

large (positive) $\Delta\bar{H}_w$. The corresponding $\Delta\bar{H}_o$ terms should be much smaller, reflecting the improved compatibility in an organic phase. For compounds of low water solubility, $\Delta\bar{H}$ would be somewhat less negative (exothermic) than $-\Delta\bar{H}_w$. This readily accounts for the $\Delta\bar{H}$ values for β - and γ -BHC (benzene hexachloride) (11) and parathion (12) in soil-water equilibria; $\Delta\bar{H}$ will be small for compounds with low $\Delta\bar{H}_w$ and may even be positive if $\Delta\bar{H}_w$ is negative. In our data, $\Delta\bar{H}$ for 1,2-dichlorobenzene is practically zero as a result of the low $\Delta\bar{H}_w$ ($S = 133$ ppm at 3.5°C; 148 ppm at 20°C), and $\Delta\bar{H}$ for 1,1,1-trichloroethane is positive ($> -\Delta\bar{H}_w$) because of the negative $\Delta\bar{H}_w$ value for this compound ($S = 1790$ ppm at 3.5°C; 1360 ppm at 20°C). These results are not compatible with an adsorption model.

Consider now the relation between G and S . Since S is a good estimator of the organic-water partition coefficients for slightly soluble organic compounds (13), we may expect to find a correlation between $\log G$ and $\log S$, similar to that between $\log G$ and $\log K$. The G values calculated on the basis of the individual soil organic matter contents for the seven compounds from this work and other nonionic compounds from the literature are shown in Fig. 2. The regression equation is

$$\log G = 4.040 (\pm 0.038) - 0.557 (\pm 0.012) \log S \quad (2)$$

with $r^2 = 0.988$ and $n = 15$ (where G is dimensionless and S is in micromoles per liter) and covers more than seven orders of magnitude in S and four orders of magnitude in G .

The close fit suggests that the makeup of organic matter in soil is not critical in determining $\log G$ values for neutral chemicals (14). Moreover, it implies that, although the uptake by other soil constituents may involve other mechanisms, their contribution will be relatively small. For instance, the uptake by clays is considerably lower than that of organic materials (11, 15).

Since a chemical's partition value depends on its relative solubilities in the two phases, the solution pH may be expected to have a strong effect on the partition coefficients of organic acids and bases. At high pH , the dissociated anion of an organic acid should be poorly distributed in soil organics because of its high water solubility and possibly the repulsion by the surface negative charge of the organic matter. At low pH , certain cationic species (for example, paraquat)

may show substantial adsorption through ion-exchange even though partitioning is not favored by their high water solubilities. Surface binding (for example, hydrogen bonding) may potentially be a factor for highly polar compounds. The contribution of these effects needs to be considered separately.

It thus appears that the uptake of neutral chemicals by soils is consistent with the hypothesis of solute partitioning to the organic content of the soil. The resulting relationship between $\log G$ and $\log S$ provides a means for estimating the soil-water distribution.

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Widmanstaetten Patterns in Josephinite, a Metal-Bearing Terrestrial Rock

Abstract. *Widmanstaetten patterns have been found in several specimens of josephinite, a complex, metamorphosed, metal-bearing rock from placers on serpentinized peridotite in southwest Oregon. The patterns, in interior less-altered regions of the specimens, are typical of exsolution textures produced during slow cooling of a homogeneous metal. The bulk composition of the metal phases indicates that the homogeneous metal must have existed at temperatures above 500°C. Josephinite Widmanstaetten patterns are the first known in terrestrial rock. We interpret them as further evidence that josephinite was derived from the mantle.*

Josephinite, which is variable in composition, contains alloys of Ni, Fe, and Co. Other phases include garnet, sulfides, and arsenides; alteration phases include magnetite and serpentine. Josephinite is found in placers of streams which originate on and traverse the Josephine Peridotite, which is the depleted mantle of an obducted ophiolite complex (1). The josephinite specimen described in this report consists primarily of Fe, Ni, and Co. The specimen, 3 cm long and 2 cm wide, has been sectioned and polished for this study.

X-ray diffractometer analyses of polished surfaces show that there are face-centered cubic (γ) and body-centered cubic (α) metal phases present. Observa-

tions of polished surfaces made with optical and scanning electron microscopes reveal that the α and γ phases are intergrown in a pattern similar to Widmanstaetten patterns found in some meteorites. Figures 1 and 2 are scanning electron microscope images of the Widmanstaetten pattern from an unetched surface. The γ lamellae are arranged with a symmetry similar to that found in a (111) section of an octahedrite meteorite. This is a Widmanstaetten pattern in the metallurgical sense. However, it differs from the Widmanstaetten patterns found in meteorites in two significant ways. The lamellae in the josephinite specimen have the γ structure, whereas lamellae in meteorites consist of

the α phase. The compositions of the phases in this josephinite Widmanstaetten pattern are very different from the compositions of the phases found in Widmanstaetten patterns of meteorites.

Electron microprobe analyses of the josephinite γ phase yielded the following values (atom percentages): Fe, 26.5 ± 0.6 ; Co, 1.8 ± 0.4 ; and Ni, 71.7 ± 0.7 ; the values for the α phase were as follows: Fe, 54.0 ± 2.2 ; Co, 45.3 ± 2.0 ; and Ni, 0.7 ± 0.2 . The values represent observed ranges of composition; values less than unity probably represent uncertainty, and values greater than unity represent a real variation in composition. Each value is the average of ten measurements. Calculation of a bulk composition from these analyses, based on a point-count analysis that showed a 1:1 ratio for the abundances of α and γ in some of the Widmanstaetten pattern-bearing regions of the josephinite specimen, yielded (atom percentages): Fe, 40.3 ± 1.7 ; Co, 23.5 ± 2.0 ; and Ni, 36.2 ± 0.7 . The analyses show that the γ phase has a composition close to FeNi_3 ; this Ni content is greater than that observed in any metal phase found in Widmanstaetten patterns of meteorites. The α phase has a composition close to FeCo ; this Co content is also considerably greater than that found in any metal phase in iron meteorites.

