SELECTED AUTHOR'S ABSTRACTS

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HIORTDAHLITE FROM KIPAWA, QUEBEC

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Hiortdahlite, $(Ca,Na,Y,RE)_3Zr_{1-x}Si_2O_7\ (F,O,OH)_2$, a member of the wöhlerite group of minerals occurs in an alkalic rock complex along with such unusual minerals as eudialyte, rinkite, mosandrite, vlasovite, britholite, and at least two new minerals. The complex is on the Kipawa River in Willedieu Township. The mineral is polysynthetically twinned but doubling or tripling of reflections on single crystal *x*-ray photography does not conform to any known twin law; it is ascribed to the intergrowth of several crystallites. The unit cell has $a = 10.95$Å, $b = 10.31$Å, $c = 7.29$Å, $\alpha = 90°19'$, $\beta = 109°02'$, $\gamma = 90°05'$, with strong pseudo-orthorhombic and pseudo-monoclinic symmetries. There is a continuum of physical properties and chemical composition from fresh to somewhat altered hiortdahlite. Fresh material has $2V + 80°$ to $-76°$, $\alpha = 1.639$, $\beta = 1.643$, $\gamma = 1.646$ and $D = 3.256$. Partly altered material has lower refractive indices and density and smaller negative $2V$.

Chemical analysis shows at least 30 elements present in determinable quantities. The unit cell is deficient in metallic cations, and this may account for the triclinic symmetry rather than the monoclinic symmetry that characterizes the rest of the wöhlerite group.

The structural formula derived from the analysis is $(Ca_{2.01}Na_{0.85}Y_{0.12})\ (Zr_{0.58}Nb_{0.02}Mn_{0.02}Ti_{0.01}Fe_{0.01}Mg_{0.01}Hf,Al_{0.01})\ [Si_{2.05}O_{7.0}]\ (F_{1.34}O_{0.41}OH_{0.13})$.

The cation deficiency appears to be concentrated in the Zr site and so the general formula of hiortdahlite may be written $Ca_2(Na,Y,RE)_1\ Zr_{1-x}[Si_2O_7]\ (O,OH,F)_2$.

AN OCCURRENCE OF COARSE HEXAGONAL PRISMS OF PYRRHOTITE, STRATHCONA MINE

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Coarse hexagonal prisms of pyrrhotite, up to 3 cm diameter, have been found within the Footwall Ore Zone at Strathcona Mine, roughly 600 feet below the norite contact within tonalitic gneisses of the footwall complex. Locally, parallel orientation of the prisms reveals itself on fracture surfaces through step-like hexagonal platelets. In detail, some unusual features of crystal growth and mineral relationships are noted; sections of euhedral hexagonal pyrrhotite contain broad (up to 1 mm) laths of similar composition along three sets of pyramidal planes; extensive development of magnetite, chalcopyrite and exsolution pentlandite occurs on basal planes of the pyrrhotite. The prisms have nucleated and grown in close association with granular monoclinic pyrrhotite, rounded subhedral magnetite, blocky pentlandite and intergranular chalcopyrite. Distribution of pyrrhotite types is demonstrated by treatment with magnetic colloid and etchants. Results of microprobe analyses and *x*-ray powder diffraction data of the major phases are presented.

Ni AND Co PARTITION RATIOS AMONG PENTLANDITE, PYRRHOTITE, AND PYRITE IN BOTH NATURAL AND SYNTHETIC SYSTEMS

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Experimental data have been obtained for the partitioning of Ni and Co between (1) pentlandite and pyrrhotite at 200, 350 and 500°C with 5, 10 and 20 wt % Ni combined with 1 wt % Co in the charges, (2) pyrrhotite and pyrite at 350, 500 and 650°C with up to 0.42 wt % Ni and 0.35 wt % Co in the charges. Partition ratios of these elements ($[\mathrm{Ni}]_{\mathrm{po}} / [\mathrm{Ni}]_{\mathrm{py}}$, $[\mathrm{Co}]_{\mathrm{pn}} / [\mathrm{Co}]_{\mathrm{po}}$, etc.) for pairs of phases vary smoothly as a function of temperature.

Ni and Co partition ratios among pentlandite, pyrrhotite and pyrite in nickel ores are evaluated in terms of the experimental data.

A NEW OCCURRENCE OF MISERITE FROM THE KIPAWA LAKE AREA, TEMISCAMINGUE CO., QUEBEC

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This silicate mineral occurs as red-brown cleavage masses, with vitreous lustre, closely associated with dark green hornblende, pink eudialyte, scapolite, and an unknown light grey mineral, in a carbonatite vein. The mineral is triclinic, with unit cell dimensions: $a = 10.099(6)$, $b = 15.996(3)$, $c = 7.367(7)$ Å, $\alpha = 96°24'$, $\beta = 111°04'$, $\gamma = 76°39'$; hardness 5.5 to 6.0; specific gravity 2.926 (meas), cleavage {100} perfect and {010} imperfect. Optically positive, $\alpha = 1.5870$, $\beta = 1.5890$, $\gamma = 1.5940$ (± 0.0002) in sodium light, 2V (meas) 65°, (calc) 64°48′, the optic plane is {100}, $Z \simeq a$, on {100} $Y \wedge c = \sim 2°$, on {010} $Y \wedge c = 11°$, shows wavy extinction and lamellar twinning. The mineral melts below 1400°C and is insoluble in HCl, HNO_3 and H_2SO_4.

Analyses by wet-chemical and microprobe methods (wt %) give the following: SiO_2 50.15, 50.20; CaO 30.99, 33.4; K_2O 4.81, 6.65; Na_2O 0.84, 0.79; MgO 0.25, nd; MnO 0.50, 0.35; FeO 0.12, 0.16; Al_2O_3 0.60, nd; Y_2O_3 4.96, 2.53; La_2O_3 0.59, 0.50; CeO_2 1.00, 1.20; Pr_6O_{11} 0.21, 0.25; Nd_2O_3 0.86, 1.20; EuO 0.04, nd; Dy_2O_3 0.58, 0.70; Er_2O_3 0.31, nd; Tm_2O_3 0.03, nd; Yb_2O_3 0.47, nd; Lu_2O_3 0.04, nd; Ign. loss 1.15; totals 99.34, 98.97. The average of these analyses gives Ca 11, K 2.3, Na 0.5, Mg 0.1, Mn 0.1, Fe 0.04, Al 0.22, Y 0.6, La 0.06, Ce 0.06, Pr 0.01, Nd 0.11, Dy 0.06, Er 0.02, Yb 0.04, H 2.3, O 47.74, close to 16 [(Ca, K, Na, Al, Y, etc.) SiO_3] for the cell content.

