

OXYGEN FUGACITY OF THE MARTIAN MANTLE FROM PIGEONITE/MELT PARTITIONING OF SAMARIUM, EUROPIUM AND GADOLINIUM

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Introduction: This study is part of an ongoing effort [1,2] to calibrate the pyroxene/melt REE oxybarometer [3] for conditions relevant to the martian meteorites. These efforts have been motivated by reports of redox variations among the shergottites [4-6]. There is fairly good agreement between fO_2 determinations using equilibria between Fe-Ti oxides [4,5] and the estimates from Eu anomalies in shergottite augites [6] in terms of which meteorites are more or less oxidized. However, there is as much as two log-units offset in fO_2 values between the results of [4,5] and [6]. One explanation for this offset is that the Eu calibration used for the shergottites was actually designed for the LEW86010 angrite [7], a silica-undersaturated basalt whose pyroxene (diopside) compositions are rather extreme. To correct this, [1] conducted experiments to calibrate the Eu oxybarometer for martian composition augite/melt pairs. Application of the natural rare earth data to the new calibration results in somewhat different fO_2 's in comparison to that of [7]. However, this difference is small compared to the discrepancy between the fO_2 determined with Eu oxybarometer technique and that from the Fe-Ti oxides method. The reason for this continued discrepancy is unclear. One possibility is that augites are non-liquidus or that the augites measured were not actually cores. To address the first possibility, the use of pigeonite rather than augite as the oxybarometer phase is considered. Towards this end we have conducted experiments on martian composition pigeonite/melt rare earth element partitioning as a function of fO_2 .

Experimental Methods: Pigeonite/melt partitioning experiments for the rare earth elements: Sm, Eu and Gd were run in a gas-mixing DelTec furnace at fO_2 s ranging from one log unit below to four log units above the iron-wüstite buffer. The simplified (i.e. $CaO+MgO+Al_2O_3+SiO_2+FeO+Na_2O$) composition was designed to produce shergottite composition pigeonites on the liquidus. This composition was doped with 1% each of Sm, Eu and Gd. Sample preparation and experimental procedures are the same as in [1]. Run products were analyzed for all elements with the SX100 EMP at NASA/JSC.

Rare earth abundances in the pigeonites determined by electron probe are low (on order of 100 ppm) and push the detection limit of the instrument. So, in addition, trace element analyses of the pyroxene and glass were conducted using the

Cameca ims 4f ion microprobe at the University of New Mexico, Institute of Meteoritics. Doped clinopyroxene and glass prepared at the JSC experimental lab were used as standards. These synthetic standards were doped only with Sm, Eu, and Gd to eliminate most isobaric interferences. The calibration curve for the REE had a correlation coefficient of better than 0.997. Ion yields for the glass and pyroxene were identical.

Results: Experimental pigeonite compositions are fairly uniform within a given run, varying generally from $En_{72-77}Fs_{19-22}Wo_{4-7}$. Fig 1 shows the average pyroxene composition for each run. The scatter in the average composition data from run to run is only slightly greater than that within a given run. Average compositions from run to run are essentially constant, displaying no discernable correlation with fO_2 . Also plotted on the quadrilateral plot are shergottite pigeonite core compositions from the literature [8]. The natural pigeonites display a compositional range from $En_{50-70}Fs_{21-32}Wo_{6-14}$. The more restricted composition of the experimental pigeonites lies at the more magnesian and lowest calcium end-member of the natural pigeonite cores and are similar to those from QUE94201 [9] and EET79001 [10].

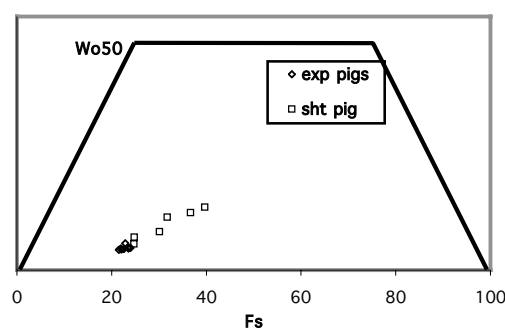


Fig 1: experimental and shergottite pigeonite compositions

The pigeonites are homogeneous in their rare earth contents within analytical error.

The ratio of D_{Eu} to $D_{(Sm,Gd)}$ (pigeonite/melt) as a function of fO_2 derived from the current experiments is shown in Fig 2. The D values and ratios are averages of multiple analyses for each run. D values were calculated from the ratio of the intensities of the rare earth element relative to Si in the pigeonite to the ratio in the glass. The error bars for the D ratios

represent the standard deviation of these ratios within a given run. $D(\text{Eu}/\text{Sm})$ and $D(\text{Eu}/\text{Gd})$ vary smoothly with $f\text{O}_2$, flattening out at both the high- and low- $f\text{O}_2$ portions of the trend as Eu becomes either dominantly tri- or di-valent, respectively. In both cases, the range of D ratios is about a factor of three.

