

Mössbauer investigations of synthetic valleriite

Nataliya I. Chistyakova · Vyacheslav S. Rusakov ·
Tatyana V. Gubaidulina · Alexey M. Gapochka ·
Andrey Yu. Bychkov

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Abstract Samples obtained as a result of the valleriite synthesis process under different conditions (temperature and proportion Cu:Fe:Mg in the initial mixture) were investigated by ^{57}Fe Mössbauer spectroscopy with attraction data of X-ray diffraction. Parameters of hyperfine interactions for valleriite were determined and crystal chemical identification of ^{57}Fe subspectra was carried out. It was found that valleriite was formed in samples synthesized at 150°C and 180°C and not formed in samples synthesized at 250°C.

Keywords ^{57}Fe Mössbauer spectroscopy · Valleriite

1 Introduction

Valleriite belong to incommensurable and modulated mixed-layer minerals. Valleriite is hydroxide-sulfides with mixed layered crystal structure. Common chemical formula of valleriite $\text{CuFeS}_2 \cdot \{n[\text{Mg,Fe}(\text{OH})_2] + m(\text{Al,Fe})(\text{OH})_3\}$, where $1.3 \leq n \leq 1.6$ and $0 \leq m \leq 0.3$. In valleriite structure double sulfide layers with iron and copper cations presented in tetrahedral sites are situated between hydroxide brucite-like layers. Sulfide layers of valleriite are constructed of tetrahedra lying on their bases, at that all tetrahedral positions are filled in with statistically distributed iron and copper atoms. In the general case in brucite-like layers of valleriite divalent and trivalent cations are located in positions with octahedral environment of OH-groups [1].

N. I. Chistyakova (✉) · V. S. Rusakov · T. V. Gubaidulina · A. M. Gapochka
Faculty of Physics, M.V. Lomonosov Moscow State University,
Moscow, Russia
e-mail: nchistyakova@yandex.ru

A. Yu. Bychkov
Faculty of Geology, M.V. Lomonosov Moscow State University,
Moscow, Russia

2 Experimental

The objects for our investigation were four series of samples obtained as a result of the valleriite synthesis process under different conditions: temperature of synthesis and proportion Cu:Fe:Mg in the initial mixture. An sulphate aqueous solution was prepared by mixing 1 M H_2SO_4 , FeSO_4 , CuSO_4 and MgSO_4 solution in different proportions Cu:Fe:Mg. Then, sulphides quantitatively precipitated by addition of Na_2S solution produced by saturation of NaOH with gaseous H_2S . This reaction produces amorphous iron and copper sulphides. Then phases were placed with its supernatant solution in steel autoclave with Teflon liner at 150°C (exp. №3), 180°C (exp. №1 and 2) and 250°C (exp. №4) for 30 days. After the recrystallization sulphide precipitate was washed with distilled water and acetone and dried. Experiment №2 differs from experiment №1 by excess of sulfide sulfur Na_2S .

The produced crystal phases up to 10 micron size were studied by electron microscope. X-ray powder diffraction patterns of the sulphides were taken with a universal X-ray diffractometer (DRON-UM1) that measures the X-ray intensity distribution for oriented and powder samples using $\text{Co-K}\alpha$ radiation with Fe filter ($V = 35 \text{ kV}$, $A = 25 \text{ mA}$). Measurements were made automatically with step 0.02° at speed of $4^\circ/\text{min}$. X-ray spectra were processed by the internal software XRAY and the Pcpdf 2003 database for the analysis of diffraction powder patterns.

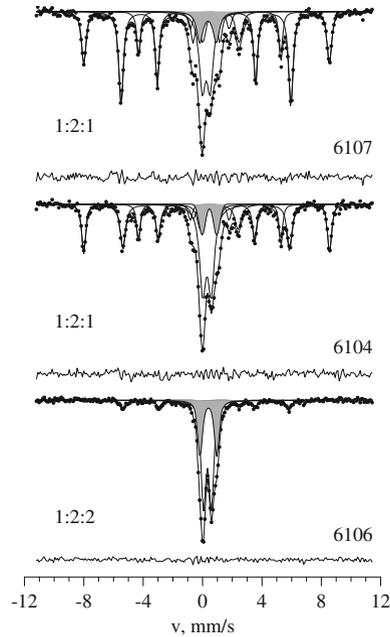
The ^{57}Fe Mössbauer study was carried out at room temperature on the spectrometer operated in constant acceleration mode and equipped with a ^{57}Co -source into Rh-matrix. The calibration was accomplished relatively $\alpha\text{-Fe}$. The program SpectrRelax from MSTools Complex was used for spectrum model fitting [2].

