Octahedral site Fe\textsuperscript{2+} quadrupole splitting distributions from the Mössbauer spectra of arrojadite

ISAMU SHINNO\textsuperscript{1,*} and ZHE LI\textsuperscript{2}

\textsuperscript{1}Graduate School of Social and Cultural Study, Kyushu University, Fukuoka 810, Japan
\textsuperscript{2}Institute of Geology, Chinese Academy of Science, Beijing 100029, China

ABSTRACT

The Mössbauer spectra of arrojadite, (K,Ba)(Na,Ca)\textsubscript{5}(Fe\textsuperscript{2+},Mn,Mg)\textsubscript{14}Al(PO\textsubscript{4})\textsubscript{12}(OH,F), at 298 and 95 K were investigated for the first time. The spectra at both temperatures were analyzed in terms of their Fe\textsuperscript{2+} quadrupole splitting distributions (QSDs). The overall QSDs at both temperatures can be interpreted in terms of five octahedral site Fe\textsuperscript{2+} QSD contributions. The quadratic elongation, $\xi$, and the variation of bond angles, $\delta$, for the different sites were calculated on the basis of the structural data obtained by Moore et al. (1981). The five QSD contributions are tentatively assigned to Fe\textsuperscript{2+} in the M3, M4, M5, M6, and M7 sites, based on the structural determination and the relation of the quadrupole splitting to the distortion of the octahedra, respectively. The Fe\textsuperscript{2+} ions are randomly distributed over the M3, M4, M5, M6, and M7 sites. In addition, Mössbauer data from arrojadite and related phosphate minerals indicate that the mean value of the isomer shift of Fe\textsuperscript{2+} in the octahedral sites in phosphate minerals is ~0.07 mm/s larger than that in silicate minerals. This difference is explained in terms of electron affinity.

INTRODUCTION

To date, many Mössbauer spectra of silicate and oxide minerals have been published, but relatively few Mössbauer studies concern phosphate minerals. Gonser and Grant (1967) first examined single and polycrystalline samples of naturally occurring vivianite, Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·8H\textsubscript{2}O; subsequently, the oxidation mechanism of vivianite has been investigated many times (Takashima and Ohashi 1968; Tricker and Ash 1979; Vochten et al. 1979; Dorman and Poullens 1980; McCammon and Burns 1980; Burns 1981). Chandra and Hoy (1967) reported that the ordered phase of ludlamite, Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}·4H\textsubscript{2}O, has a Mössbauer spectrum with two hyperfine fields below 15 K. Lithium orthophosphate, LiFe\textsubscript{0.8}Mn\textsubscript{0.2}PO\textsubscript{4}, orders antiferromagnetically at low temperature (Schideler and Terry 1969). Kostiner (1972) reported the Mössbauer parameters for the phosphate minerals tripleite, zwieselite, triploidite, and wolfeite. The cation distributions of the ternary orthophosphates, (Zn, Fe, Mo\textsubscript{0.5}Ni, Mn, Co), and (Co, Fe),(PO\textsubscript{4})\textsubscript{2}, having the farringtonite structure were investigated by Nord and Ericsson (1985) and Nord et al. (1985). The cation partitioning in hydrothermally prepared sarcopsites (Fe,Mn,Co,Mg)\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} was analyzed by means of X-ray powder diffraction and \textsuperscript{57}Fe Mössbauer spectroscopy (Ericsson et al. 1986; Charalampides et al. 1988). All of the above studies provide useful information on the crystal chemistry and bonding in phosphate minerals.

The arrojadite-dickinsonite family constitutes an alkali transition metal phosphate group. Several mineralogical studies on arrojadite-dickinsonite were carried out (Headden 1891; Ziegler 1914; Quensel 1937; Mason 1941; Guimarães 1942; Lindberg 1950). Moore and Ito (1979) analyzed 12 samples of the family and proposed the general formula $XY_5M$ Al(PO\textsubscript{4})\textsubscript{12}(OH,F), where $X = $ large cations such as K\textsuperscript{+}, Ba\textsuperscript{2+}, Y = (Na\textsuperscript{+}, Ca\textsuperscript{2+}) and $M = $ (Fe\textsuperscript{2+}, Mn\textsuperscript{2+} and Mg\textsuperscript{2+}). Moore et al. (1981) determined the crystal structure for the series using single-crystal X-ray diffraction. In this study, intrinsic Fe\textsuperscript{2+} QSDs were extracted from Mössbauer spectra of arrojadite at 298 and 95 K, and the iron distributions over the different sites are determined.

EXPERIMENTAL METHODS

The sample occurs as large cleavable masses in a granitic pegmatite from India associated with feldspar, quartz, muscovite, beryl, and spodumene. The purity of the arrojadite was checked using X-ray diffraction and no other phases were found. Its chemical composition was analyzed using a Cameca SX51 electron microprobe. The analyses were carried out on six arrojadite crystals with colors ranging from olive to grass green. The average composition is Na\textsubscript{2}O 6.83 (6.13–7.85), K\textsubscript{2}O 1.84 (1.70–1.88), FeO 28.33 (27.60–28.79), MgO 1.18 (1.01–1.24), Al\textsubscript{2}O\textsubscript{3} 2.45 (2.35–2.51), P\textsubscript{2}O\textsubscript{5} 41.71 (40.32–43.10), total 99.69 wt% (97.05–102.28), where the brackets denote the ranges. The chemical formula can be written as K\textsubscript{0.81}(Na\textsubscript{4.60}Ca\textsubscript{0.95})\textsubscript{5.55}(Mn\textsubscript{14.34}Fe\textsubscript{8.23}Mg\textsubscript{0.61})\textsubscript{13.18}Al\textsubscript{1.00}(P\textsubscript{12.25}O\textsubscript{48})(OH,F), based on 48 O atoms in the formula unit.

* E-mail: Shinno@rc.kyushu-u.ac.jp

0003-004X/98/1112–1316$05.00