The strongest lines of the powder pattern (Co*K*, Fe filter, 114.6 mm camera, intensities by densitometer) are: $15.\underline{6}$, 60, (010); 3.470, 50, (122); $3.\underline{1}4$, 100b, ($\bar{2}30$,050,+); 2.825, 55 (032); 2.377, 65, ($4\bar{2}2$); 1.845, 55, (500); 1.641, 80, ($\bar{1}82$); 1.589, 50, ($3\bar{5}2$).

PHASE RELATIONS IN THE CHALCOPYRITE REGION OF THE Cu-Fe-S SYSTEM

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Detailed studies of sulphide ores and of the central portion of the synthetic Cu-Fe-S system show that there exist a number of phases at room temperature. Deviations from chalcopyrite stoichiometry on the metal-rich side (*i.e.* metal to sulphur ratio exceeding unity), result in the formation of at least three distinct, but closely related structures. These differ in their degree of metal addition and ordering to the cubic high-temperature modification of chalcopyrite ($a = 5.26$Å). The high-temperature modification itself has not been found to occur in nature.

In the case of Cu > Fe ($Cu_{1.125}Fe_{1.0}S_{2.0}$), a phase with a *cubic* unit cell $a = 10.593$Å is formed and this corresponds to the mineral talnakhite ($\simeq Cu_{18}Fe_{16}S_{32}$). The structure of this mineral has been determined by single crystal *x*-ray diffraction techniques as being that proposed for the β-phase of Hiller & Probsthain (1956). For $Cu \simeq Fe$ ($Cu_{1.125}Fe_{1.125}S_{2.0}$), a phase with a *tetragonal* unit cell is formed which appears equivalent to the γ-phase of Hiller & Probsthain (1956). Both synthetic and natural single crystals have been used in the identification of this phase. A third phase has $Cu < Fe$ ($Cu_{1.0}Fe_{1.25}S_{2.0}$) and preliminary *x*-ray diffraction powder analysis shows that it agrees closely with that of an expanded tetragonal cell of chalcopyrite.

The inclusion of these additional phases in the Cu-Fe-S diagram give rise to significant tie-line changes. One important practical aspect of the elucidation of the phase relations in this system is that the behaviour of these phases in the flotation process might be different from that of chalcopyrite.

A TWO-PHASE MAGNESIAN CLAY SHOWING ONE-PHASE PHYSICAL PROPERTIES RELATED TO STEVENSITE, CEROLITE, AND MIXED-LAYER TALC-SAPONITE MINERALS

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A fibrous clay from a pegmatite located in serpentinite at Věžná, Czechoslovakia, has a chemical composition close to that of stevensite (defect talc structure with rather regularly interstratified montmorillonite-like layers), uncontaminated cerolite (disordered defect talc structure with irregularly interstratified montmorillonite-like layers), and regular 1 : 1 mixed-layer talc-saponite minerals of Alietti and Veniale & v.d. Marel. The cation exchange capacity and exchangeable cations are close to those of stevensite and mixed-layer talc-saponite. The clay is homogeneous in optical microscope, with *n* between 1.530 and 1.540. Differential thermal treatment shows two major (130 and 850°C) and one minor (230°C) endothermic effects. X-ray powder data indicate the presence of talc and saponite as separate phases, with probable minor admixture of cerolite. IR absorption spectrum corresponds to that of stevensite, cerolite, and/or mixture of talc and saponite. After boiling in 10 N HCl at 70°C/6 hours the *x*-ray reflections of saponite disappear, the IR-spectrum becomes that of talc, and 13.3 wt. % MgO is leached into solution.

The chemical composition and some physical properties could be those of a single phase, as is the regular mixed-layer talc-saponite, stevensite, and cerolite, but the *x*-ray study reveals at least two separate phases. This indicates the large influence of grain size and aggregation on the physical properties of Mg-hydrosilicates, and stresses the necessity of *x*-ray work and quantitative chemical analysis for recognition of stevensite, mixed-layer talc-saponite minerals, cerolite, and multiphase mixtures.

MINOR ELEMENT VARIATION IN PYRRHOTITE FROM FALCONBRIDGE MINE — AN AID IN GEOLOGICAL INTERPRETATION

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The low-temperature breakdown of the $Fe_{1-x}S$-$Ni_{1-x}S$ monosulphide solid solution, although not detected to date in "dry" experimental work on the system Fe-Ni-S, is required by the mineral assemblage pyrrhotite-pyrite-pentlandite. It is also indicated by the coexisting pair low-Ni monoclinic pyrrhotite — pentlandite, the most common mineral assemblage in Sudbury ores, since any other low-Ni pyrrhotite would be too sulphur-poor to invert to the monoclinic form at low temperatures. Once the solid solution breaks down, the nickel content of the pyrrhotite coexisting with pentlandite will be a function of the temperature of final equilibration; that is, it may serve as a geothermometer.

With this in mind, the nickel content of pyrrhotite from the Falconbridge Mine, Sudbury, has been determined by electron probe microanalysis. A range was found from 0.1% to 1.2%; the amount present is strongly dependent on the immediate geology and on the distance from the breccia sulphide zone.

The cobalt contents of both pentlandite and pyrrhotite were also determined. That of pyrrhotite seems relatively constant in the specimens studied (0.1%), probably insufficient to complicate the use of the nickel content as a geothermometer. Pentlandite, on the other hand, shows a marked variation in cobalt content (0.9% to 2.6%) ; this also seems to be dependent on the distance from the breccia sulphide zone.

A reliable and commonly available geothermometer for the Sudbury ores and associated rocks may ease the difficulties in interpretation of the geological history of the area, or may suggest new possibilities for interpretation and for exploration. Specifically, the nickel content of pyrrhotites from either side of the breccia sulphide zone, and from the breccia sulphide zone itself, are combatible with pre-ore faulting along this zone. This fault zone provided a channel for movement, and a site for deposition, of the breccia sulphides.