3 Results and discussion

Samples obtained as a result of the valleriite synthesis process at temperatures equal to 150°C , 180°C and 250°C and different proportions Cu:Fe:Mg in initial mixture were investigated by ^{57}Fe Mössbauer spectroscopy. X-Ray powder diffraction data are in a good agreement with data obtained in [3] for synthetic valleriite. It was found that all investigated samples are multiphase. We note that valleriite phase was not detected in samples synthesized at 250°C . The ^{57}Fe Mössbauer spectra of investigated samples are present on Figs. 1, 2 and 3.

In all experimental Mössbauer spectra of samples synthesized at 150°C and 180°C quadrupole doublets with values of Mössbauer line shift $\delta = 0.39 \div 0.54 \text{ mm/s}$ and quadrupole shift $\varepsilon = 0.46 \div 0.56 \text{ mm/s}$ were obtained (shaded subspectra on Figs. 1, 2, 3). The subspectrum with the parameter values corresponds to Fe^{2+} cations located in the positions of a tetrahedral environment of sulfur atoms [4]. Since it is known that sulfide layers of valleriite are constructed of tetrahedra, at that all positions are filled in with statistically distributed iron and copper atoms, we can assume that this quadrupole doublet corresponds to Fe atoms in sulfide layers of valleriite. Besides, subspectra with similar values of hyperfine parameters were obtained earlier in Mössbauer spectra of natural valleriite from North Korea and Sweden [5, 6]. In [7] analogue quadrupole doublets with $\delta = 0.42 \div 0.48 \text{ mm/s}$ and quadrupole splitting $\Delta = 2\varepsilon = 0.81 \div 1.28 \text{ mm/s}$ also were detected in Mössbauer spectra of natural valleriite and were interpreted as subspectra of sulfide layers of

Fig. 1 The ^{57}Fe Mössbauer spectra of samples synthesized at different proportion Cu:Fe:Mg and $t = 180^\circ\text{C}$ (exp. №1)



valleriite. Mössbauer spectra of valleriite in [8] were processed by four quadrupole doublets. The doublet with similar parameters $\delta = 0.42 \div 0.42 \text{ mm/s}$ and $\Delta = 1.12 \div 1.32 \text{ mm/s}$ was attributed to Fe^{2+} atoms and doublets with $\delta = 0.24 \div 0.41 \text{ mm/s}$ and $\Delta = 0.74 \div 0.89 \text{ mm/s}$ – to Fe^{3+} in sulfide layer respectively. The fourth doublet with $\delta = 0.22 \div 0.28 \text{ mm/s}$ and $\Delta = 0.30 \div 0.28 \text{ mm/s}$ corresponded to Fe^{3+} in the hydroxide lattice.

In all spectra of investigated samples (Figs. 1, 2, 3) central quadrupole doublets with average values of hyperfine parameters $\delta \approx 0.30 \text{ mm/s}$ and $\varepsilon \approx 0.30 \text{ mm/s}$ and low-intensity quadrupole doublets with parameters $\delta \approx 1.1 \text{ mm/s}$ and $\varepsilon \approx 1.2 \text{ mm/s}$ were detected. These subspectra respectively correspond to tri- and divalent iron cations located in octahedral environment of oxygen atoms [4]. Since hydroxide brucite-like layers of valleriite may contain both Fe^{3+} and Fe^{2+} atoms, detected doublets can be attributed to valleriite brucite-like layers. On the other hand in accordance with [8] the first doublet can also be consistent with tetrahedrally coordinated Fe^{3+} atoms in sulfide layers. Moreover relative intensities of quadrupole doublets corresponding to divalent Fe cations are much lower than relative intensities of quadrupole doublets corresponding to trivalent Fe cations. But it should be noted that according to [9] parameters of hyperfine interactions of ^{57}Fe nuclei in pyrite FeS_2 are the values $\delta \approx 0.30 \text{ mm/s}$ and $\varepsilon \approx 0.30 \text{ mm/s}$. Therefore central quadrupole doublet in experimental spectra may correspond to sulfide phase, which is not related to valleriite.

