The crystal chemistry of iron-nickel thiospinels

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Abstract

The crystal chemistry and mineralogical properties of the thiospinels of the series polydymite (Ni_3S_4)–violarite ($FeNi_2S_4$)–greigite (Fe_3S_4) have been studied using synthetic and natural samples and emphasizing the intermediate compositions ("violarites," $(Fe, Ni)_3S_4$). In the series Ni_3S_4–$FeNi_2S_4$, increasing iron correlates with increasing thermal stability, a nearly linear decrease in a and increase in reflectance (R% at 589 nm), although spectral reflectance curves show more complex behavior. Mössbauer spectra of ^{57}Fe for a series of compositions between $Fe_{0.25}Ni_{2.75}S_4$ and $FeNi_2S_4$ consist essentially of a doublet with a small isomer shift and quadrupole splitting, the former increasing with increasing iron (0.23–0.53 mm/sec). This is interpreted as low-spin Fe^{2+} in the octahedral sites, although further examination of the spectra suggests a possible contribution from iron ($\sim 18\%$) in tetrahedral coordination. These data are in agreement with bonding models previously proposed for the thiospinels.

Although electron microprobe analyses of natural samples indicate that solid solution extends completely from Ni_3S_4 to Fe_3S_4, bonding models suggest that compositions more iron-rich than $FeNi_2S_4$ may be metastable. The formation of such possibly metastable compositions, the observation in this work of violarites which are 1–2 wt.% sulfur-poor relative to stoichiometric M_3S_4, and the confusion over the low-temperaure phase relations involving violarite are all attributed to its formation by alteration of pre-existing minerals (notably pentlandite). Reaction mechanism and kinetics are therefore crucial in the formation of this mineral in nature.

Introduction

The thiospinel (or sulfospinel) minerals are a group which exemplify a number of problems of general interest in sulfide mineralogy. This contribution is part of a program of study of the thiospinels by the authors and aimed at a fuller understanding of their crystal chemistry, thermochemistry, phase relations and occurrence. Although the mineral thiospinels, M_3S_4 sulfides where M can be Fe, Co, Ni, Cu, Cr, In and possibly Pt, are named according to ideal end-member compositions, extensive solid solutions are common involving two major and one (or sometimes two) minor cations. Previous work (Vaughan et al., 1971; Vaughan and Craig, 1978; Craig et al., 1979a, 1979b) has shown that the thiospinel series carrollite ($CuCo_2S_4$)–linnaeite (Co_3S_4)–polydymite (Ni_3S_4)–violarite ($FeNi_2S_4$) is characterized by extensive solid solution. The present work is concerned with the polydymite–violarite series although natural compositions of this series also frequently contain some of the Co_3S_4 (linnaeite) molecule. For simplicity in this paper, all iron-nickel thiospinels

((Ni,Fe)$_3$S$_4$ with or without other minor cations) will be termed "violarites," except for the endmembers, polydymite (Ni_3S_4) and greigite (Fe_3S_4). These are all metallic minerals, the properties of which have been described in terms of bonding models by Vaughan et al. (1971) and Vaughan and Tossell (1981). Violarites are quite common secondary minerals in pentlandite-bearing ores (Misra and Fleet, 1974) and constitute at least locally important sources of nickel. Greigite occurs commonly only in recent sediments.

Synthetic violarites: structure, composition and properties

The violarites have the familiar spinel crystal structure which is based on a cubic close-packed sulfur sublattice with half the octahedral sites and one-eighth of the tetrahedral sites occupied by cations (Lundqvist, 1947). The cubic unit cell contains eight AB_2S_4 formula units and there are, therefore, one tetrahedral (A) cation site and two octahedral (B) cation sites per formula unit which are occupied. The tetrahedral A sites are regular but the octa-

hedral B sites show trigonal distortion along different [111] directions of the cubic unit cell. Each sulfur atom is four-coordinated to three cations in octahedral B sites and one cation in a tetrahedral A site as shown in Figure 1.

