Chlorine/Bromine Ratios in Fracture-filling Aqueous Alteration Products in Nakhla Olivine

S. R. Sutton,[1,2] M. N. Rao,[3,4] G. Dreibus,[3] D. S. McKay,[4] H. Wänke,[3]
S. Wentworth,[5] M. Newville,[2] T. Trainor,[2] G. J. Flynn[6]
[1]Department of Geophysical Sciences, The University of Chicago, Chicago, IL, U.S.A.
[2]Consortium for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL, U.S.A.
[3]Max-Planck-Institute, Mainz, Germany
[4]National Aeronautics and Space Administration (NASA), Johnson Space Center (JSC), Houston, TX, U.S.A.
[5]Lockheed Martin, NASA, Houston, TX, U.S.A.
[6]Department of Physics, State University of New York (SUNY), Plattsburgh, NY, U.S.A.

Introduction

During early Martian history, volcanic emanations contributed large excesses of volatiles, including halogens, sulfur, and water, to the Martian crust. These chemically reactive elements had undergone extensive redistribution over time as the result of various surface processes on Mars [1]. A study of halogens (particularly Cl/Br ratios in secondary mineralization products) may provide valuable insights to help in understanding the nature of the alterations caused by the aqueous activity in the Martian surface environment. Dreibus and Wänke [2] used neutron activation to study glasses and bulk samples of several SNC (i.e., composed of shergottite, nakhlite, and chassigny classes) meteorites and arrived at a Cl/Br ratio of ~110 for the Martian surface materials.

Nakhla probably offers the most diverse suite of aqueous precipitates to be found among the SNC meteorites. Numerous veins of hydrous clay within olivine grains are present in Nakhla [3, 4]. Bridges and Grady [5] and Wentworth and McKay [6] observed massive concentrations of halite of probable Martian evaporitic origin in association with siderite and anhydrite in interstitial areas in Nakhla. Dreibus et al. [7] reported Cl/Br ratios from 104 to 550 in three Nakhla fragments and found that 90% of the Cl and Br was readily leachable from this material. Their Nakhla leachate ratio was 580. Their analysis of an attached salt grain yielded a ratio of 5440, similar to that in table salt. Xirouchakis et al. [8] found 20 ppm Br in glass veins in Los Angeles shergottite by means of x-ray fluorescence (XRF) measurements made with the x-ray microprobe (beamline X26A) at Brookhaven National Laboratory.

In this study, we examine whether a Cl/Br ratio similar to that cited in Dreibus and Wänke [2] is present in products of secondary mineralization generated as a result of aqueous alteration in some SNC meteorites. We studied the Cl/Br ratios in fracture-filling materials in veins in Nakhla olivines (thin sections) by using the x-ray microprobe facility [9] at the GeoSoilEnviro Consortium for Advanced Radiation Studies (GSECARS) sector to determine Br contents and by using scanning electron microscopy (SEM)-based energy-dispersive x-ray (EDX) measurements to determine Cl contents at the same sites in the veins.

Methods and Materials

Samples

The Nakhla specimen consisted of a 30-μm-thick section on glass prepared at NASA-JSC. This thin section was prepared from the Nakhla sample obtained as a part of the consortium studies organized by M. Grady by using minimal amounts of aqueous solvents. Previous work on this filling material with electron-based techniques had produced semiquantitative concentrations for other elements, including Fe and Cl. An attempt was made here to conduct the synchrotron XRF measurements on the same (as well as adjacent) spots analyzed previously. Electron micrographs were available for this registry purpose. X-ray microprobe analyses were made on the thin section "as is."

X-ray Microprobe Analysis

The GSECARS x-ray microprobe consisted of an APS undulator x-ray source, a silicon (111) cryogenic monochromator, Kirkpatrick-Baez microfocusing mirrors [10], and a germanium solid-state fluorescence detector. A 3-μm-diameter x-ray beam was used. XRF maps in "region-of-interest" mode were made of the areas of interest, then full XRF spectra of high Br concentration spots were collected. Dwell times for the latter were typically 5 min.

As the Nakhla thin section was prepared on a conventional glass slide, there was a high fluorescence background from impurities in this material. Fortunately, the Br fluorescence from the glass was small compared to the signal from the alteration material (<10%), and a correction for this background could readily be made.

Bromine concentrations were computed by using Fe as an internal reference element. Because the x-ray beam penetrates the entire thickness of the thin section, the Fe fluorescence measured at each spot is derived not only from the weathering material but also potentially from the underlying host material (olivine). For accurate Br content determinations, knowledge of the proportions of these two phases in the analysis volume is required. The average Fe content along the beam trajectory was obtained from the ratio of the Fe fluorescence at the spot to that from the adjacent olivine (50% FeO) [3]. The Fe content of the weathering material was nearly constant in these regions as determined by EDX (Region 1 = 16.8 wt% Fe, Region 2 = 17.0 wt% Fe). These Fe contents fall at the low end of the range observed by Gooding et al. [3] for the compositions that they interpreted as likely smectites. The proportion of each phase in the beam was then computed from this average Fe content and the Fe contents of the two phases (end members). This approach allowed bromine concentrations in the weathering materials themselves to be computed.

Results and Discussion

Elemental maps were obtained for three distinct fracture zones containing weathering material. They were denoted Regions 1-3. Figure 1 shows these maps for Regions 1 and 2. It can be seen that there is a negative correlation between Fe and Br (i.e., Fe is more concentrated in the host olivine, and Br only occurs in the fracture-filling material).

