

**FINE-SCALE VARIATIONS IN EUCRITIC PYROXENE FeO/MnO: PROCESS VS. PROVENANCE.** D. W. Mittlefehldt<sup>1</sup>, T. J. Barrett<sup>2</sup>, L. Le<sup>3</sup>, Z. X. Peng<sup>3,4</sup>, E. L. Berger<sup>5</sup> and D. K. Ross<sup>3,6</sup>, <sup>1</sup>NASA Johnson Space Center, Houston TX, USA ([david.w.mittlefehldt@nasa.gov](mailto:david.w.mittlefehldt@nasa.gov)), <sup>2</sup>The Open University, Milton Keynes, UK, <sup>3</sup>Jacobs JETS-NASA Johnson Space Center, Houston TX, USA, <sup>4</sup>California State University, Northridge CA, USA, <sup>5</sup>GCS-Jacobs JETS-NASA Johnson Space Center, Houston TX USA, <sup>6</sup>UTEP-CASSMAR, El Paso TX, USA.

**Introduction:** Most asteroidal igneous rocks are eucrite-like basalts and gabbros, composed mostly of ferroan low- and high-Ca pyroxenes and calcic plagioclase, plus smaller amounts of silica (most commonly tridymite), ilmenite, chromite, troilite, Ca-phosphate, metal and sometimes ferroan olivine. Eucrite-like mafic rocks are fragments of the crusts of differentiated asteroids, and most are likely from 4 Vesta [1].

Oxygen isotopic compositions of meteorites are important indicators of genetic relationships [2]. Eucrite-like basalt Northwest Africa (NWA) 011 is anomalous in O isotopic composition compared to other eucrites and is thought to be from different asteroid [3]. Current analytical methods allow smaller O isotopic differences to be resolved [4, 5]; for example, Ibitira differs from the eucritic  $\Delta^{17}\text{O}$  mean by 0.171 ‰, 20 times the uncertainty of the mean (Fig. 1). Some eucrite-like mafic rocks have even smaller O-isotopic anomalies (Fig. 1). Here, “normal” eucrites are indistinguishable from the group mean O isotopic composition; “anomalous” eucrites are distinguishable.

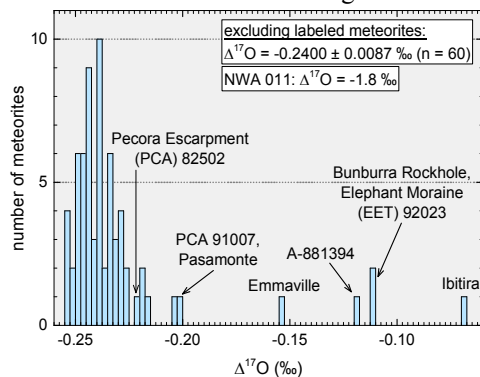


Figure 1. O-isotopic compositions of eucrite-like mafic meteorites; Open University data from [5-10].

The FeO/MnO ratios of planetary basalts can be used to fingerprint the source body. This ratio is relatively invariant during most igneous processes and is inherited from its source region with little modification [11]. Low-Ca pyroxenes in Ibitira and NWA 011 have FeO/MnO ratios that are resolvable from those of most eucritic-like basalts, supporting formation on different asteroids [3, 12]. The efficacy of the FeO/MnO ratio as a diagnostic of source body was demonstrated through comparison of basalts from the Earth, Moon, Mars, Vesta and the angrite parent asteroid, where large differences in pyroxene and/or olivine FeO/MnO are pre-

sent [11]. Modifications imposed by igneous processes are small secondary effects in this comparison.

Our analytical protocol allows precision of better than 2% (1 $\sigma$  standard deviation) on FeO/MnO to be achieved for homogeneous eucritic pyroxenes [12]. Our data have resolvable differences in pyroxene FeO/MnO for some anomalous eucrite-like mafic rocks, but not all [8, 10, 13]. For example, Emmaville differs from the eucritic  $\Delta^{17}\text{O}$  mean by 0.087 ‰, roughly 10 times the uncertainty of the mean (Fig. 1), but its pyroxene FeO/MnO is indistinguishable from those of normal eucrites [8]. Further, some normal, eucrite-like mafic rocks have distinct pyroxene FeO/MnO ratios, whilst others show internal variations in FeO/MnO [14]. Here we begin to address the utility and limitations of using FeO/MnO ratios as source-body vs. formational process indicators when differences in this ratio are small.