The mineral assemblages and the nickel content of the pyrrhotite can be shown to place narrow limits on the Fe : Ni : S ratios of the sulphide melt.

PHASE RELATIONS AND PS_2-T VARIATIONS IN THE Fe–Ni–S SYSTEM

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Knowledge of phase relations within the Fe–Ni–S system have now been extended from liquidus temperatures to 200°C. Partial pressures of S_2 in equilibrium with various phases and phase assemblages have been determined by means of the pyrrhotite and electrum tarnish methods at intervals between 900° and 400°C.

Phase relations in the Fe–Ni–S system are dominated by the $Fe_{1-x}S$–$Ni_{1-x}S$ monosulphide solid solution (Mss) which spans the central portion of the system from liquidus temperatures to below 300°C. Reduction of the composition limits of the Mss on cooling from liquidus temperatures may result in exsolution of pyrite, violarite, and vaesite on the sulphur-rich side or pentlandite, or millerite on the sulphur-poor side. Final decomposition of the Mss results from withdrawal from the Ni–S join below 282°C and separation into two separate Mss phases (with Fe : Ni ratios about 2 : 1) below 275 ± 25°C. Pyrite-pentlandite tie lines are established below 225 ± 25°C. Typical Sudbury ore compositions initially crystallize as homogeneous Mss (+ magnetite) which exsolves, on cooling, chalcopyrite, pentlandite, and pyrite. Nickel-rich ores may crystallize initially at low temperatures as millerite-violarite assemblages or result from decomposition of Ni-rich Mss compositions.

The partial pressure of S_2 coexisting with various Mss compositions range over several orders of magnitude at most temperatures but would vary for a typical Sudbury ore (sulphide content of 57% Fe, 5% Ni, 38% S) as: 1100°C-10^{-1} atm, 900°C-10^{-3} atm, 600°C-10^{-6} atm, 400°C-10^{-11} atm. The partial pressure of S_2 over assemblages containing Mss + violarite is $10^{-4.8}$ atm at 450°C, $10^{-6.0}$ atm at 400°C, and $10^{-8.5}$ atm. at 300°C. These data plus an estimated entropy of violarite, $S_{298} = 46.0$, permit formulation of free energy equations for the reactions: $\frac{1}{2}Fe + Ni + S_2 = \frac{1}{2}FeNi_2S_4$ ($\Delta G = 69{,}575 + 41.9T$, 25° — 450°C), $2(FeS\,.\,2NiS) + S_2 = 2FeNi_2S_4$ ($\Delta G = 57{,}900 + 59.4T$, 300 — 450°C). The partial pressure of S_2 over the assemblage pentlandite + FeNi, $10^{-14.0}$ atm at 500°C and $10^{-17.8}$ atm at 400°C, and an estimated entropy of pentlandite, $S_{298} = 120.8$, yield the free energy equation for the reaction, $9/4(Fe,Ni) + S_2 = \frac{1}{4}(Fe,Ni)_9S_8$ ($\Delta G = -80{,}800 + 39.7T$, 25°–500°C).

CHALCOPYRITE SOLID SOLUTION : $Cu_{1+x}\ Fe_{1+x}\ S_2$

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Samples with atomic ratios Cu : Fe : S of 1.04 : 1.04 : 2.00 and 1.11 : 1.11 : 2.00 were heated between 365° and 500°C for 22 months. A single, homogeneous, polycrystalline phase was obtained in each case. The only lines we observed on the Debye-Scherrer patterns were those of chalcopyrite. We first interpreted both compositions as metal addition to the chalcopyrite crystal structure, in line with the observed increase in cell volume (*Carnegie Institution of Washington Year Book* **69,** 306, 1970). The excess metal atoms, when placed in the tetrahedral position 8c, 0,0,z with $z = 0.75$, in space group $I\bar{4}2d$, give calculated powder-line intensities in agreement with the observed ones. Calculated densities for the stoichiometric and the two non-stoichiometric compositions did not, however, fall on a straight line; the straight-line drawn through the first two points leads to a predicted density of 4.45 g/cm³ for $Cu_{1.11}Fe_{1.11}S_{2.00}$ as compared with its calculated density of 4.35 g/cm³.

The recent results of Cabri & Hall throw light on this discrepancy: the $Cu_{1.11}Fe_{1.11}S_{2.00}$ composition is likely to belong to that tetragonal phase which is found by them to be distinct from chalcopyrite.

THE STRUCTURAL FORMULA OF PENTLANDITE

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Literature data (Shewman & Clark, 1970*) on synthetic pentlandite compositions permit determination of the types of solid solutions encountered. The data here used refer to samples quenched from 600°C and to x-ray powder patterns taken at 25°C from which $d(155,333)$ values were obtained. The compositions are recalculated on the assumptions of pure addition or pure omission solid solutions. In the Table $n = \frac{1}{2}$.

#	wt % S	*Me* addition $(Fe_nNi_n)_{9+x}S_8$ x	S omission $(Fe_nNi_n)_9S_{8-y}$ y	d(Å) ±0.0003	V(Å³) ±0.5
(1)	32.55 ±0.20	0.280	0.241	1.946_4	1034.5
(2)	32.23 ±0.20	0.000	0.000	1.944_7	1031.8
(3)	34.00 ±0.30	—0.307	—0.282	1.942_8	1028.8

The cell volume shows an increase with decrease in sulphur content, a result which can only be interpreted as metal-addition solid solution. The decrease in cell volume with increase in sulphur content, on the other hand, indicates metal-omission solid solution. The formula must be written:

$$(Fe,Ni)_{9\pm x}S_8$$

The combination of small amounts of sulphur omission with metal addition for # (1) and the reverse for # (3) cannot be ruled out but is unlikely for structural reasons. The sulphur atoms are in pseudo close-packing so that there is little tendency for sulphur vacancies and no room for sulphur additions; the metal atoms, however, occupy only ⅛ of all available octahedral and ½ of all available tetrahedral sites. Thus metal atoms should readily add to unoccupied octahedral sites and vacate normally occupied tetrahedral sites.