The thiospinels, like the oxide spinels, have normally been referred to the cubic space group $Fd3m$, but Grimes (1972) has suggested that the space group $F\bar{4}3m$ may be more appropriate to many of these compounds. This is consistent with evidence that the octahedrally coordinated metal ions may be "off-center" and displaced along [111] directions. Higgins et al. (1975) have found evidence from X-ray diffraction that the thiospinels carrollite, linnaeite and siegenite possess a symmetry lower than $Fd3m$ but consistent with several other cubic space groups, including $F\bar{4}3m$. Grimes (1974), on the other hand, examined powder diffraction data and found only a slight improvement in fitting of the data when the space group $F\bar{4}3m$ was applied to $CuCo_2S_4$, whereas for many oxide spinels the improvement was appreciable. Other studies have also found that cation ordering on octahedral sites in $Fe_{0.76}Yb_{2.16}S_4$ (Tomas and Guittard, 1977) and on tetrahedral sites in $FeIn_2S_4$ (Hill et al., 1978) reduces those thiospinels to $F\bar{4}3m$ symmetry. Uncertainty remains, therefore, regarding the precise structure of the thiospinels but there seems to be at least some evidence to support a structure with lower symmetry than $Fd3m$.

Although in oxide spinels, divalent and trivalent cations occur in tetrahedral and octahedral sites giving *normal* and *inverse* spinel types, the assignment of formal oxidation states to the cations in thiospinels is not straightforward. This is further discussed for the violarites in relation to Mössbauer data presented in the following section. Structural variations as a function of composition in the series Ni_3S_4–$FeNi_2S_4$ (–Fe_3S_4) will also be discussed more fully in a later part of this paper but the most readily monitored changes are those which occur in the unit-cell parameter.

Precise measurements of the unit-cell dimension of compositions between Ni_3S_4 and $FeNi_2S_4$ were undertaken on synthetic samples during this work. Violarite thiospinels were synthesized by conventional silica tube techniques (Kullerud, 1971; Vaughan and Craig, 1978) and by means of the multiple reaction techniques previously used for violarite synthesis (Craig, 1971). Reagents used were 99.999 + % pure iron, nickel and sulfur as shown by supplier's (ASARCO) analyses. Iron was reduced in a stream of hydrogen at 700°C before being used in the experiments which were performed in nichrome wound resistance furnaces controlled to within ±3°C. Following initial reaction and homogenization as $(Fe, Ni)_{1-x}S$ at 700°C, sulfur was added and samples were annealed at 300°C. Quenched charges were examined by reflected light microscopy and electron microprobe analysis as well as X-ray powder diffraction. Electron microprobe data were obtained using either an ARL-EMX or an ARL-SEMQ instrument at 15 kV accelerating voltage and 0.15 µA sample current. Synthetic NiS and FeS were used as standards. In the cell dimension measurements, National Bureau of Standards silicon ($a = 5.43088Å$) was used as an internal standard.
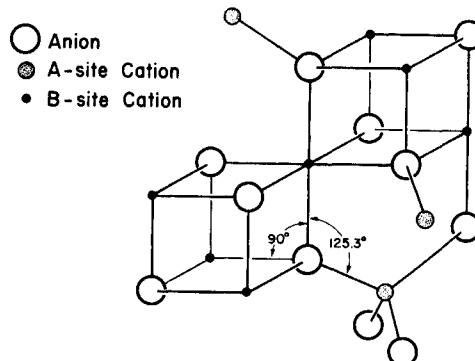
Spinel Structure

Fig. 1. The spinel crystal structure showing the relationships between cations in octahedral and tetrahedral coordination.

The variation in cell parameter with composition in the series Ni_3S_4–$FeNi_2S_4$, is shown in Figure 2. The data show a linear variation throughout most of the series although with a slight flattening out at the $FeNi_2S_4$ end. Greigite, Fe_3S_4, has a much greater cell parameter ($a = 9.876Å$) than any of the values shown here and the effect of nickel substitution in greigite on cell parameters is not known at present.

The compositional limits and stabilities of synthetic violarites can be considered with reference to the Fe–Ni–S ternary system and the $FeNi_2S_4$–Ni_3S_4 pseudobinary join. The latter shows that complete Ni_3S_4–$FeNi_2S_4$ solid solution exists below 356°C; above 356°C Ni_3S_4 decomposes and only successively more iron-rich compositions are stable to a maximum temperature of 461°C at the $FeNi_2S_4$ end (Craig, 1971). It is to be emphasized that compositions more iron-rich than $FeNi_2S_4$ have not been synthesized.

