) [4-7]. The sediment ages of ~470 Ma [8] coincide with the refined age of the breakup event 470±6 Ma [9]. Abundant SEC grains in contemporaneous conodont-dated sediments from China were reported [10]. Chromite is the only meteoritic mineral that survived sediment diagenesis. EDS analyses of the extraterrestrial chromites (ECs) yield minor element concentrations consistent with concentrations in chromites from modern L and LL chondrites, however, some terrestrial alteration was suspected [4-7,10]. These observations led to the hypothesis that the ECs were part of direct fragments of the breakup event [5-7,10]. This is supported by very short cosmic-ray exposure ages (0.1 – 1 Myrs) of nine fossil meteorites from Sweden which correlate inversely with sediment ages, and therefore originated from one source and a single event [11]. Also, size measurements of pseudomorphed chondrules, which are preserved in some fossil meteorites, compare best with chondrule sizes of modern L chondrites [12].

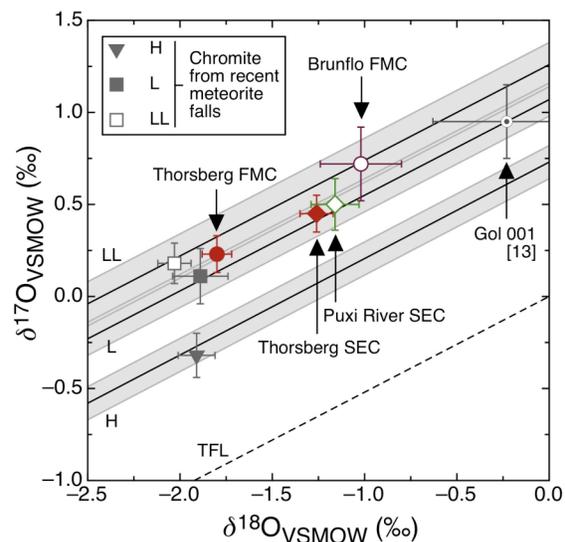
A bulk O isotopic analysis of chromites from the well-characterized fossil meteorite Gol 001 (Österplana 029) from Thorsberg was reported to be consistent with recent L and LL chondrites [13]. However, a bulk analysis requires about 100 grains and would mix heterogeneous samples. Bulk analysis cannot be applied to many other chromites from fossil meteorites (FMC) nor to SECs, mostly fragments of fossil micrometeorites [14,15], because grains are too small and each SEC grain might have a different origin.

Here, we present high-precision O isotope SIMS analyses of FMCs and SECs, which require only single grains to achieve the same accuracy and precision reported by [13]. One major advantage of SIMS is to analyze individual chromite grains to test if they de-

rived from single sources while avoiding diagenetic alteration or phases. The goal of this study is to test the hypothesis that the chromites from fossil meteorites and micrometeorites from Ordovician sediments deposited 0.1–5 Myrs after the L chondrite parent body breakup are related to this event.

**Samples:** We studied 18 chromite grains from 9 fossil meteorites from the Thorsberg quarry in southern Sweden, 4 grains of the fossil meteorite Brunflo from the Gärde quarry in central Sweden, 19 SEC grains from the Golvsten and Sextummen beds at Thorsberg, and 9 SEC grains from the Y9 and P6a beds at Puxi River in south central China. The Chinese Y9 and P6a beds were correlated earlier to the same conodont zone as the Sextummen bed at Thorsberg by Schmitz et al. [10]. Extracted chromites were mounted in epoxy together with the newly established chromite standard UWCr-2.

**Analytical Methods:** We used the Wisc-SIMS Cameca IMS-1280 with three Faraday Cups in multi-collection mode [17,18]. A primary Cs<sup>+</sup> beam was set to a spot size of 10×15 μm with current of ~5 nA. The



**Figure 1.** Weighted averages of O isotopic data of chromite from fossil meteorites (FMC) and sediments (SEC) from Thorsberg (southern Sweden), Brunflo FMC (central Sweden), Puxi River SEC (China) and chromite from modern H, L, and LL chondrites. Errors are based on 2SD errors of individual analyses. Mass-dependent fractionation lines are drawn for terrestrial (TFL), and for average compositions of group H, L and LL chondrites [16] with their standard deviations (shaded boxes).

[ $^{16}\text{O}^1\text{H}$ ] signal was recorded after each analysis to correct for its tailing ( $\sim 20$  ppm) interference on  $^{17}\text{O}^-$ ; data with large OH corrections  $>0.5\%$  were rejected (uncertainty  $< 0.1\%$ ). We used chromite and spinel ( $\text{MgAl}_2\text{O}_4$ ) standards to correct for instrument drift and bias, and matrix effects. In order to improve the precision of  $\Delta^{17}\text{O}$  ( $=\delta^{17}\text{O}-0.52\times\delta^{18}\text{O}$ ) from single spot analyses, each spot was analyzed twice. Raw  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values in the second sequence in each spot were fractionated whereas the raw  $\Delta^{17}\text{O}$  value was identical to the first sequence. Thus  $\delta^{18}\text{O}$  is calculated from just the first analysis, while  $\Delta^{17}\text{O}$  is calculated from both analyses for better precision. Six sample spots were bracketed with 12 standard spots within a single sequence. We achieved spot-to-spot reproducibility (2SD) of  $\sim 0.3\%$  for  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ , and  $\sim 0.25\%$  for  $\Delta^{17}\text{O}$ . This precision allows us to distinguish H ( $\Delta^{17}\text{O} = 0.73\pm 0.09\%$ ) from L and LL ( $\Delta^{17}\text{O} = 1.07\pm 0.18\%$  1SD;  $1.26\pm 0.24\%$  2SD, respectively, [16]) chondrites.