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* Shewman, R.W. & Clark, L.A., Pentlandite phase relations in the Fe-Ni-S system and notes on the monosulphide solid solution. *Canada J. Earth Sciences,* **7,** 67, (1970).

THE REPRESENTATION OF MINERAL ASSEMBLAGES COEXISTING WITH BIOTITE ON THE BIOTITE COMPOSITION SURFACE

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Mineral assemblages of quartz-bearing pelitic rocks may be shown approximately in the tetrahedron K_2O–Al_2O_3–FeO–MgO. Four-phase assemblages including biotite will be represented by subtetrahedra having one corner on the biotite composition surface. Volumes representing three-phase assemblages will subtend a line on the biotite composition surface and volumes representing two-phase assemblages will subtend an area. Thus mineral compatibilities in the presence of biotite may be shown by a subdivision of the biotite composition surface. This method is particularly useful in potassium-poor rocks not containing muscovite.

HAUCHECORNITE FROM THE VERMILION MINE, SUDBURY DISTRICT, ONTARIO

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Hauchecornite from the Vermilion Mine, Sudbury District, Ontario, has *x*-ray data similar to those for the Westphalian mineral. Electron microprobe analyses of Sudbury hauchecornite gave: Ni 44.90, Co 0.35, Fe 1.45, Bi 26.56, Sb 0.17, As 4.41 and S 22.05 wt. %. Similar analyses of Westphalian material gave: Ni 46.87, Co 0.37, Bi 22.30, Sb 7.83, As 0.25 and S 22.63 wt. %. The ideal chemical composition may be expressed as $(Ni,Co,Fe)_9\ (Bi,As,Sb)_2S_8$. The Sudbury mineral is the arsenian variety and the Westphalian mineral is the antimonian variety. Electron microprobe studies of Westphalian hauchecornite revealed inclusions of millerite, bismuthinite, galena, gold, bismuthian-arsenian-ullmanite and antimonian gersdorffite. The VHN, with a 50 g load, for Sudbury hauchecornite is 516-655 kg/mm^2 and for the Westphalian material 447-655 kg/mm^2. Reflectance values for various wavelengths for hauchecornite from both localities are summarized below:

Wavelength	(nm)	470	546	589	650
Sudbury	Max.	43.0	47.1	49.2	51.6
	Min.	41.6	46.2	48.2	50.8
Westphalia	Max.	42.1	44.9	46.1	48.5
	Min.	41.3	44.1	46.0	47.9

CRYSTALLIZATION OF THE SUDBURY NICKEL IRRUPTIVE WITH SPECIAL REFERENCE TO MAGNETITE AND ILMENITE

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Petrologically the south range of the Nickel Irruptive contrasts strongly with the north (and east) range. The extreme upper part of the south range norite and the overlying upper gabbro and micropegmatite resemble the felsic norite and overlying oxide-rich gabbro and micropegmatite of the north range. The marginal norite of the south range is similar, in some respects, to the mafic norite which is developed intermittently around the outer margin of the north range. However, the vast bulk (lower 2500 ft.) of the south range norite is missing from the north range.

Hypersthene, augite and plagioclase in all rocks except those from the margins show compositional variations similar to the normal cryptic variation found in gravity-stratified differentiated intrusions. Cryptic variation opposite to normal is found in the marginal quartz-rich and mafic norites and is attributed to more rapid cooling of the marginal zones.

The south range is thought to have been up-faulted 3 miles with respect to the north range (Stevenson & Colgrove 1968) so that it represents rocks that crystallized at a deeper level within the Irruptive.

Magnetite and ilmenite occur throughout the Nickel Irruptive. The magnetite almost invariably contains oriented lamellae of magnetite and/or hematite. The upper and oxide-rich gabbros and the micropegmatite contain between 1 to 10 percent oxides with magnetite far in excess of ilmenite. The felsic and south range norites contain 0.1 to 2 percent oxides with ilmenite in excess of magnetite. The mafic norite, a unit developed intermittently around the perimeter of the north range of the intrusion, contains 0.5 to 1 percent oxide (largely magnetite) while the quartz-rich norite, developed continuously along the margin of the south range, contains the same amount of oxide, largely ilmenite.

Electron microprobe data on magnetite, coupled with estimates of the proportion of ilmenite lamellae developed within grains, indicates that magnetite from the upper levels of the Irruptive was very much richer in titanium at the time of its crystallization than that from lower levels. Chromium shows the reverse trend. Magnetite from the upper part of the mafic norite contains 8 to 13 percent Cr_2O_3 but this decreases rapidly to less than 2 percent across the 10-50 ft transition zone between the mafic and overlying felsic norite and then falls more gradually to less than 0.2 percent in the micropegmatite. Magnetite from the upper part of the quartz-rich norite and lower south range norite is also rich in Cr_2O_3 (3-5 wt %) and this decreases upwards to less than 1.5 percent half way up this unit. These variations in magnetite composition support previous evidence (Naldrett *et al.* 1970) of cryptic variation in the Irruptive.

The final partitioning of iron and titanium between magnetite and ilmenite occurred at high ($\simeq$ 900°C) temperatures on the north range and much lower ($<$ 600°C) temperatures on the south range, indicating a very different cooling history for the two ranges. This is consistent with the hypothesis that the Irruptive is funnel-shaped and that the south range is a section through a deeper, thicker portion of the funnel.

IRON AND SULPHUR IN BASALTIC LIQUIDS

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One of the most important considerations in developing models for the formation of magmatic-sulphide ore deposits is the solubility of sulphur in silicate melts of basic composition. The sulphur solubility is very low in these melts and depends upon the temperature, pressure, activity of the various volatile species, and the bulk chemical composition of the melt.

In the present study, the solubility of sulphur, in a melt of basaltic composition coexisting with an immiscible sulphide (Fe-S-O) melt, has been determined by experiments (1200°C) conducted at oxygen fugacities (10^{-9}-10^{-12} atmospheres) are sulphur fugacities ($10^{-0.8}$-$10^{-2.8}$ atmospheres) controlled by mixtures of CO, CO_2 and SO_2. The maximum amount of sulphur which is soluble in a balsatic melt is strongly dependent on the concentration of ferrous iron and to a lesser extent on the concentration of other basic oxides (CaO, MgO, etc.). At a constant activity of ferrous oxide the concentration of ferrous oxide increases with increasing titania and decreases with increasing alkali.