Phase relations in the Fe–Ni–S system have been established at high temperatures by the work of Kullerud (1963), Naldrett et al. (1967) and Misra and Fleet (1973). Craig (1971) found that the $FeNi_2S_4$ endmember becomes
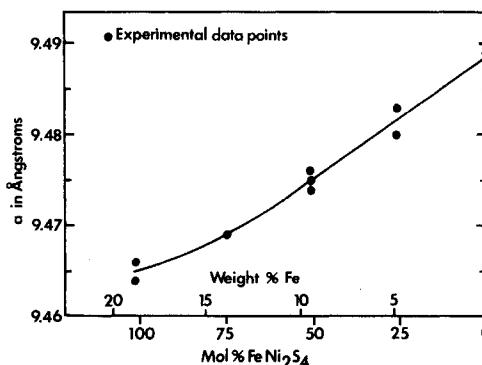

Fig. 2. Variation in unit cell parameter (a) with composition between $FeNi_2S_4$ and Ni_3S_4. The unit cell parameter of Fe_3S_4 is 9.876Å.

stable below 461°C with tie lines to nickeloan pyrite (Fe, Ni)S_2, ferroan vaesite (Ni, Fe)S_2 and the monosulfide solid solution (Fe, Ni)$_{1-x}$S. At lower temperatures, with the breakdown of the monosulfide solid solution (mss) below 300°C, phase relations involving violarites are still confused since conflicting evidence is available from experimental studies and the examination of natural assemblages. In particular, confusion exists over whether pyrite–millerite or pentlandite–violarite constitute the stable assemblage (Graterol and Naldrett, 1971; Craig, 1973; Keele and Nickel, 1974; Hudson and Groves, 1974; Misra and Fleet, 1974).

Certain mineral properties of the violarites synthesized in this work have also been studied. In particular, measurements have been made of the spectral reflectance of compositions between Ni_3S_4 and $FeNi_2S_4$. Measurements were made with the Reichert Spectral Microphotometer using a WTiC standard approved by the Commission on Ore Microscopy. The data are presented in Figure 3 and show that at 589 nm there is a systematic decrease in reflectance from $FeNi_2S_4$ to Ni_3S_4 (Fig. 3a). Spectral reflectance curves between 420 and 640 nm wavelength (Fig. 3b) show appreciable dispersion with maxima towards the red end of the spectrum. The correspondence of the shapes of the dispersion curves with compositional variation accounts for the subtle, although readily observable, color variations observed in violarites.

Fig. 4. Mössbauer spectra for violarites of varying iron content; the zero of the velocity scale is the center of gravity of an iron foil spectrum.
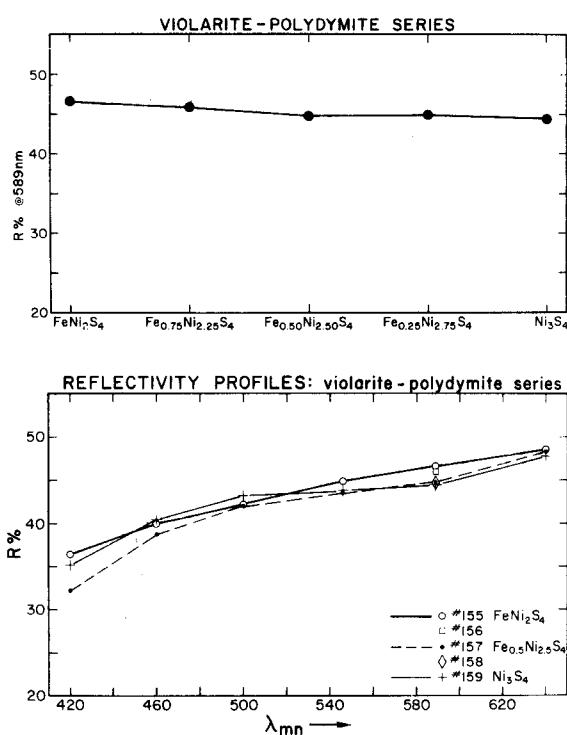