The model fitting and analysis of measured experimental spectra showed that all synthesized samples contained considerable (relatively the total iron content in the sample) amounts of chalcopyrite CuFeS_2 . Zeeman sextet with parameters $\delta \approx 0.24 \text{ mm/s}$ and hyperfine magnetic field on ^{57}Fe nuclei $H_n \approx 350 \text{ kOe}$ in Mössbauer

Fig. 2 The ^{57}Fe Mössbauer spectra of samples synthesized at different proportion Cu:Fe:Mg and $t = 180^\circ\text{C}$ (exp. №2)

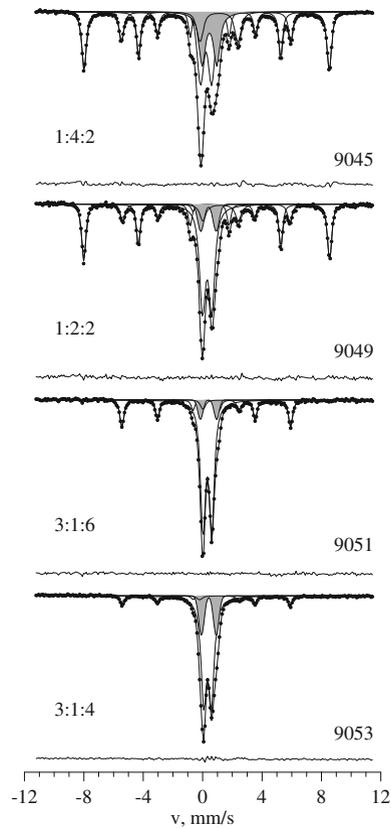
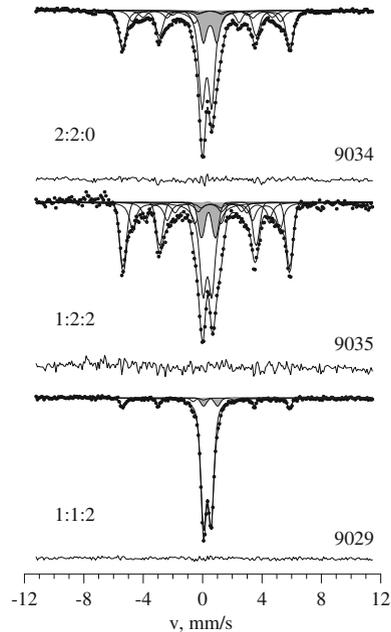


Fig. 3 The ^{57}Fe Mössbauer spectra of samples synthesized at different proportion Cu:Fe:Mg and $t = 150^\circ\text{C}$ (exp. №3)



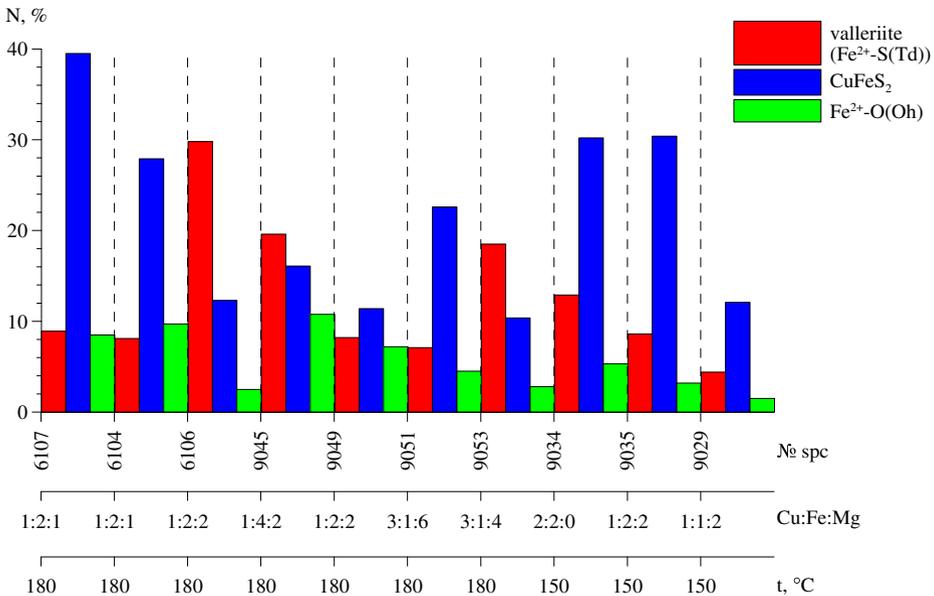


Fig. 4 Relative intensities of obtained subspectra of ^{57}Fe atoms in different phases depending on Cu:Fe:Mg proportion in initial mixture and synthesis temperature. The estimation of statistical errors of relative intensities is about 1–2%