**FeO/MnO:** Divalent Fe and Mn are homologous species; their identical charge and similar ionic radius (78 vs. 83 pm; octahedral coordination) allow them to substitute for each other in mineral structures with similar levels of distortion to the crystal structure. They have similar mineral/melt partition coefficients for ferromagnesian silicates [15]. For the degrees of fractionation typical of basaltic suites, little change to magma FeO/MnO is incurred. Eucrite-like basalts were formed at an oxygen fugacity near the iron-wüstite buffer, and had variable, but poorly documented, S contents [1, 15]. Small differences in  $f_{\text{O}_2}$  or  $f_{\text{S}_2}$  could lead to resolvable differences in pyroxene FeO/MnO as Fe, but not Mn, is partitioned between the silicate, metal and sulfide phases. Redox and silicate-sulfide interactions leave clear petrological signatures that allow us to distinguish secondary, parent-body processes, from primary differences due to provenance. Two examples: high-S magmas result in loss of FeO to FeS coupled with systematically decreasing pyroxene FeO/MnO with crystallization (normal eucrite Queen Alexandra Range (QUE) 94484 [16]); subsolidus redox results in pyroxenes with very low FeO/MnO ( $18.9 \pm 0.4$ ) and high modal abundances of Fe metal and silica (normal eucrite Elephant Moraine (EET) 87542 [14]).

**Eucritic Pyroxenes:** Eucrite-like basalts crystallized pigeonite on their liquids, which evolved to au-

gite with fractionation [15]. The majority of a eucrites' Fe and Mn are in pyroxene. Comparison of pyroxene FeO/MnO can, therefore, be a robust proxy for bulk-rock FeO/MnO. The large  $\text{Ca}^{2+}$  cation only occupies the pyroxene M2 site, whilst  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  preferentially fill the M2 site, with the filling order of the latter being  $\text{Mn}^{2+} > \text{Fe}^{2+}$ . The slightly smaller radius of  $\text{Fe}^{2+}$  indicates that the filling order for the M1 site is  $\text{Fe}^{2+} > \text{Mn}^{2+}$  [17]. Thus,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  partition differently in low-Ca and high-Ca pyroxenes. Most eucrite-like mafic rocks underwent variable degrees of thermal metamorphism engendering exsolution of high-Ca pyroxene from pigeonite, resulting in augite or diopside lamellae in a low-Ca pyroxene host for the most metamorphosed rocks [18]. This can lead to fractionation of FeO/MnO between the phases (e.g., Asuka (A-) 881394, Fig. 2). We compare only low-Ca pyroxene compositions in order to minimize problems associated with FeO/MnO partitioning between pyroxene types.

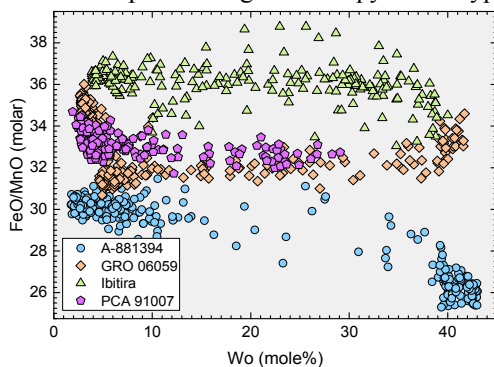


Figure 2. FeO/MnO vs. Wo for pyroxene analyses of cumulate gabbro A-881394, and basalts Grosvenor Mountains (GRO) 06059, Ibitira and Pecora Escarpment (PCA) 91007.

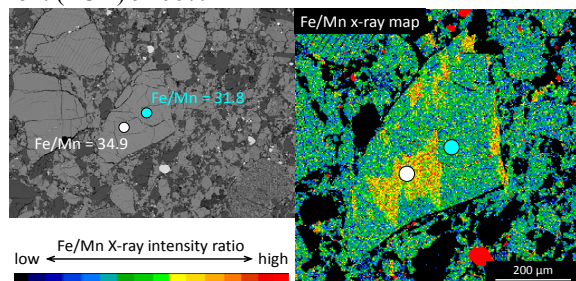


Figure 3. Variation in FeO/MnO within a single grain fragment in GRO 06059.