Fig. 3. Spectral reflectance data for violarites: (a) variation of reflectance at 589 nm with composition; (b) spectral reflectance curves for different compositions.
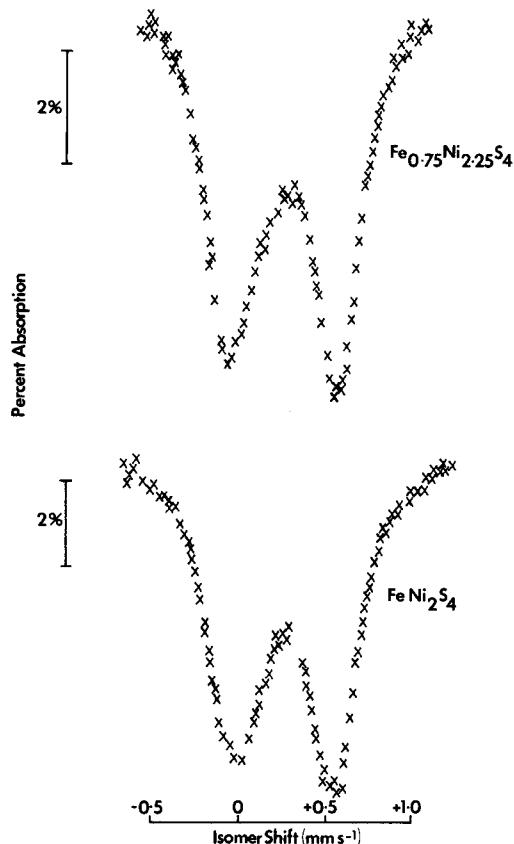
Mössbauer studies of synthetic violarites

Synthetic violarites of compositions $FeNi_2S_4$, $Fe_{0.75}Ni_{2.25}S_4$, $Fe_{0.5}Ni_{2.5}S_4$ and $Fe_{0.25}Ni_{2.75}S_4$ have been studied using ^{57}Fe Mössbauer spectroscopy. Room temperature spectra were obtained using a standard spectrometer with ^{57}Co as the source of γ-rays. The spectrometer was calibrated using iron foil and isomer shift data quoted are all relative to the center of gravity of the iron spectrum taken as zero.

The Mössbauer spectrum of $FeNi_2S_4$ (Fig. 4) consists essentially of a quadrupole doublet with a small isomer shift and splitting (Table 1). This is in agreement with previous reports of Mössbauer data for this thiospinel end-member (Vaughan et al., 1971; Townsend et al., 1977). The spectrum can be fitted to a simple doublet as shown in Figure 5. In this and all the other attempts at computer fitting of the spectra, the program used was that written by Stone (see Bancroft et al., 1967) which provides a least-squares fit of overlapping Lorentzian peaks. Parameters obtained from the fitting procedures are presented in Table 1. This simple doublet has a small isomer shift (0.28 mm/sec) and quadrupole splitting (0.54 mm/sec) which has

Table 1. ^{57}Fe Mössbauer data for synthetic violarites and related sulfides (all data with the absorber at room temperature unless otherwise stated).

Composition		Isomer Shift (mm sec^{-1})*	Quadrupole Splitting (mm sec^{-1})
(a) Synthetic violarites-two peak fits (x^2 values ~354)			
$FeNi_2S_4$		0.29 (±0.01)	0.54 (±0.02)
$Fe_{0.75}Ni_{2.25}S_4$		0.28 (±0.01)	0.59 (±0.02)
$Fe_{0.50}Ni_{2.50}S_4$		0.26 (±0.01)	0.62 (±0.01)
$Fe_{0.25}Ni_{2.75}S_4$		0.23 (±0.01)	0.61 (±0.02)
(b) Synthetic violarite-four peak fits (x^2 value 268)			
$FeNi_2S_4$ [82% area] (a)		0.25 (±0.015)	0.56 (±0.01)
[18% area] (b)		0.38 (±0.015)	0.48 (±0.02)
(c) Related sulfides**			
FeS_2 (pyrite)		0.31 (±0.002)	0.61 (±0.06)
$(Fe,Ni)_9S_8$(pentlandite)			
(tetrahedral site Fe)		0.36 (±0.002)	0.37 (±0.002)
Fe_3S_4 (greigite)			
at 4.2K	(a)	0.70	0.30
		(H_{loc} = 322 Kgauss)+	
	(b)	0.45	0.40
		(H_{loc} = 465 Kgauss)+	
	(c)	0.40	0.0
		(H_{loc} = 486 Kgauss)+	

* all isomer shifts quoted relative to the centre of gravity of an iron foil spectrum as zero

** see Vaughan and Craig, 1978, for data sources

+ internal magnetic field at the iron nucleus

intensity of the two major peaks. (The low velocity peak has ~52 to ~54% of the total intensity). Although there are a number of possible explanations for this asymmetry, the most obvious would be that a second quadrupole doublet is present and the experimentally observed envelope results from a superimposition of the two doublets. Attempts at computer fitting were therefore undertaken employing two quadrupole doublets. This results in significantly better fits (e.g., χ^2 for $FeNi_2S_4$: 2 peak fit = 354; 4 peak fit = 268) and the four peak fit for $FeNi_2S_4$ is illustrated in Figure 6 with data presented in Table 1. The second doublet comprises 18% (±4%) of the overall intensity. It is possible that this doublet represents iron in tetrahedral sites in violarite. Since the material is a metallic, Pauli paramagnetic phase, such iron should be comparable to that in the tetrahedral sites in pentlandite (see Table 1) and the values do show reasonable agreement with those reported for pentlandite.