spectra (Figs. 1, 2, 3) is related to ^{57}Fe atoms in chalcopyrite. Besides, in samples 6104, 6107, 9045 and 9049 hematite was detected. In samples 9034 and 9035 admixture of magnetically ordered phase with values of hyperfine magnetic fields H_n about 245 kOe and 310 kOe were exhibited.

The diagram, which shows relative intensities of detected subspectra corresponding to sulfide layers of valleriite, chalcopyrite and Fe^{2+} cations in octahedral environment of oxygen atoms is presented on Fig. 4. The most relative amount of valleriite formed in samples 6106, 9045 and 9053 synthesized at 180°C and with following proportions Cu:Fe:Mg in initial mixture 1:2:2, 1:4:2, 3:1:4. The comparison of two samples synthesized with equal proportions Cu:Fe:Mg = 1:2:2 but at different temperatures 180°C and 150°C (samples 6106 and 9035) shows (Fig. 4) that relative content of valleriite in samples 6106 significantly exceeds relative content of valleriite in sample 9035, i.e. in sample which was synthesized at higher temperature (180°C). Samples 6106 and 9049 were synthesized at equal temperature (180°C) and proportion Cu:Fe:Mg = 1:2:2. However the relative content of phases is different in these samples (Fig. 4). Apparently this is due to excess of Na_2S in synthesis process of sample 9049 as compared with sample 6106.

4 Conclusions

It was found that valleriite was formed at synthesis temperatures 150°C and 180°C and not formed at higher temperature (250°C). Most relative amount of valleriite

was contained in samples synthesized at 180°C and with proportions Cu:Fe:Mg in initial mixture equal to 1:2:2, 1:4:2, 3:1:4.

It was shown that hyperfine parameters values of subspectra corresponding to the sulfide layers of valleriite are $\delta = 0.39 \div 0.54$ mm/s and $\varepsilon = 0.46 \div 0.56$ mm/s. In Mössbauer spectra of samples synthesized at 150°C and 180°C quadrupole doublets with parameters $\delta \approx 1.1$ mm/s and $\varepsilon \approx 1.2$ mm/s were detected and these subspectra could correspond to iron positions in the hydroxide layers of valleriite.

References

1. Organova, N.I.: *Crystal Chemistry of Incommensurable and Modulated Mixed-layer Minerals*. Nauka, Moscow (1989)
2. Rusakov, V.S.: *Mössbauer Spectroscopy of Locally Inhomogeneous Systems* Institute of Nuclear Physics. National Nuclear Center of the Republic of Kazakhstan, Almaty (2000)
3. Iiishi, K., Tomisaka, T., Kato, T., Takeno, S.: *Am. Mineral.* **55**, 2107 (1970)
4. Reiff, W.M.: Mixed oxidation states and averaged electronic environments in iron compounds. In: Gruverman, I.J., Seidel, C.W. (eds.) *Mössbauer Effect Methodology*, vol. 8. L. Plenum Press, NY (1973)
5. Chistyakova, N.I., Gubaidulina, T.V., Rusakov, V.S.: *Czechoslov. J. Phys.* **56**(Suppl.E), E123 (2006)
6. Gubaidulina, T.V., Chistyakova, N.I., Rusakov, V.S.: *Bull. Russ. Acad. Sci. Phys.* **71**(9), 1269 (2007)
7. Shan, Q., Zhengmin C., Yanjing, C.: *Chin. Sci. Bull.* **41**, 1982 (1996)
8. Waanders, F.B., Pollak, H., Lachmann, G.: *S. Afr. J. Sci.* **95**(9), 387 (1999)
9. Vaughan, D., Craig, J.: *Mineral Chemistry of Metal Sulfides*. Cambridge University Press, Cambridge, London-New York-Melbourne (1978)