INTRODUCTION. Terrestrial weathering can render troublesome effects in the mineralogical, chemical and isotopic analyses of meteorites that might confound their cosmochemical interpretations [1]. Nonetheless, the scientific community's supply of new meteorite specimens continues to grow principally through weathered "finds" recovered from Antarctica and other remote locations where natural conditions have favored meteorite concentrations. Therefore, it is important to establish reliable methods for rapidly and quantitatively measuring the degree of weathering of a given meteorite specimen. For Antarctic meteorites, an A-B-C scale serves as a visual assessment of the relative rustiness of whole specimens [2]. "A" represents very little rust while "C" indicates abundant rust; a subscript "c" is added if evaporite (salt mineral) deposits are seen. Even if it could be extended to non-Antarctic finds, the A-B-C-e system remains subjective and inadequate for quantitative studies.

In the present work, we evaluate differential scanning calorimetry (DSC) as a weatherometer method using L-chondrites as a test case. DSC is quantitative, rapid (1-2 hr per analysis), uses small samples (10-20 mg), and is sensitive to weathering products in stony meteorites, including oxyhydroxides, salts and clays.

SAMPLES AND METHODS. Samples were selected from the U.S. Antarctic meteorite collection [2] for L3 and L6 chondrites which had been chemically analyzed by Jarosewich [3]. Non-Antarctic comparison samples, also previously analyzed by Jarosewich [3], included the Khohar (L3) and Saratov (L4) falls, the Ioka (L3) find, and the Holbrook, Arizona (L6) chondrite, which has been analyzed as both a fall (1912) and find (1931, 1968) [4-6]. Point counts of meteorite thin sections were used to determine volumetric abundances of Ni-Fe metal, sulfides, silicates, and "rust." For the Antarctic specimens, additional point counts for fractures were made with rectilinear grids overlain on photographs of the original rock specimens.

DSC analyses were performed on splits of homogenized powders analyzed by Jarosewich [3] and Holbrook powders from Gooding [6]. For each analysis, 10-12 mg of powder in an aluminum oxide crucible was heated from 300-1000 K at 10 K/min under 20 cm³ Ar/min in a Perkin-Elmer DSC-7. The sample was cooled to room temperature, weighed, and then re-heated. Empirical corrections for bulk heat-capacity effects were made by subtracting second-heat data from first-heat data; the residual consisted of peaks from nonreversible phase transitions and chemical reactions. A zinc standard (NIST SRM-2221) was run regularly for instrument calibration. Reference analyses were performed on ferric oxides and oxyhydroxides as well as on minerals representative of Antarctic evaporites (nonsesquioxide, gypsum, and epsomite).

RESULTS. Fig. 1 shows a positive trend of modal rust (from our point counts) with bulk Fe_{total}/(Fe⁹ + FeS) computed from chemical analyses by Jarosewich [3] for Antarctic samples, or by Mason and Wiik [4] and Gibson and Bogard [5] for Holbrook samples. Fig. 1 confirms that rust accumulates as metallic iron and troilitic (FeS) corrode but also underscores the limitations of existing A-B-C categories as broad and indefinite indices of the corrosion trend.

The DSC contrast between fresh and weathered specimens is illustrated in Fig. 2 for Holbrook but essentially the same features characterize Antarctic L-chondrites. "Weathering product" peaks are attributable primarily to ferric oxyhydroxides; the "rust" peak (Fig. 2) corresponds to unresolved dehydration peaks from FeO(OH) polymorphs, including goethite, lepidocrocite, and akaganite. Broad peaks at 350-400 K reveal more poorly crystallized ferric oxyhydroxides akin to ferrihydrite, 5Fe₂O₃·9H₂O. Fundamental peaks for maghemite (γ-Fe₂O₃) or magnetite (Fe₃O₄) appear weak or absent; peaks for hematite (α-Fe₂O₃) are fundamentally weak and not easily detected at low abundance. Fig. 3 shows that the DSC "rust" peak covaries with the bulk iron ratio more coherently than does the modal rust volume. Therefore, the DSC "rust" peak is a
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Figure 2. Residual DSC heat-flow data for fresh (1912 fall) and weathered (1931 find) samples of the Holbrook (L6) chondrite. Each curve represents a smooth spline drawn through about 1200 data points. The troilite peak corresponds to the α/β solid-state inversion of primary FeS. The "rust" peak represents dehydration of Fe(OH) polymorphs.

Figure 3. Covariation of DSC integrated "rust" peak with bulk iron ratio. Error bars on the Holbrook points represent standard deviations of triplicate analyses. Antarctic finds are measurably more oxidized than documented falls.

useful proxy for the abundance of ferric iron, and hence the degree of oxidative weathering, in each sample. For the Antarctic sample suite, there is no obvious increase in DSC rust index with declining 26Al activity [2] (a proxy for terrestrial residence age) except in a false sense when the ALHA77011 (L3) group is indiscriminately included.

The ALHA77011 (L3) pairing group [7] scatters widely regardless of which weathering index (modal rust, iron ratio, or DSC rust) is selected. Possible explanations are that (a) the various stones were exposed at the glacial surface for different lengths of time, (b) the size (i.e., surface-to-volume ratio) of each stone moderated diffusion-driven reactions, or (c) fractures controlled penetration of water and atmospheric gases. In our data, DSC rust index does not correlate with mass but rust appears to positively covary with fracture abundance (Fig. 4), supporting hypothesis (c).