Additional doublets may also arise through different next-nearest-neighbor coordination, as observed by Reidel and Karl (1981) for tetrahedral site Fe^{2+} ions in the system $FeCr_2S_4$-Fe_3S_4. However, although such differences produce large changes in quadrupole splitting, the changes produced in isomer shifts are very small compared to those observed here. Also, attempts to obtain a consistent trend in parameters and in the intensity of the second doublet with varying Fe:Ni ratio proved unsuccessful. Another possibility is that some octahedral site iron has been oxidized to Fe^{3+}. This also seems unlikely as every precaution was taken in sample preparation to prevent oxidation. However the parameter of the second doublet ((b) in Table 1) in the $FeNi_2S_4$ spectrum are very similar to those as-

been interpreted as due to low-spin Fe^{2+} in the octahedral sites in the spinel structure (Vaughan et al., 1971). Townsend et al. (1977) reported thermoelectric power and magnetic susceptibility results for violarite in addition to Mössbauer spectra at temperatures down to 5 K. All the results unambiguously show that violarite exhibits metallic, Pauli paramagnetic behavior. The assumption that the iron in $FeNi_2S_4$ occurs as low-spin Fe^{2+} in octahedral sites is supported by the correlation in isomer shift and quadrupole splitting values with low-spin Fe^{2+} in pyrite (see Table 1).

If this simple interpretation of the Mössbauer spectrum of $FeNi_2S_4$ is accepted, two-peak fits can be applied to the spectra from the compositions which contain successively smaller amounts of iron (Fig. 4). The results (Table 1) show that with successive decrease in iron content there is a systematic decrease in isomer shift and increase in quadrupole splitting (0.28 mm/sec–0.23 mm/sec and 0.53 mm/sec–0.61 mm/sec respectively). This could be interpreted as the result of changes in the occupancy of next-nearest-neighbor (cation) sites producing slightly more asymmetric electronic environments around the nucleus, and slight changes in the s electron density at the nucleus.

Closer examination of the spectra of the violarites shown in Figure 4 shows a distinct, though small, difference in
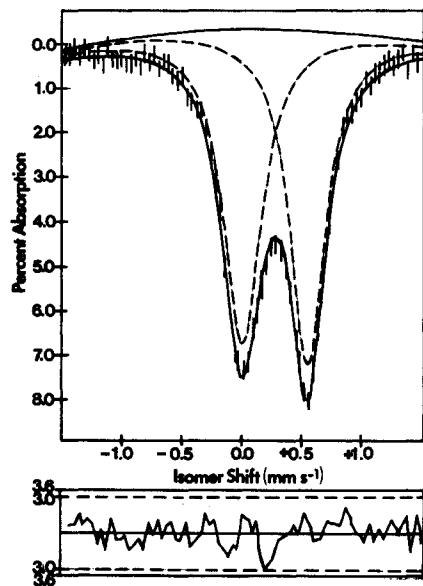

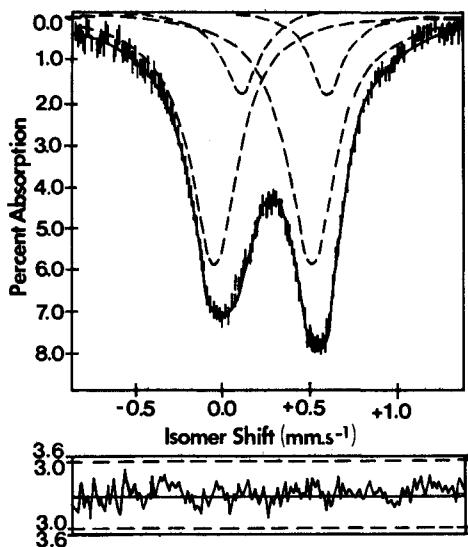Fig. 5. Computer fit of a simple doublet to the Mössbauer spectrum of $FeNi_2S_4$.