Resolvable differences in low-Ca pyroxene FeO/MnO can occur within a given eucrite-like mafic rock. We have found that the majority of low-Ca pyroxene grains in the normal basaltic eucrite GRO 06059 have FeO/MnO of  $31.5 \pm 0.3$ , within the range of normal eucrites, whilst a subset of analyses has FeO/MnO of  $34.9 \pm 0.4$ , in between those of anomalous basalts PCA 91007 ( $33.3 \pm 0.5$ ) and Ibitira ( $36.3 \pm$

$0.4$ ) (Fig. 2) [10, 12]. The different pyroxene FeO/MnO ratios can be found within individual grain fragments. Elemental mapping shows that the differences are caused by irregular zoning patches in the pyroxenes (Fig. 3). These high FeO/MnO zones are more magnesian ( $\text{mg}\# 39.0 \pm 0.3$  vs.  $37.6 \pm 0.4$ ), less calcic (Fig. 2), have higher Al ( $0.0118 \pm 0.0016$  vs.  $0.0089 \pm 0.0015$  apfu), lower Mn ( $0.0336 \pm 0.0003$  vs.  $0.0371 \pm 0.0007$  apfu), but are indistinguishable in Fe.

**Discussion:** We have identified several cases where variations in pyroxene FeO/MnO within normal eucrites is equivalent to, or larger than, the difference between normal and anomalous eucrites such as PCA 91007 (Fig. 2) [10]. In all such cases, detailed petrological study allows us to identify the cause and assess the likelihood that a given eucrite-like mafic rock is distinct from normal eucrites in FeO/MnO. Nevertheless, there are issues that require consideration. For example, high-Ca pyroxene lamellae in A-881394 have much lower FeO/MnO than the low-Ca pyroxene hosts (Fig. 2). The primary pyroxene would have had an FeO/MnO intermediate between these, making firm conclusions regarding provenance from comparisons with eucrite-like rocks that are less metamorphosed somewhat uncertain.

**Key Point:** Precise, low-Ca pyroxene FeO/MnO ratios can be used to distinguish eucrite-like mafic rocks from different source asteroids even when variations in this ratio are small as long as petrologic observations are used to understand any variations caused by parent asteroid processes.

**References:** [1] Mittlefehldt D. W. (2015) *Chem. Erde Geochem.*, 75, 155. [2] Clayton R. N. et al. (1976) *Earth. Planet. Sci. Lett.*, 30, 10. [3] Yamaguchi A. et al. (2002) *Science*, 296, 334. [4] Wiechert U. H. et al. (2004) *Earth Planet. Sci. Lett.*, 221, 373. [5] Greenwood R. C. et al. (2005) *Nature*, 435, 916. [6] Greenwood R. C. et al. (2017) *Chem. Erde Geochem.*, 77, 1. [7] Scott E. R. D. et al. (2009) *Geochim Cosmochim. Acta*, 73, 5835. [8] Barrett T. J. et al. (2017) *Meteoritics & Planet. Sci.*, 52, 656. [9] Bland P. A. et al. (2009) *Science*, 325, 1525. [10] Mittlefehldt D. W. et al. (2016) *LPS XLVII*, Abstract #1240. [11] Papike J. J. (2003) *Am. Mineral.*, 88, 469. [12] Mittlefehldt D. W. (2005) *Meteoritics & Planet. Sci.*, 40, 665. [13] Mittlefehldt D. W. et al. (2017) *LPS XLVIII*, Abstract #1194. [14] Mittlefehldt D. W. et al. (2015) *LPS XLVI*, Abstract #1933. [15] Stolper E. (1977) *Geochim. Cosmochim. Acta*, 41, 586. [16] Mittlefehldt D. W. et al. (2015) *78<sup>th</sup> Met. Soc.*, Abstract #5342. [17] Cameron M. and Papike J. J. (1981) *Am. Mineral.*, 66, 1. [18] Takeda H. and Graham A. L. (1991) *Meteoritics*, 26, 129.