The concentration of sulphur in a saturated basaltic liquid varies from 0.05 wt % S at 6 wt % FeO to 1.9 wt % at 45 wt % FeO. Using the sulphide capacity function to relate the oxygen fugacity, the sulphur fugacity, and the composition of the liquid, four processes are considered in the formation of an immiscible sulphide liquid from a silicate liquid. These are decreasing solubility with decreasing temperature, increasing concentration of sulphur in the silicate melt by sulphurization or crystallization of sulphur-free phases, oxidation of ferrous iron, and changing bulk composition of the magma.

THE MAFIC NORITE AND THE SUB-LAYER: THE PETROLOGY OF THE BASAL ZONE OF THE SUDBURY NICKEL IRRUPTIVE

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The mafic norite, an orthopyroxene-rich rock with poikilitic plagioclase, lies at the base of the Sudbury Irruptive along its north range. Previously it has been established that the mafic norite is distinct both modally and in the composition of its minerals from the overlying felsic norite and the relationship between the two has been unclear. Cryptic trends in pyroxene and magnetite compositions and gradational contacts indicate that the mafic norite is part of a continuous sequence with the main layers of the Irruptive. The relatively sharp gradation between the mafic and felsic norites is attributed to a resurgence of felsic norite magma over the top of the mafic norite.

The sub-layer consists of sulphide bodies, breccias and various fine-grained gabbros and norites in sharp contact with mafic norite or separated from it by footwall rocks. The sub-layer basic rocks, being richer in augite and poorer in quartz than the main Irruptive norites, are modally distinct. Orthopyroxenes in the sub-layer have higher $Fe/Fe + Mg$ ratios (reaching 0.36 in the Fecunis Lake gabbro) than in mafic norite. The sub-layer and main Irruptive magmas appear to have been derived separately.

Xenocrysts and anomalously magnesian orthopyroxene ($Fe/Fe + Mg$ ratio of 0.29, as in mafic norite) at the top of the sub-layer gabbro suggest contamination by incorporation of overlying mafic norite. The sub-layer is therefore considered younger than the main Irruptive. It has been confirmed that mineralization is associated with the sub-layer rather than the main Irruptive, which contains minor amounts of sulphides. Several ore bodies in Levack Township occur directly below sub-layer basic rocks where they form thick lobes or embayments.

AN INVESTIGATION OF THE SOLUBILITY OF INDIUM IN HYDROTHERMALLY SYNTHESIZED GALENA AND SPHALERITE

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The solubility of indium in galena between 350° and 550°C and in sphalerite between 500° and 650°C was studied by means of a hydrothermal crystal synthesis method. Since indium occurs in trace amounts in both minerals, radioactive tracers were used to determine indium contents of the synthesized crystals. Large single crystals were grown from aqueous solutions containing radioactive In^{114m} and were analyzed by comparing the activity of the indium-doped crystals with that of a standard. For sphalerite indium-activated luminescence was also used as a measure of indium incorporation.

The solubility of indium in galena increased from approximately 17 ppm at 350°C to 100 ppm at 550°C. In sphalerite, indium solubility increased from approximately 25 ppm at 500°C to 240 ppm at 600°C and then decreased to 50 ppm at 650°C. The solubility data for galena agree well with data on the indium content of natural galena; however, natural sphalerite analyses yield considerably higher indium contents than those determined in this study. Thus, it is believed that the discrepancy between the experimental results and the natural occurrences can be explained by the fine dispersion of an indium-bearing phase, or the metastable incorporation of excess indium within crystallographically controlled sectoral zones.

METASTABLY CO-EXISTING CHALCOPYRITE SOLID SOLUTIONS

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Chalcopyrite solid solutions (cp_{ss}), annealed above about 550°C in equilibrium with pyrite, unmix upon cooling to a very fine intergrowth (20 microns or less) of two optically distant phases. Electron microprobe analyses of the two phases place them within the projected cp_{ss} field (Yund & Kullerud 1966) at the annealing temperature. Preliminary x-ray diffraction data suggest both phases give the intense powder lines of chalcopyrite, plus weak lines that do not belong to chalcopyrite or pyrite, the latter always being present after quenching. A bright yellow, anisotropic phase forms regions of lenticular shape that plot close to $Cu = Fe$ in the cp_{ss} field. The other, darker, phase has a bluish-grey tinge, forms interstitially to the bright phase, and generally contains very fine lamellae of the bright phase. The dark phase may be either Cu- or Fe-rich depending on the composition of the original charge. Analyses of dark phases plot along the full length of the sulphur-saturated boundary of the cp_{ss} field. When the starting material was chalcopyrite ($CuFeS_2$) the quenched products were pyrite and a chalcopyrite-type phase that unmixed to a bright Cu–Fe phase and a darker $Cu > Fe$ phase When the starting chalcopyrite grains contained small amounts of pyrite and pyrrhotite, the products were pyrite and the chalcopyrite-type phase which unmixed to the bright Cu — Fe phase and a dark $Fe > Cu$ phase. The phases appear to form metastably; no experimentally defined or natural stability fields are known for these co-existing chalcopyrite phases.

THE PARTITION OF SOME BASE METALS BETWEEN CO-EXISTING IRON SULPHIDE AND IRON SILICATE LIQUIDS

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Base metals are generally present in magmas in very small quantities and probably do not form primary crystalline phases at magmatic temperatures. In magmas where an immiscible sulphide liquid, composed mostly of FeS with some FeO, is present, the base metals partition between silicate and sulphide liquids. In our study we have added Co, Ni, Cu, Zn and Pb to mixtures within the iron sulphide — iron oxide — silica system corresponding to the iron-fayalite-tridymite-silicate liquid-sulphide liquid-vapor invariant point. All runs were made at 1150°C, 10 degrees above the invariant temperature in the base metal-free system. The quenched liquids have been analysed with the microprobe.