Fig. 6. Computer fit of two doublets to the Mössbauer spectrum of $FeNi_2S_4$.

signed by Reidel and Karl (1981) to high-spin Fe^{3+} ions in octahedral sites in $Fe_{1+x}Cr_{2-x}S_4$.

The Mössbauer spectrum of greigite (Fe_3S_4), the pure iron analogue of violarite, contrasts strongly with the violarites (Vaughan and Ridout, 1971). At 4.2 K, it has been resolved into three sets of six-line magnetic hyperfine spectra attributed to high-spin Fe^{3+} ions in tetrahedral A sites and octahedral B sites. Greigite is, therefore, an inverse spinel and the sulfur analogue of magnetite as also confirmed by the work of Coey et al. (1970) although they observed only a single species on the octahedral sites as a result of electron hopping between "Fe^{2+}" and "Fe^{3+}".

Natural violarites: compositions, occurrence and associations

During this work the compositions of numerous natural violarites (as well as certain of the coexisting sulfides) have been determined by electron microprobe analysis using the instruments and standards already described. In addition, numerous analyses have been assembled from data already in the literature. These data are presented in Table 2.[1] Compositions of natural iron-nickel thiospinels are also plotted on Figure 7 in terms of relative amounts of Ni_3S_4–Fe_3S_4–Co_3S_4 endmembers since minor cobalt is frequently present in violarites. A very important observation immediately seen from this diagram is that, unlike the synthetic iron-nickel thiospinels which do not form compositions more iron-rich than $FeNi_2S_4$, the natural samples show a complete compositional range from Ni_3S_4 to

[1] To obtain a copy of Table 2, order Document AM-85-275 from the Mineralogical Society of America, Business Office, 2000 Florida Ave., N.W., Washington, D.C. 20009. Please remit $5.00 in advance for the microfiche.

Fe_3S_4. Misra and Fleet (1974) have already reported natural "violarite" compositions indicating a solid solution extending to nickel contents as low as 17 atomic percent; the data in Figure 7 show essentially complete violarite–greigite solid solution. For Figure 7 perfect M_3S_4 stoichiometry is assumed but the nature and extent of any variation in M:S ratio in this series can also be considered using a triangular Fe–Ni–S plot as shown in Figure 8. It is remarkable that of the 74 analyses shown here, only two plot in the field of excess sulfur. A few of the analyses lie on the line joining stoichiometric $FeNi_2S_4$ and Ni_3S_4 but most are sulfur-deficient by 1–2 wt.% sulfur. This strongly suggests a real trend to sulfur-poor compositions in natural violarites, an observation first noted by Desborough and Czamanske (1973) and later supported by Misra and Fleet (1974) and by Craig and Vaughan (1976). Like Misra and Fleet (1974) we find no clear evidence to support the alternative stoichiometry of $(Fe, Ni)_9S_{11}$ suggested by Desborough and Czamanske (1973). A note of caution should be added, however, because most natural violarites are extremely porous and many of the microprobe analyses reported have totals less than 98%. Any preferential loss of SK_α X-rays as a result of the porosity would bias the results shown in Figure 8. Nevertheless, the consistency of low sulfur contents observed by so many workers suggests that it is a real phenomenon.

Polydymite is an uncommon mineral known primarily from scattered occurrences in hydrothermal vein deposits. Violarite, on the other hand, is a widespread and well-known secondary mineral formed in the weathering of nickeliferous pyrrhotite ores associated with mafic rocks. In such occurrences, it is generally present as rims on hypogene pentlandite where it apparently forms through the selective removal of cations from the pre-existing structure.
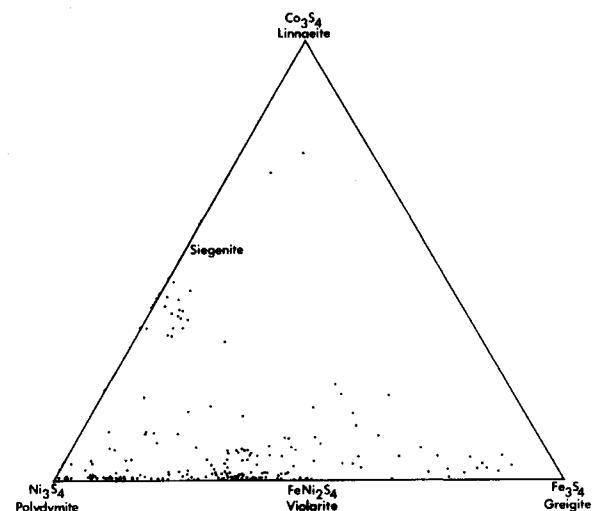

