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FOR

Direct determination of europium valence state by XANES in extraterrestrial merrillite. Implications for REE crystal chemistry and martian magmatism.

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Analytical Approach

BSE images and K_α x-ray maps of phosphates in the samples were made using the Institute of Meteoritics' JEOL JXA-8200 electron microprobe (EMP) operating at an accelerating voltage 15 kV and a beam current of 100 nA. In particular, K_α x-ray maps for F, Cl, Fe, Na, and Mg were collected on the EMP to explore the distribution of elements in the merrillite, and the chemical heterogeneity of the merrillite. Following the identification and documentation of phases, samples were repolished and quantitative point analyses were conducted using the JEOL JXA-8200 electron microprobe using a beam current of 20 nA and a ~5 μm spot size. Both Cl and F counts were monitored during analysis to account for migration of these two elements during electron beam – sample interactions (Stormer et al. 1993). Grains with the steepest and most irregular slopes were discarded from the data set (Stormer et al. 1993). Analyses were standardized using C.M. Taylor Company mineral and metal standards (http://www.2spi.com/catalog/standards/ taylor/ index.shtml). Stoichiometric constraints were used to determine the quality of the datasets, and detection limits were calculated at the 3σ level. A summary of results of the electron microprobe analyses are presented in Table 1. The arrangement of this table follows that used by Jolliff et al. (1993, 2006).

Trace element concentrations (La, Ce, Nd, Sm, Eu, Dy, Er, Yb and Sr) were determined following the analytical approach of Shearer et al. (2008, 2010) using a Cameca ims 4f ion probe at the University of New Mexico.. The ion probe analyses involved repeated cycles (10 cycles per analysis) of peak counting on the isotopes of selected trace elements. Absolute concentrations of the trace elements were calculated using the empirical relationship between measured peak/$^{42}Ca^{+}$ ratios, normalized to known CaO content in the standards. Analyses of these selected trace elements by ion microprobe have a precision of better than 10%. Trace element standards used for these analyses included a well-documented Durango apatite and an apatite standard from Oak Ridge National Laboratory and the University of New Mexico. A summary of results of the ion microprobe analyses are presented in Table 1.

References

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Stormer J. C., Jr., Pierson M.L. and Tacker R.C. (1993) Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis. American Mineralogist 78, 641-648.

scroll down for Table

Table 1. Summary of electron and ion microprobe analyses of merrillite from martian basalts.

	Los Angeles Map C, Point 4	QUE 94201 Grain 1, Point 11	NWA 2986 Grain 1, Point 12	LAR 06319 Grain 1, Point 9
	Oxide Concentrations (wt. %)			
P_2O_5	44.95	45.56	46.32	45.64
SiO_2	BDL	BDL	BDL	BDL
TiO_2	BDL	BDL	BDL	BDL
Al_2O_3	n/a	n/a	n/a	n/a
FeO	5.17	6.17	3.10	2.58
MnO	0.17	0.22	0.11	0.09
MgO	1.86	0.36	2.09	2.29
CaO	47.20	46.58	46.87	46.70
SrO	BDL	BDL	BDL	BDL
Na_2O	1.23	0.47	1.32	1.50
Y_2O_3	BDL	BDL	0.13	0.12
La_2O_3	0.022	0.001	0.026	0.027
Ce_2O_3	0.048	0.002	0.058	0.061
Pr_2O_3	n/a	n/a	n/a	n/a
Nd_2O_3	0.039	0.004	0.050	0.053
Sm_2O_3	0.017	0.003	0.022	0.022
Eu_2O_3	0.006	0.001	0.007	0.007
Gd_2O_3	n/a	n/a	n/a	n/a
Tb_2O_3	n/a	n/a	n/a	n/a
Dy_2O_3	0.025	0.006	0.028	0.028
Ho_2O_3	n/a	n/a	n/a	n/a
Er_2O_3	0.013	0.003	0.014	0.013
Tm_2O_3	n/a	n/a	n/a	n/a
Yb_2O_3	0.012	0.003	0.011	0.010
Lu_2O_3	n/a	n/a	n/a	n/a
SO_3	BDL	BDL	BDL	BDL
F	BDL	BDL	BDL	BDL
Cl	BDL	BDL	0.03	BDL
Total	100.76	99.37	100.17	99.14
-O=F				
Total Y+REE $_2O_3$				
P	13.82	14.15	14.12	14.06
Si	BDL	BDL	BDL	BDL
Ti	BDL	BDL	BDL	BDL
Sum(P,Si,Ti)	13.82	14.15	14.12	14.06
Al	n/a	n/a	n/a	n/a
Fe^{+2}	1.57	1.89	0.93	0.78
Mn^{+2}	0.05	0.07	0.03	0.03
Mg	1.01	0.20	1.12	1.24
Ca	18.36	18.30	18.08	18.20
Sr	BDL	BDL	BDL	BDL
Na	0.86	0.33	0.92	1.06
partial sum	21.86	20.79	21.09	21.31
Y+REE	0.02	0.00	0.05	0.05
S	BDL	BDL	BDL	BDL
SumCations	21.88	20.80	21.14	21.36
F	BDL	BDL	BDL	BDL
Cl	BDL	BDL	0.02	BDL

Notes: n/a = not analyzed, BDL = below detection limit. Values in red were analyzed via ion microprobe and represent average values for a particular grain.