Prior to SIMS, concentrations of 8 elements (Fe, Cr, Mg, Al, Ti, V, Mn, Zn) were determined with WDS by Cameca SX-51 EPMA. SEM images were acquired before and after SIMS analyses.

**Results and Discussion:** Oxygen isotopic compositions of chromites from modern H (Guareña, Hessle), L (Ergheo) and LL (St-Séverin) chondrites were analyzed with identical conditions. Their  $\Delta^{17}\text{O}$  values are consistent with corresponding group averages [16] and demonstrate the reliability of our analytical method (Figure 1). Weighted average data of Thorsberg FMC are similar to those of Ergheo (L5) chromite (Fig. 1). The average  $\Delta^{17}\text{O}$  values of Thorsberg FMC ( $1.17\pm 0.09\%$ , mean errors of weighted average based on individual 2SD, unless noted otherwise), Brunflo FMC ( $1.25\pm 0.16\%$ ), Thorsberg SEC ( $1.10\pm 0.09\%$ ), Puxi River SEC ( $1.11\pm 0.12\%$ ) are consistent with L and LL group averages and the previously reported bulk analysis of Gol 001 FMC ( $1.07\pm 0.10\%$ ,  $2\sigma$ ; [13]). The scatter (1SD) of  $\delta^{18}\text{O}$  values from individual chromite grains within fossil meteorites is  $\leq$  analytical uncertainties. This implies that the original meteorites are well equilibrated. Only Brunflo FMC displays grain-to-grain variability in  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$   $\sim 2\times$  the analytical uncertainty along a mass-dependent fractionation line, i.e. the 1SD of  $\Delta^{17}\text{O}$  is only  $0.01\%$ . Such variability is in line with a less equilibrated type as proposed by [19]. The  $\delta^{18}\text{O}$  variability between Thorsberg SEC ( $<0.3\%$  1SD) and P6a Puxi River SEC ( $<0.2\%$ ) is small, whereas Y9 Puxi River SEC  $\delta^{18}\text{O}$  varies more ( $\sim 1\%$  1SD). However, the variability of  $\Delta^{17}\text{O}$  values among all analyzed SEC grains from Sweden and China, and FMC grains from Sweden is consistent with analytical uncertainty ( $0.10\%$ , 1SD).

We conclude that all analyzed SEC and FMC grains are closely related and may have originated in the same parent body.

EPMA analyses of the Ordovician EC grains gave element abundances (Cr, Fe, Mg, Al, Ti, V, Mn, Zn) consistent with chromites of modern L and LL chondrites [20]. The Cr, Fe, and Zn wt%-concentrations are variable in some grains and show inverse correlation of FeO+ZnO with  $\text{Cr}_2\text{O}_3$  as reported by [5,7]. A comparable variation and correlation is also observed in chromite data from modern ordinary chondrites [20], implying this reflects mainly a parent body process. We observe a weak negative correlation of  $\delta^{18}\text{O}$  with FeO+ZnO only in Thorsberg SEC grains, however, no correlation of any element concentration with  $\Delta^{17}\text{O}$  was observed within our precision. These observations indicate that no significant alteration of these grains occurred on Earth.

**Conclusions:** Values of  $\Delta^{17}\text{O}$  are indistinguishable within analytical uncertainty and provide evidence that SEC grains from contemporaneous sediments in Sweden and China are genetically closely related to each other and to chromites from fossil meteorites from Sweden. The  $\Delta^{17}\text{O}$  values of all samples match L and LL group  $\Delta^{17}\text{O}$  averages. Concentrations of Cr, Fe, Mg, Al, Ti, V, Mn, and Zn are consistent with modern L and LL group chromite. We also confirm the recent conclusion [19] that Brunflo has a L or LL chondrite composition. Terrestrial alteration did not affect the O isotopic composition of the chromites. This study provides an important piece of evidence, in line with all previous work, to corroborate the hypothesis that the abundant ECs in mid-Ordovician sediments are debris of the L chondrite parent asteroid breakup event.

**References:** [1] Heymann D. (1967) *Icarus* 6, 189 [2] Bogard D.D. (1995) *MAPS* 30, 224 [3] Haack H. et al. (1996) *Icarus* 119, 182 [4] Schmitz B. et al. (1996) *EPSL* 145, 31 [5] Schmitz B. et al. (2001) *EPSL* 194, 1 [6] Schmitz B. et al. (2003) *Science* 300, 961 [7] Schmitz B. and Häggström T. (2006) *MAPS* 41, 455 [8] Cooper R.A. and Sadler P.M. (2004) in: Gradstein F. et al. (eds.) *A Geologic Time Scale 2004*, pp. 165 [9] Korochantseva E.V. et al. (2007) *MAPS* 41, 113 [10] Schmitz B. et al. (2008) *Nat. Geosci.* 1, 49 [11] Heck P.R. et al. (2004) *Nature* 430, 323 [12] Bridges J.C. et al. (2007) *MAPS* 1781 [13] Greenwood R.C. et al. (2007) *EPSL* 262, 204 [14] Heck P.R. et al. (2008) *MAPS* 43, 517 [15] Meier M.M.M. et al. (2009) *LPSC XL*, this vol. [16] Clayton R.N. et al. (1991) *GCA* 55, 2317 [17] Kita N.T. et al. (2007) *LPS XXXVIII*, Abs. #1981 [18] Kita N.T. et al. (2009) *Chem. Geol.* subm. [19] Alwmark C. and Schmitz B. (2009) *MAPS* in press [20] Wlotzka F. (2005) *MAPS* 40, 1673

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