In the simplest form, the base metals may be considered to enter the silicate liquid as oxides and the sulphide liquid as sulphides:

$$\begin{array}{ccccccc} \mathit{Me}\mathrm{S} & + & \mathrm{FeO} & = & \mathit{Me}\mathrm{O} & + & \mathrm{FeS} \\ \text{Sulphide liquid} & & \text{silicate liquid} & & \text{silicate liquid} & & \text{sulphide liquid} \end{array}$$

Runs were made using varying, but small, amounts of each base metal to determine if partitioning was constant at low levels of concentration of base metals. With addition of up to 5 weight percent of the base metal, partition of each base metal between the two liquids appeared to be linear. Preliminary values for partition coefficients calculated as wt. % base metal in silicate liquid to that in sulphide liquid are: Co 0.20, Ni 0.007, Cu 0.03, Zn 3.0 and Pb 0.50. These coefficients indicate that Ni and Cu are strongly partitioned into the sulphide liquid whereas Co and Pb are only moderately so, and Zn shows preference for the silicate liquid.

EXPERIMENTAL INVESTIGATIONS OF SOME SULPHIDE-SILICATE REACTIONS IN THE HYDROTHERMAL TEMPERATURE RANGE

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Preliminary investigations have been performed at 700°C and 1 Kb confining pressure to determine the behaviour of such common minerals as garnet, epidote and potassium feldspar in the presence of H_2O and S. Garnet of three analysed compositions characteristically produced cordierite, iron sulphide and anhydrite as primary products. Recrystallization of those garnets containing large amounts of the grossular molecule was marked. In the garnet + H_2O + S reactions pyrrhotite or pyrrhotite + pyrite or pyrite alone formed depending on the ratio of almandine end-member to S. The cordierite produced was Fe-poor. These experiments did not produce iron oxides. Similar reactions involving analysed epidote produced iron sulphides, anorthite, grossular and anhydrite. It was found that two analysed K-feldspars containing Fe and Pb respectively did not react with H_2O and S over a one month period.

EVIDENCE FOR AN INVARIANT EQUILIBRIUM AT 1005 ± 3°C IN THE Fe-Ni-S SYSTEM

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Quenching experiments conducted in evacuated, silica-glass tubes were used to define an invariant assemblage involving monosulphide solid solution (Mss), vaesite (Ve), metal-rich liquid (L_1), sulphur-rich liquid (L_2) and vapor (V), near the Ni-S binary in the sulphur-rich portion of the Fe-Ni-S system. High temperature phase relations in the Ni-S binary have been revised to be consistent with the phase relations in the ternary system. The temperature and sulphur vapor pressure of the invariant equilibrium are estimated to be 1005 ± 3°C and 100 atmospheres. The compositions of the condensed phases have been corrected for sulphur loss at the temperature of heating. The following ternary peritectic-type reaction is proposed at the invariant temperature (vapor present) :

$$L_1 + L_2 \overset{\text{cooling}}{\rightleftarrows} Ve + Mss$$

Isothermal sections below, at, and above the invariant temperature are presented.

COEXISTING COPPER SULPHIDES AND NICKEL SULPHIDES IN ORE AND THE P-T CONDITIONS OF THEIR FORMATION

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COMPOSITION AND ORIENTATION OF CLINOPYROXENE EXSOLUTION LAMELLAE IN BUSHVELD TYPE ORTHOPYROXENE

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Identification of clinopyroxene lamellae in Bushveld-type orthopyroxene from the Greenhills Complex, New Zealand, has been made on the basis of partial analysis by electron microprobe and by unit cell determination by prolonged exposure to *x*-rays of single crystals of orthopyroxene. Lamellae averaging $Ca_{42}Mg_{47}Fe_{11}$ in composition with an approximate unit cell *a* 9.79Å, *b* 8.90Å, *c* 5.29Å, β106°14′ occur in orthopyroxene $Ca_2Mg_{67}Fe_{31}$ with unit cell *a* 18.28Å, *b* 8.85Å, *c* 5 20Å. The lamellae share *c* and *b*-axes with host orthopyroxene.

EQUILIBRIA BETWEEN IRON-RICH SILICATES AND IRON AND NICKEL-BEARING SULPHIDES

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Equilibria represented by the following reactions have been studied in silica tubes:

$$2FeSiO_{3(\text{in Fe-Mg pxn})} + S_2 \rightleftarrows 2FeS_{(\text{in po})} + SiO_2 + O_2 \quad \ldots\ldots \quad (i)$$

$$NiSi_{1/2}O_{2(\text{in Ni-Fe ol})} + FeS_{(\text{in Mss})} \rightleftarrows FeSi_{1/2}O_{2(\text{in Ni-Fe ol})} + NiS\ (\text{in Mss}) \quad (ii)$$

Both reactions were studied in the presence of excess quartz and magnetite, reaction (i) at 980°C and reaction (ii) at 900°C. The method was designed so that a single experiment approached equilibrium from both sides of the reaction.

Our results for reaction (i) indicate that an Fe-Mg pyroxene with composition $Ens_{45} \pm 2\%$ is in equilibrium at 980°C with pyrrhotite containing 47.2 at. percent Fe. We find that for reaction (ii) the distribution coefficient, K_D is 33.2 ± 3.4 where

$$K_D = \left(\frac{N_{FeSi_{1/2}O_2}}{N_{NiSi_{1/2}O_2}} \times \frac{N_{NiS}}{N_{FeS}} \right)$$

Thermodynamic calculations suggest that the equilibria for both reactions may be strongly temperature dependent. Our results for reaction (i) should represent equilibrium reached in hypersthene and pyrrhotite-bearing rocks that also contain quartz and magnetite. Assuming olivine to be an ideal solid solution our results for reaction (ii) should apply to sulphide-bearing ultramafic rocks, in which the sulphides have similar metal : sulphur ratios as those in our experiments.

NICKELIFEROUS SMYTHITE—COMPOSITION, DIAGNOSTICS AND OCCURRENCES

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Nickeliferous smythite, with composition approximating $(Fe,Ni)_{3.3}S_{4.0}$ has been found in five Canadian occurrences. It is invariably associated with monoclinic pyrrhotite, and usually occurs as flame-like forms in the pyrrhotite, generally around grain margins or along fractures. In reflected light, smythite is bireflecting, and similar in appearance to pyrrhotite, but with appreciably higher reflectance: at a wavelength of 546 mm, smythite has $Rm = 41.8\%$, whereas pyrrhotite has $Rm = 36.6\%$. Smythite has a microhardness of VHN 388; pyrrhotite, VHN 277. Smythite has a consistently higher nickel content than the pyrrhotite with which it is associated, most analyses giving a ratio of about 2.5 : 1. The maximum nickel content found in smythite to date is 7.5 wt % Ni.

