Raman spectroscopy of titanomagnetites: Calibration of the intensity of Raman peaks as a sensitive indicator for their Ti content

PAVEL ZININ,1,* LISA TATSUMI-PETROCHILOS,2 LYDIE BONAL,1 TAYRO ACOSTA,1 JULIA HAMMER,2 STUART GIDER,3 AND MIKE FULLER1

1Hawaii Institute of Geophysics and Planetology, Honolulu, Hawaii 96822, U.S.A.
2Department of Geology and Geophysics, University of Hawaii, Honolulu, Hawaii 96822, U.S.A.
3Department of Earth and Environmental Sciences-Geophysics, Munich University, Munich 80333, Germany

ABSTRACT

A systematic study of the Raman spectra of the titanomagnetite solid-solution series (Fe3−xTixO4) for x = −0.0, 0.2, 0.4, and 0.6 has been conducted. The samples showed combinations of five previously predicted Raman peaks at −190, 310, 460, 540, and 670 cm−1 that correspond to vibrational modes with Tg(1), Eg, Tg(3), Tg(2), and Ag, respectively. The calibration of Raman spectra for titanomagnetite with known values of Ti concentrations reveals a strong dependence of relative intensity for the Tg(2) and Tg(3) modes on Ti concentration. The most prominent feature is the appearance and increase in the relative intensity of a Tg(3) peak above x = −0.2. On the other hand, the Raman peak for the Tg(2) mode gradually diminishes as Ti increases and nearly disappears at x = −0.6. Combining the two relative intensities potentially provides a sensitive indicator of Ti content. The technique was applied to study titanomagnetite in grains from Hana Volcanics and melatroctolite from Rhode Island.

Keywords: Titanomagnetites, Raman spectroscopy, Fe-Ti oxides, spinel

INTRODUCTION

Iron-titanium oxide minerals are fundamental to paleo, rock, and environmental magnetic studies because they are the most common magnetic phases on Earth and serve as important carriers of the paleomagnetic record (Buddington and Lindsley 1964; Lindsley 1991; Rohrbach et al. 2007). The magnetic, electrical, and thermodynamic properties of these minerals depend on the concentration and distribution of Fe and Ti among sites of different symmetry in the structure (Lindsley 1976). Two Fe-Ti oxide solid-solution series are relevant for magnetic studies—the titanomagnetite (TM) and the titanohematite-hemoilmenite series (Franke et al. 2007). TM is the cubic spinel series between the magnetite (Fe3O4) and ulvöspinel (Fe2TiO4) end-members. The general TM formula is Fe3−xTixO4, where x is the mole fraction of the ulvöspinel component. Hereafter, TM compositions will be given as “TMx,” for example TM60 for x = 0.6.

The Raman spectra of the end-members of the titanomagnetite solid solution, magnetite (deFaria et al. 1997; Degiorgi et al. 1987; Gasparov et al. 2000; Shebanova and Lazor 2003a, 2003c; Verble 1974), ulvöspinel, and of some intermediate Ti compositions (Wang et al. 2004) are available. However, a systematic study of the changes of the line positions and their relative intensities as Ti is substituted into magnetite does not appear to have been reported. Here, we describe a study on the Raman spectroscopy of the titanomagnetites to see whether variation in chemical bonding can be used for their identification. Raman spectroscopy is commonly used for characterization in chemistry and materials science because the vibrational information gathered is very specific for the chemical bonds in molecules. Moreover, the most recent Raman microscopes have mapping capabilities that allow them to reveal the distribution of mineral phases with high spatial and spectral resolutions (Zinin et al. 2007). Raman spectroscopy can also be used as a tool to detect minerals remotely (Sharma et al. 2010). The proper identification of the Raman spectra of TM minerals may be of importance particularly now, when FeTi oxides were found in the Gusev crater on Mars (McSween et al. 2004). In the future, TM minerals may be identified using a remote Raman spectrometer.

The TM composition is an important parameter in studies on the magnetism of terrestrial and extraterrestrial materials. In planetary science applications, it has an additional advantage in that it can be measured remotely. In terrestrial work, Curie points are commonly used to determine the composition of these magnetic phases (Akimoto 1962). However, Curie points generally reflect bulk rock properties and do not provide insight for individual grains or intra-grain compositional variation in a sample. Determination of the composition of individual Fe-Ti oxide grains can also be made with electron microprobe techniques, electron backscatter diffraction in scanning electron microscopy (Franke et al. 2007), and X-ray diffraction (Madsen et al. 2009). However, all these techniques require special sample preparation and cannot be used in remote determinations of the Ti content of titanomagnetites.

We present results for the composition parameter x, defined by (Fe3−xTixO4), with x = −0.0, 0.2, 0.4, and 0.6, namely TM0, TM20, TM40, and TM60. The results from our systematic study were used to quantify the Ti content variations within and between titanomagnetite grains in a basaltic sample from the Hana volcano on Maui Island in the Hawaiian chain and in a melatroctolite sample from Cumberland, Rhode Island.

* E-mail: zinin@soest.hawaii.edu