CONCLUSIONS. DSC offers a rapid method for measuring the degree of oxidative weathering of ordinary chondrites. With further development, the method could probably be extended to other types of chondrites and achondrites. For a given terrestrial residence age, weathering of Antarctic chondrites may be strongly influenced by fracture abundance.

ICP-MS TRACE ELEMENT ANALYSIS OF UREILITES: EVIDENCE FOR MIXING OF DISTINCT COMPONENTS. A.H. Spitz* Department of Geosciences, University of Arizona, Tucson, AZ 85721 USA.

Eleven ureilites were analysed using the inductively coupled plasma-mass spectrometer (ICP-MS) in the laboratory of J. Ruiz, University of Arizona: ALHA78019, ALHA87262, EET 87511, LEW 85328, LEW 85440, META78008, PCA 82506 and Y-790981, Hajmah, Kenna and North Haig. Trace element concentrations determined for the ureilites were: Co, Cu, Zn, Ga, Se, Rb, Sr, Y, Mo, Cs, Ba, Hf, W, Re, Ir and Pb. These elements were chosen because of their geochemical properties and the ability of the ICP-MS to determine their concentrations. Specifics of the method are found in (1). Multiple analyses were made of these ureilites with the exception of ALHA78019, ALHA87262 and North Haig. Results for individual samples were quite variable and demonstrate the heterogeneous nature of ureilites vis-à-vis trace elements. Averaged results for each main group ureilite are shown in Figure 1.

RESULTS: Data Variability. Multiple counts of the same sample in an experiment produced results within 5% for the majority of elements. There are, however, significant (meaning real, not statistical) differences among some replicate analyses of a particular ureilite. Average standard deviations are as low as 7% for Zn and as high as 40% for W. Only limited literature data exists with respect to replicate measurement for individual ureilites and these corroborate the ICP-MS results. The variability noted for light rare earth element (LREE) concentrations extends to other trace elements as well.

Lithophile elements. The lithophile elements measured include both volatile and refractory elements. The element concentrations range from about 0.005 to 0.9 x CI (CI values from (3)). The range of lithophile element concentrations is greater than those for chalcophile and siderophile element concentrations. A suggestion of correlation between the volatile element Rb and the refractory element Ba exists. North Haig has higher lithophile element concentrations than the main group ureilites (MGU).

Chalcophile elements. Zn is the most consistent of elements measured for the ureilites and is approximately 1.0 x CI. Average values of Pb and Se have similar ranges of concentration values for the ureilites while Cu has a somewhat more extensive range. The depletions displayed may reflect volatility controls as well as igneous compatibility constraints. No other studies have analysed for Pb concentrations in ureilite so no comparison to previous work can be made. No statistically significant correlations exist between chalcophile elements or between chalcophile and siderophile elements. North Haig has similar chalcophile element concentrations to the MGU.

Siderophile elements. The refractory element concentrations determined in this study (Mo, W, Re and Ir) vary from 0.1 to 3.0 x CI. The volatile siderophile elements (Co and Ga) are more depleted and range from 0.2 to 0.9 x CI. Running a simple linear regression analysis on the ureilite siderophile elements (refractory versus volatile) indicated that no correlations existed among the siderophile element for all ureilites. This was in contrast to correlations determined for neutron activation analysis (NAA) data (2,4,5,6,7,8,9). The reason for this became obvious when examination of element correlations was made graphically using both the data obtained in this research and those available in the literature from the previous NAA studies.

On the plot of Ir (ppb) versus Ga (ppm) (Figure 2), two distinct groups of ureilites are evident (Trend 1 = Kenna to ALHA77257, Trend 2 = META78008 to ALHA81101). These trends clearly indicate some processing mechanism, be it mixing or igneous, which relate the ureilites within each group. These groups do not correspond to groups based on nickel content, fayalite content, oxygen or nitrogen isotopic groupings, weathering or shock classifications. Some of the members of these groups do correspond, however, to the Sm-Nd systematic groupings of Goodrich et al. (10): Kenna, Novo Urei and ALHA77257 (Goodrich et al. Group 2) lie on Trend 1 and ALH 82130, LEW 85440, META78008 and PCA 82506 (Goodrich et al. Group 1) lie on Trend 2. This is the first instance of any grouping found in one line of research agreeing with the groups determined in another area of study. These trends in all probability represent mixing lines (igneous processing does not produce trends such as these) and may, therefore, indicate separate contributors at possibly different times in the ureilite parent body (UPB) history, e.g. two siderophile-rich components but one more refractory-rich, one more volatile-rich. These trends may be recording the contribution of impactors to the original ultramafic ureilite rock. Alternatively, they could indicate different parent bodies for these meteorites (a less attractive option based on other lines of evidence for complex origin (2,10)).
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DISCUSSION: A hypothesis for ureilite formation based on these Ir and Ga data and the Sm-Nd data includes formation of the ureilite ultramafic rock at 4.55 Ga and disturbance of the UPB at a later date. Trend 2 represents unaffected ureilites, trend 1 members reflect the disturbance at 3.74 Ga seen in the Sm-Nd data. A significant impact which may have caused the metasomatic activity on the UPB reflected in the Sm-Nd isotope data may have also established a different siderophile trend and affected other isotopic systems such as oxygen and nitrogen. The trace element data presented here indicate that the combination of the models which propose igneous processing and impact events (as suggested by 11 and 12) as the drivers for the chemical and physical characteristics of ureilites presents the most attractive alternative. Neither simple models of ureilites as primitive, non-processed meteorites nor models of igneous processing without mixing of additional material can account for the observations.


Figure 1: Element Concentrations
Figure 2: Ir versus Ga concentrations