Fig. 7. Compositions of natural iron-nickel thiospinels shown in terms of Fe_3S_4–Ni_3S_4–Co_3S_4 endmembers to illustrate the variation in cation contents (for sources of data see Table 2).
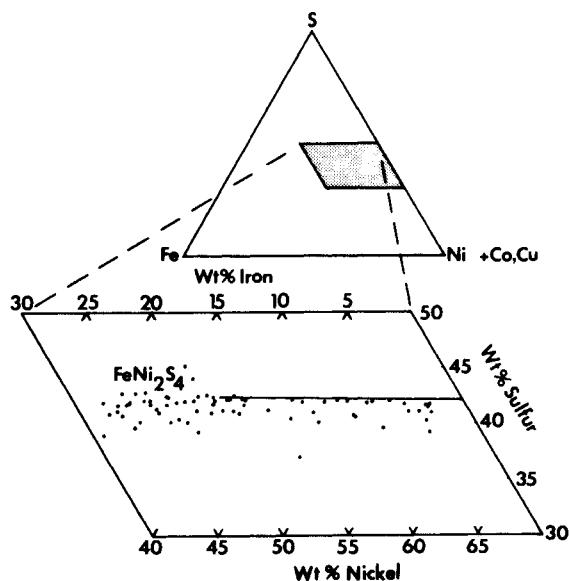
Fig. 8. Compositions of natural iron-nickel thiospinels shown in terms of Fe, Ni and S content (for sources of data, see Table 2).

these models have been supported by molecular orbital calculations in the cases of Co_3S_4, $CuCo_2S_4$ and Fe_3S_4 (Vaughan and Tossell, 1981). Since the highest energy levels containing electrons (and the lowest empty levels) are those associated with the transition metal $3d$ orbitals, only those need be considered in detail. Schematic energy level diagrams for the $3d$ orbitals in Ni_3S_4, $FeNi_2S_4$ and Fe_3S_4 are shown in Figure 9. In Ni_3S_4 and $FeNi_2S_4$, the lower energy $3d$ levels (t_{2g}, e) are considered as filled with electrons, whereas the higher energy levels (comprised of e_g and t_2-type orbitals) which are antibonding in character overlap to form delocalized bands of collective electrons (σ_A^* and σ_B^* from cations on A and B sites). In Ni_3S_4, the σ^* band contains 6 electrons per formula unit, whereas with substitution of iron in the series Ni_3S_4–$FeNi_2S_4$, the number drops to 4 at $FeNi_2S_4$. No fundamental change occurs in the electronic structures of thiospinels in this polydymite–violarite series. Furthermore, the systematic changes in properties in the series can be directly linked to the electron occupancy of this σ^* band (Vaughan et al., 1971)—correlations further substantiated by the more detailed data on properties presented in this paper. Thus, the systematic increase in cell parameter from $FeNi_2S_4$–Ni_3S_4 (Fig. 2) correlates with the increasing electron occupancy of the antibonding orbitals of the σ^* band which are more proximal to the sulfur ligands tending to push these away. The systematic decrease in reflectance at 589 nm along the same series (Fig. 3a) can also be related to a decrease in the available empty levels in the σ^* band; levels into which electrons may be excited resulting in high absorption coefficients and high reflectances (Burns and Vaughan, 1970; Vaughan et al., 1971). The stabilities of these thiospinels have also been discussed in terms of the bonding models and the lower thermal stability of polydymite ($353 \pm 3°C$) compared to violarite ($461 \pm 3°C$) related to the greater electron occupancy of the σ^* band in polydymite (Vaughan et al., 1971).

The Mössbauer data presented for the violarites in this paper have been used to suggest that some iron may occur in tetrahedral sites in these minerals. Such substitution would not affect the electron occupancy of the σ^* band so that the correlations noted above would remain valid. Further detailed spectroscopic studies are required to confirm the presence of iron in tetrahedral coordination in violarites and determine if its distribution is dependent on the conditions (annealing temperature, time) of formation.