A CHEMICAL STUDY OF THE GOLDING-KEENE PEGMATITE AND ADJACENT GNEISSES, YORK RIVER AREA, ONTARIO

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The Golding-Keene pegmatite, a large very coarse-grained nepheline-albite body, and the surrounding heterogeneous nepheline-plagioclase gneisses have been mapped and extensively sampled by diamond drilling. Over 800 feet of 1⅜ inch core have been obtained, including two holes through the pegmatite. Microprobe analyses of minerals and atomic absorption analyses of split drill core intersections have been performed with a view to providing chemical data necessary to any theory of origin and in particular to test the hypothesis that the pegmatite represents a low-melting fraction of the adjacent gneisses.

The bulk composition of a major portion of the pegmatite does not lie at the minimum of the "nepheline syenite system" but rather on the line joining the nepheline solid solution and albite compositions near the cotectic line at ne 62, ks 9, qz 29. Gneiss compositions cluster around ne 62, ks 17, qz 21. Using a modified norm calculation, the pegmatite may be interpreted as having formed by partial melting of the enclosing gneisses. It is not feasible to directly derive a pegmatite such as the Golding-Keene from typical nepheline syenite magma.

SPINEL-MICA PARAGENESIS IN THE THOMPSON NICKEL BELT, MANITOBA

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Chromian spinels from the Thompson Nickel Belt range in composition from zincian chromian hercynite to zincian chromite. They are found in association with micas as inclusions in massive pyrrhotite-pentlandite ore, in narrow bands and segregations between the ore and biotite selvages, and in mica-sillimanite layers in the wall rocks adjacent to the massive sulphides. The chromian spinels have mottled appearance, some are zoned, and vary in colour from pale yellow through honey-brown to deep red. An electron probe microanalysis indicated the following relationships between the colour and their chemical composition: (1) the pale yellow variety contains the highest concentrations of alumina and zinc: $(Mg_{0.05}Fe_{0.55}Zn_{0.4})(Al_{1.6}Cr_{0.4})O_4$; it is rimmed by (2) the reddish spinel which is composed dominantly of chromite and contains minor ferric iron oxide; and (3) the brown variety which has an intermediate chemical composition and occurs in intergrowths with the yellow and red spinels. The spinels contain about 0.1 per cent nickel and are closely associated with orange-brown biotite. The biotite encloses spinel or in turn is enclosed in the spinel. Selvages between the massive sulphides and silicate xenoliths consist mainly of reddish-brown biotite and minor greenish muscovite, and chlorite. The micas and chlorite genetically related to Ni and Cr mineralizations contain from ten to hundred times more Ni and Cr than these minerals from common rocks. The variations in chemical composition of the chromian spinels and of the micas can probably be used as indicators of associated base metals mineralization.

A COMPARISON OF TRACE ELEMENTS AND SULPHUR ISOTOPES OF SULPHIDE MINERALS IN "ECONOMIC" AND "BARREN" SULPHIDE DEPOSITS OF THE FLIN FLON-SNOW LAKE REGION

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The Flin Flon-Snow Lake region comprises a belt of metamorphosed Precambrian volcanic and intrusive rocks over 100 miles long containing many base metal sulphide deposits with varying amounts of pyrite, pyrrhotite, arsenopyrite, chalcopyrite, sphalerite and galena. These are the "economic" deposits. In addition to these there are numerous "barren" sulphide deposits which are sometimes mineralogically similar but are composed mainly of iron sulphides.

A geochemical study of trace elements such as Ni, Co, Se and Te and sulphur isotopes in sulphides of both "economic" and "barren" types has been made. The results suggest that these data may be useful in distinguishing between the two types of deposits in exploration programs. Some comments are presented on the modes of formation of the two types of deposits.

SULPHUR ISOTOPES AT SUDBURY

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Previous sulphur isotope studies of Sudbury ores are reviewed and discussed in the light of more recent data on meteorites and igneous rocks. New analyses of coexisting pyrrhotite (po), chalcopyrite (cp) and pentlandite (pn) from various ore types at Sudbury display the following trends: a) δS^{34}(po) is generally greater than δS^{34}(cp); Δpn-po $= \delta S^{34}(pn) - \delta S^{34}(po)$ varies from + 0.8 to 0.1. Highest fractionation (lowest temperatures) are found in the deep zone of Strathcona, and the deepest ores at Frood, farthest from the irruptive. No absolute temperatures can be assigned, but some assemblages show fractionations consistent with crystallization from a magmatic sulphide-rich liquid.

The isotopic composition (δS^{34}) of ore from south range deposits is significantly lighter (more S^{32}-rich) than north range (Strathcona, Levack) ores. All ores are significantly heavier than meteoric (and thus presumably primitive mantle-derived) sulphide, and suggest considerable fractionative loss of sulphur from some parts of the intrusive prior to final separation and/or crystallization of the sulphide liquid. This probably occurred prior to the main separation of sulphide-rich liquid from silicate melt and may have been caused by significent isotopic fractionation between sulphide crystals (po,cp) and sulphur-rich liquid in which Δ sulphide xls-sulphide liquid ≤ 0. No exogenous source of sulphur is indicated by isotopic data.

APSLEY FORMATION, ONTARIO, ORTHOGNEISS OR PARAGNEISS?

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Biotite-microcline-oligoclase-quartz gneisses are commonly mapped as "paragneiss", as a consequence of their stratigraphic conformity with calcareous metasediments. Before metamorphism, such gneisses were either sandstones or silicic volcanics. In the absence of geological criteria for the origin of the Apsley formation, chemical indices were sought.

Major element abundances in 53 Apsley analyses, considered singly or in various linear combinations show variations similar to about 600 analyses of sandstones and a similar number of over-saturated igneous rocks. Comparison of Cr, V, Ni, Y, Sc, Zr, Sr, Ba abundances gives similar conclusions, as do element rations such as Ca/Sr, V/(Fe + Mg).