Table 1 summarizes the bromine concentrations, which ranged from 96 to 215 ppm, with a mean value of 151 ppm and standard deviation of 49 ppm. The Br background measured from the olivine itself, representing the contribution from Br in the glass substrate, was equivalent to 10 ppm. The data were corrected for this background.

The chlorine concentrations for Regions 1 and 2 shown in Table 1 (0.88 and 0.68 wt%, respectively) were derived from EDX measurements of the same regions by Rao et al [1]. For Region 3, the average Cl concentration of the other two regions (0.8 wt%) was used. (Cl contents of the Nakhla weathering material in this thin section varied only at the ~20% level.) The Cl contents used here agree well with those of Gooding et al. (0.66 wt% average) [3].

The resulting Cl/Br ratios ranged from 37 to 71, with a mean of 55 and standard deviation of 13. These ratios are about a factor of two lower than the ~110 value arrived at by Dreibus and Wänke [2] for shergottite meteorites and glasses. The difference between the Cl/Br ratio of 55 deduced in this study for the Martian aqueous alteration products in Nakhla olivine veinlets, the ratio of 104 measured in the bulk sample [7], and the ratio of ~110 determined for the basaltic shergottites [2] is statistically

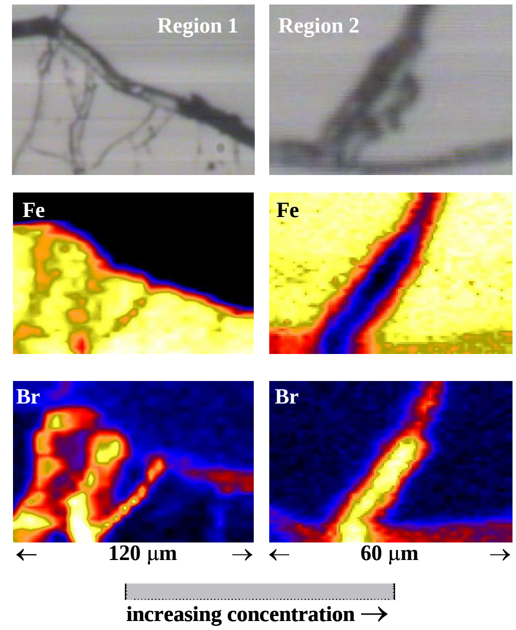

FIG. 1. Images of Region 1 (left column) and Region 2 (right column) on the Nakhla thin section. Top = optical micrograph, middle = Fe, bottom = Br.

Table 1. Chlorine and bromine microanalysis results.

Location	Bromine (ppm)	Chlorine (%)	Cl/Br
Region 1			
Map1-spot1	196	0.88	45
Map1-spot2	134	0.88	66
Region 2			
Map2-spot1	108	0.68	63
Map2-spot2	96	0.68	71
Map2-spot3	114	0.68	60
Region 3			
Map3-spot1	215	0.80	37
Map3-spot2	195	0.80	41
Mean	151	0.77	55
Standard deviation	49	0.09	13

significant. On the basis of Viking XRF measurements on Martian soil, Clark and Baird [11] estimated a value of ~100 ppm Br for the Martian soil. By using a Cl content of 0.6% for the Martian soil and Pathfinder measurements [12], we obtain a ratio of ~60 for the Martian soil. This value is in agreement with the Cl/Br ratio of 55 determined for the aqueous alteration products in Nakhla olivine veinlets in this study.

Our mean Cl/Br ratio is lower than the modern terrestrial sea water value of about 290 and the Earth's crust of 280 by about a factor of five [13]. These results show that the secondary altered material in Nakhla veinlets and grain boundaries is pristine, extraterrestrial, and akin to the Martian soil.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

This article appeared in S. R. Sutton, M. N. Rao, G. Dreibus, D. S. McKay, H. Wänke, S. Wentworth, M. Newville, T. Trainor, and G. J. Flynn, "Chlorine/ bromine ratios in fracture-filling aqueous alteration products in Nakhla olivine," Lunar and Planetary Science Conference XXXIII, paper 1278 on CD-ROM (2001).

[1] M. N. Rao et al., Icarus (in press, 2001).
[2] G. Dreibus and H. Wänke, Meteoritics **20**, 367-380 (1987).
[3] J. L. Gooding et al., Meteoritics **26**, 135-143 (1991).
[4] A. H. Treiman et al., Meteoritics **28**, 86-98 (1993).
[5] J. C. Bridges and M. M. Grady, Earth Planet. Sci. Lett. **176**, 267-279 (2000).
[6] S. J. Wentworth and D. S. McKay, Lunar and Planetary Science Conference XXX, paper 1946 (1999).
[7] G. Dreibus et al., Meteoritics & Planet. Sci. A **33** (1999).
[8] D. Xirouchakis et al., Geochim. Cosmochim. Acta (in press, 2001).
[9] S. R. Sutton et al., Lunar and Planetary Science Conference XXX, paper 1656 (1999).
[10] P. E. Eng et al., Society of Photo-optical Instrumentation Engineers (SPIE) Proc. **3449**, 145 (1998).
[11] B. C. Clark and A. K. Baird, Geophys. Res. Lett. **6**, 811-815 (1979).
[12] R. Rieder et al., Science **278**, 1771-1774 (1998).
[13] H. Wänke et al., in *Arch. Geochemistry*, edited by Kröner et al. (Springer, Berlin, Germany, 1984) pp. 1-24.