The electronic structure of greigite illustrated in Figure 9 contrasts strongly with the polydymite–violarite series. The model shown here incorporates the results of the molecular orbital calculations of Vaughan and Tossell (1981). Greigite contains localized $3d$ electrons with unpaired spins which are coupled antiferromagnetically at lower temperatures. This essentially more "ionic" substance has a much larger cell parameter than the violarites and the large number of electrons in antibonding orbitals contribute to its instability. Vaughan et al. (1971) suggested that the lack of experimental solid solution between $FeNi_2S_4$ and Fe_3S_4 is due to this fundamental difference in electronic structure.
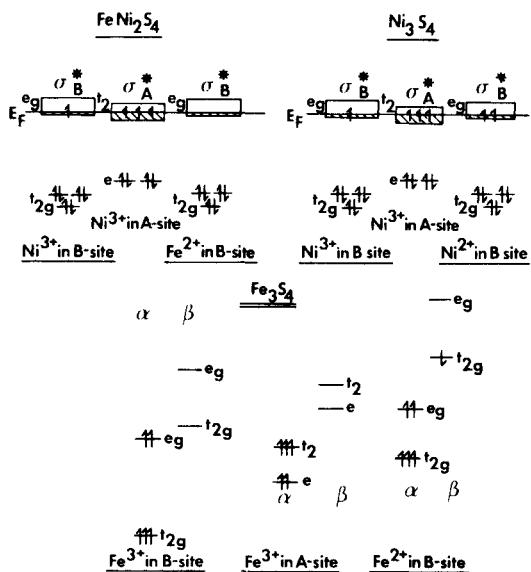
Nickel (1973), Misra and Fleet (1974), and Imai et al. (1978) have noted that the iron/nickel ratios (and even the cobalt contents) of these secondary violarites are largely a function of the initial pentlandite composition. Consequently, many violarites exhibit iron/nickel ratios far in excess of the 1/2 stoichiometry seen in synthetic violarites and expected from crystal chemical considerations. Nickel (1973) has further suggested that very iron-rich compositions result from replacement of pyrrhotite (possibly nickeloan pyrrhotite). The thermodynamic stability of these iron-rich compositions is neither known nor probably consequential in terms of their formation and persistence. Misra and Fleet (1974) have noted that the similarities of the crystal structures readily permit conversion of pentlandite to violarite regardless of stabilities. This same ease of conversion may also account for the problem of what constitutes stable low temperature assemblages. The trends of tie lines in higher temperature experiments and the associations observed in what are interpreted as hypogene millerite occurrences suggest that pyrite and millerite may coexist stably at low temperature. On the other hand, the common occurrence of secondary violarite forming on pentlandite in weathered ores has been interpreted as indicating a stable violarite–pentlandite tie line at low temperature. It appears likely that pyrite + millerite represents thermodynamic stability but that pendlandite + violarite represents a common situation in nature because of the ready conversion of pentlandite to violarite.

Discussion

The crystal chemistry of thiospinel minerals has been discussed in terms of qualitative molecular orbital and band theory bonding models by Vaughan et al. (1971) and

Fig. 9. Schematic energy level diagrams for the $3d$ orbitals in Ni_3S_4, $FeNi_2S_4$ and Fe_3S_4. α and β refer to spin directions of the electrons; E_F is the Fermi level.

The new data show that although $FeNi_2S_4$–Fe_3S_4 solid solution is not observed in synthetic (high temperature) experiments, it is observed in natural phases (Fig. 7). This is not necessarily in conflict with the proposed electronic structure theory for thiospinels, since the compositions between $FeNi_2S_4$ and Fe_3S_4 are very likely to be metastable. They occur in small quantities and frequently result from the alteration of pre-existing pentlandite—the "predominant mode of formation of violarite" (Misra and Fleet, 1974). There is increasing evidence to show the importance of reaction mechanisms and kinetic factors in the formation of sulfides at low temperatures (e.g. Putnis, 1976; Putnis and McConnell, 1980). The metastable transformation of pentlandite to violarite would readily explain the occurrence of iron-enriched violarites and also the frequently observed sulfur-poor compositions (Fig. 8) which lie on the pentlandite site of the stoichiometric violarite composition. It is not surprising, therefore, that the low temperature phase relations involving violarite are controversial. Furthermore, Nickel (1973) has suggested that the compositions of secondary violarites are not dependent upon stability but rather upon the initial phase replaced or altered.

The properties of compositions between $FeNi_2S_4$ and Fe_3S_4 are particularly interesting and attempts to synthesize these in aqueous media are underway. Such materials must exhibit a transition from delocalized to localized d-electron behavior at some point in the series. It is interesting to note that such a transition has been observed in $CuCr_{2-x}V_xS_4$ thiospinels (Robbins et al., 1970).

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