Discriminant function analysis helps distinguish the origin of many paragneisses.

PRIMARY SULPHIDE PHASES PRECIPITATED FROM MAGMAS: THEIR NATURE AND CAUSES OF PRECIPITATION

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Ore minerals preserved as isolated solid inclusions in silicate minerals provide unchanged samples of primary phases precipitated from magmas. In rocks of the granodiorite-monzonite-granite suite, magnetite is ubiquitous, and pyrite almost ubiquitous, as primary inclusions in quartz and feldspar. Evidence of the time of their precipitation is not conclusive, but their distribution suggests both are early phases to appear on the liquidus and that they remain there throughout the crystallization interval.

The presence of pyrite limits the crystallization temperatures of most salic igneous rocks below 743°C, the invariant temperature for the assemblage pyrite + pyrrhotite + sulphur liquid + sulphur vapor. The appearance of both pyrite and magnetite on the liquidus requires that any hydrothermal fluids evolved must be saturated with respect to both phases, placing close restraints on the activities of sulphur (a_{S2}) and oxygen (a_{O2}) in the fluids and thereby controlling their potentials as ore forming fluids.

Other primary sulphide phases, in decreasing frequency of occurrence, are chalcopyrite, the breakdown products of a digenite-bornite solid solution, pyrrhotite, (in some granodiorites from the Sierra Nevada, and in feldspar phenocrypts of ash-flow tuffs from the Jemez Mountains, New Mexico) and molybdenite.

Experimental determination of sulphide solubility in magmas demonstrates that the controlling variables are bulk composition of the magma, temperature and the partial pressures of oxygen and sulphur. Pressure is apparently not an important variable throughout the crustal pressure range except in-so-far as it affects the H_2O-contents and thereby the bulk compositions of magmas. Increasing the H_2O-content decreases the sulphide solubility. Changing H_2O pressures and falling temperatures appear to act with equal efficacy in controlling sulphide precipitation during crystallization of hydrous magmas.

ORIGIN OF THE ONAPING TUFF FORMATION, SUDBURY, ONTARIO

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The Onaping consists, at its base, of erratically distributed volcanic breccia and lapilli tuff; this grades up through mixed lapilli tuff and ash-sized tuff into the siltstone and slate of the overlying Onwatin formation. Despite this size grading in the Onaping tuff, it is for the most part strikingly non-bedded, free from the laminated bedding associated with air-fall tuffs and the flowage features of lavas. The Onaping is definitely of pyroclastic origin but because it lacks bedding its origin has always been a problem.

Recent recognition of the widespread occurrence of ash-flow tuffs has led to a re-examination of the Onaping, which possesses similar features. The Onaping appears to comprise an ash-flow field of large areal extent consisting of several ash-flow units. This field is comparable in size to some of the more extensive ash-flow fields in the eastern United States and New Zealand. As in these younger fields, welding has been extensive, and although in many places metamorphism has made recognition of early textures and minerals difficult, it is still possible to identify original vitroclastic textures and minerals produced by devitrification and vapor-phase crystallization.

The great lateral extent and tremendous volume of material in the Onaping ash-flow field precludes eruption from single domes or craters, and it is thought that the vent or vents supplying the material for the field must have been principally of the fissure type.

SOME ELECTRON MICROPROBE OBSERVATIONS ON SERPENTINE MINERALS

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The serpentine minerals found in serpentinized ultramafic rocks have been identified, using the microbeam *x*-ray diffraction camera in conjunction with the petrographic microscope. The textures they form have been classified into: (1) primary textures, characterized by recognizable pseudomorphs after the original minerals; and (2) secondary textures, characterized by non-pseudomorphic, interlocking, or interpenetrating features.

Electron microprobe traverses for Mg, Fe, Al and Si on primary lizardite mesh textures, in partly serpentinized peridotite, indicate that there is a great variation in composition between adjacent textural units. However, similar traverses in completely serpentinized peridotite indicate that a uniformity of composition exists between adjacent textural units. Primary lizardite hourglass textures also have a uniform composition between units. The lizardite bastites, associated with lizardite mesh textures, in both partly and completely serpentinized peridotites, tend to have a fairly uniform composition.

The secondary textures tend to be more complex mineralogically than the primary textures; secondary chrysotile, lizardite, 6-layer serpentine and antigorite all have been observed, but their individual compositions vary little across the areas traversed.

Fracture-filling veins were found to be composed of chrysotile, lizardite, and 6-layer serpentine. The composition of the serpentine in some of these veins is influenced strongly by the composition of the host serpentine, but in others the composition of the host serpentine has had little influence.

EMPIRICAL RESTRAINTS ON THE CHEMISTRY OF SERPENTINIZATION IN ALPINE-TYPE OLIVINE-ENSTATITE-SPINEL PERIDOTITE

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Serpentinization of olivine-enstatite peridotite is subject to the restraints of a density decrease from about 3.20 to 2.60 gm/cc, and a 10 to 14 per cent addition of water, and can be accomplished by: (1) 35 to 40 per cent increase in volume and minimal leaching of primary constituents, or (2) constant volume replacement and massive removal of magnesia and silica in solution.

Chemical data obtained from partially serpentinized alpine-type ultramafic masses in the Cassiar belt of northern British Columbia indicate that Mg/Fe ratios for dunites and peridotites have not been significantly altered by the serpentinization process. If Fe is locally fixed by secondary formation of magnetite, the implication is clear that Mg must also remain fixed. Slightly lower $(MgO + FeO)/SiO_2$ ratios in highly serpentinized rocks reflect silica addition during serpentinization rather than magnesium removal.

The chemical evidence supports the view that serpentinization of alpine-type peridotite has proceeded by simple addition of H_2O and minor SiO_2, minimal leaching of MgO and significant volume increase in the order of 30 to 40 per cent. Much of this expansion must occur in a vertical direction during the upward tectonic transport of peridotite masses in the orogenic environment. Pervasive serpentinization is regarded as a gradual process that results from incremental additions of water and silica derived from adjacent country rocks during the tectonic ascent of ultramafic masses through the sialic crust.