MAGNETIC ORDERING IN THE NATURAL ORTHOPYROXENE Fe$_{0.87}$Mg$_{0.13}$SiO$_3$. By A. Wiedemann$^a$, J.R. Regnard$^b$ and S.S. Hafner$^b$.

$^a$DORF. CENG 85X F-38041 Grenoble, $^b$University Marburg, Marburg, F.R.G.

In the crystal structure of orthopyroxene Fe$_{0.87}$Mg$_{0.13}$SiO$_3$ two nonequivalent positions $M_1$ and $M_2$ of oxygen octahedra are occupied by Fe$^{2+}$ and Mg$^{2+}$ with a preference of Fe$^{2+}$ for the more distorted $M_2$ site. In the unit cell edge sharing octahedra build up four ribbons of infinite length along the c axis well separated from each other ($d=4.9\ \text{Å}$). Each ribbon consists of two linear chains of $N_2$ which enclose a zigzag chain of $M_4$ (Virgo and Hafner, Amer. Mineral. 1970 55, 201). Investigations of the magnetic properties of the natural pyroxene Fe$_{0.87}$Mg$_{0.13}$SiO$_3$ were performed on a polycrystalline sample of 100 mg. The powder susceptibility follows a Curie-Weiss law with $\Theta_p = 34\ \text{K}$ and $\mu_{eff} = 5.24\ \mu_B$, indicating large orbital contributions. $\chi$ exhibits an inflection point at $T_N = 26\ \text{K}$ reflecting an antiferromagnetic ordering. The onset of long range magnetic order at $T_N$ was confirmed by neutron diffraction. The propagation vector is $\mathbf{k} = [000]$ indicative for a collinear magnetic structure.

The ESR studies revealed no Cu$^{2+}$ signals for covellite over the whole temperature range and Cu$^{2+}$ signals for Cu$_4$Bi$_4$S$_9$ at $T = 173\ \text{K}$ ($g=1.91$) and for idaite at $T = 96\ \text{K}$ ($g=1.87$). Because of the charge balance of these phases, mixed valence state of Cu ($\sim 1.5+$) has to be suggested at temperatures without an ESR signal. This suggestion is verified in the case of idaite showing mixed valence state for Fe ($\sim 2.5+$) by Mössbauer studies with an isomer shift of $\delta = 0.35$ for tetrahedrally coordinated Fe. ESR studies on the phases kobellite and Cu$_4$Fe$_{1.2}$Bi$_{10.8}$S$_{22}$ show paramagnetic signals for Cu$^{2+}$ over the whole temperature range with $g=2.01$ and 2.019 respectively.

Mössbauer studies lead to Fe$^{2+}$ in both cases. An empirical term for the mixed valence state and/or the valence of 2+ for Cu in positive charge deficient sulfosalts is proposed.