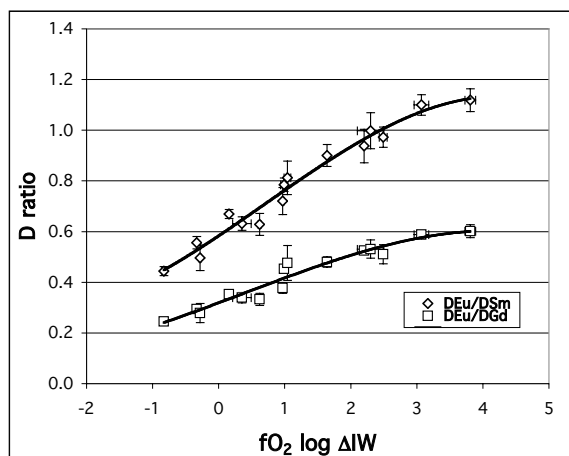


Fig 2: The ratio of D_{Eu} to $D_{(\text{Sm},\text{Gd})}$ (pigeonite/melt) as a function of $f\text{O}_2$ derived from the current experiments

Discussion: Applying fig. 2 data to D ratios from measured Sm, Eu and Gd concentrations in selected shergottite pigeonite cores [11] and whole rocks [12] gives the $f\text{O}_2$ for each meteorite at the time of initial pigeonite crystallization. These values are plotted in Fig 3 against the $f\text{O}_2$ s derived from Fe-Ti oxides for comparison. The use of this pigeonite-core rare earth data set [11] is intended for illustration purposes only as it was not collected with this application in mind. The core values were arrived at by taking the lowest rare earth values measured in the pigeonites. The first formed pigeonites will have the highest Mg content, so that lower rare earth concentrations should correlate with higher Mg values. This cannot be confirmed for the pigeonite-core data set.

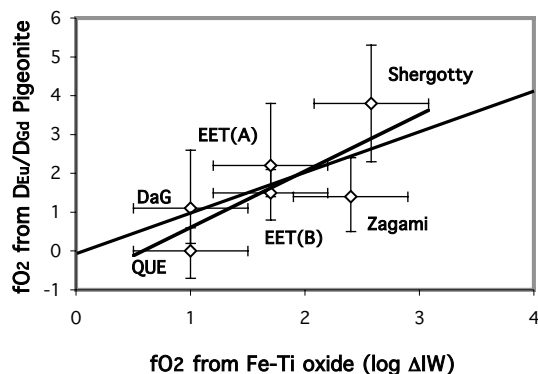


Fig 3: $f\text{O}_2$ from $D_{\text{Eu}}/D_{\text{Gd}}$ (Pigeonite) versus $f\text{O}_2$ from Fe-Ti oxybarometer

Caveats aside, there is, to first order, good agreement between the $f\text{O}_2$ s determined from the Eu-anomaly method with the calibration presented here and those using the Fe-Ti oxide method. As with the previous studies, the same $f\text{O}_2$ trend is seen among the meteorites using both methods. There is a subtle tendency for the values to be shifted from the 1:1 correspondence line depending on $f\text{O}_2$. The $f\text{O}_2$ for QUE94201, the most reduced meteorite, determined by the Eu-oxybarometer is significantly (greater than error) lower than that determined by Fe-Ti oxides. Likewise, the $f\text{O}_2$ for Shergotty, the most oxidized meteorite, determined by the Eu-oxybarometer is higher (although slightly within error) than that determined by Fe-Ti oxides. This is similar to, although much subtler than, the trend seen using the augite calibration of [1]. In that case the more reduced the meteorite from either method, the greater the difference in the $f\text{O}_2$ between the two methods. With the exception of Shergotty, the most oxidized meteorite, the $f\text{O}_2$ from the augite Eu oxybarometer is always lower than that from the Fe-Ti method. As well, Zagami lies off of the 1:1 correlation curve. This may, in part, be due to poorly determined whole-rock values for the Eu/Gd and Eu/Sm ratios. The similarity of results between the two methods leads us to believe that we are on the right track in the use of pigeonite for the $f\text{O}_2$ determination and that the calibration is applicable. However, we should expect, in some instances, differences in the $f\text{O}_2$ s arrived at from the two methods for a given meteorite. The pigeonite cores (along with olivine) should be the first phases to crystallize from the magma. Fe-Ti oxides would be expected to crystallize somewhat later. If significant assimilation of more oxidized crustal material occurs subsequent to the onset of pigeonite crystallization, we would expect that the oxides would yield a higher $f\text{O}_2$.

Further work on this subject is concentrating on identification of the truly first formed pigeonite and augite cores in basaltic shergottites and analysis with both SIMS and LAM-ICPMS methods in an effort to produce the best rare earth ratios and to reduce the associated error. Further experiments are also under way to cover the range of martian pigeonites.

References: [1] Musselwhite, D.S. et al (2003), *MAPS*, in review. [2] McCanta et al., (2003) *GCA*, in review. [3] Philpotts, J. A. (1970) *EPSL*, **9**, 257-268 [4] Herd C. et al. (2001) *Am. Min.*, **86**, 1015-1024. [5] Herd C. et al (2002) *GCA*, **66**, 2025-2036. [6] Wadhwa, M. (2001) *Science* **291**, 1527-1530 [7] McKay, G.A. et al. (1994). *GCA*, **58**, 2911-2919. [8] McSween, H.Y. Jr. and Treiman, A.H. (1998) In *Planetary Materials MSA Wash, D.C.* [9] McSween, H.Y. Jr et al. (1996) *GCA* **60**, 4563-4569. [10] McSween, H.Y. Jr. and Jarosevich, E. (1983) *GCA* **47**, 1501-1513 [11] Wadhwa M. et al. (1994) *GCA* **58**, 4213. [12] Meyer, C. (2003) NASA/ JSC Pub #27672.