It is known that FeNi_3 has a superlattice, giving it the L1_2 structure; it is, therefore, designated γ' . Moreover, FeCo is known to have a superlattice, giving it the B2 structure; it is designated α' .

Figure 3 is the Fe-Co-Ni ternary diagram (2-4). Figure 4 is a temperature-composition section along the solid line between FeCo and FeNi_3 in Fig. 3.

Lamellae of the γ' phase are parallel over distances of several millimeters in the polished sections of josephinite; this parallelism indicates that the areas that are now comprised of Widmanstaetten patterns were once homogeneous, single crystals before exsolution took place. Some of the Widmanstaetten pattern-bearing regions have more than 50 percent α phase; their bulk compositions plot to the left of the midpoint of the temperature-composition section shown in Fig. 4. A temperature of more than 500°C is needed in order for the metal of these regions to exist as homogeneous, single crystals of γ phase from which the Widmanstaetten patterns formed by exsolution.

The fact that lamellae in the josephinite Widmanstaetten patterns are the γ' phase, rather than the α phase as in

meteorites, suggests that the γ' phase precipitated earlier than the α phase. If exsolution took place during equilibrium conditions, this sequence could not have happened because a metal having the bulk composition that we determined would enter the $\alpha + \gamma$ two-phase region upon cooling, before entering the $\gamma + \gamma'$ or the $\alpha + \gamma'$ two-phase regions. However, if the bulk composition was cooled metastably below the temperature of the eutectoid (Fig. 4), γ' could precipitate first, producing a texture similar to that observed by Widge and Goldstein (4) when they heated a metastable α_2 phase. Because of higher diffusion rates, the γ' phase is more likely to precipitate before the α phase (5).

The lamellae usually have straight boundaries with the α phase. However, line-profile electron microprobe analyses revealed another γ phase, having irregular boundaries with the α phase, between the lamellae and the α phase (see Fig. 2). Its composition ranges from $\text{Fe}_{29.6}\text{Co}_{3.1}\text{Ni}_{67.2}$ to $\text{Fe}_{25.7}\text{Co}_{11.6}\text{Ni}_{62.7}$, in contrast

with the uniform composition (FeNi_3) of the lamellae. Within these regions the Ni content increases toward the lamellae and the Co content increases toward the α phase. We interpret this material to be the earlier γ phase from which precipitation of γ' and α had not gone to completion.

The regions of the α phase consist of two body-centered cubic phases having two different compositions: $\sim \text{Fe}_{51.9}\text{Co}_{47.4}\text{Ni}_{0.6}$ and $\sim \text{Fe}_{55.9}\text{Co}_{43.5}\text{Ni}_{0.6}$. The first phase occurs as irregular polygons, and these are surrounded by the second phase. We interpret this texture to have resulted from further exsolution within the α phase; if so, one of these phases should be ordered and the other disordered. This arrangement is consistent with the experimental data of Viting (3) but must be confirmed by diffraction studies with a transmission electron microscope of the α phase assemblage.

Many of the γ' lamellae have fine lines made up of many small grains of iron magnesium silicate, parallel to the edges

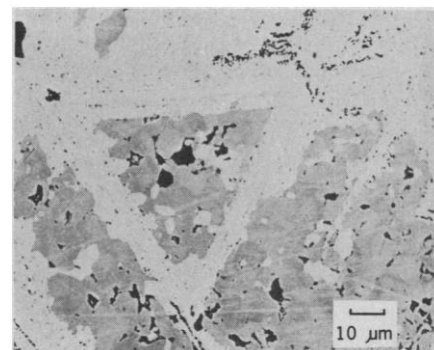
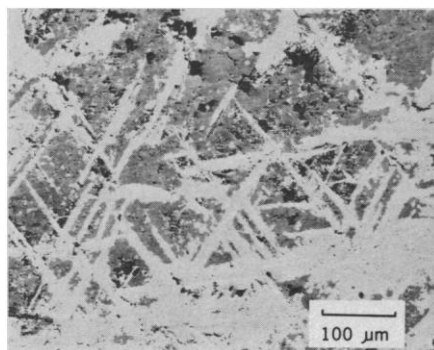


Fig. 1 (left). Scanning electron microscope image, produced by backscattered electrons in the composition mode, of the josephinite Widmanstaetten pattern. The light gray regions are the γ phase; the darker gray regions are the α phase; black areas are the iron cobalt chloride. Fig. 2 (right). Same as Fig. 1 but with greater magnification.

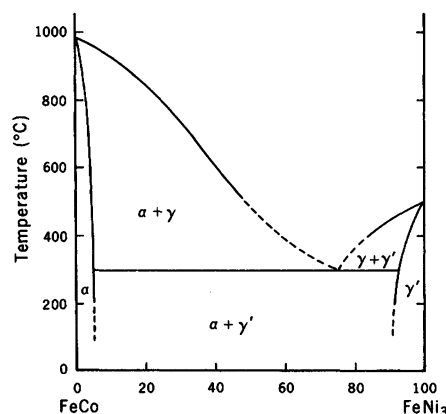
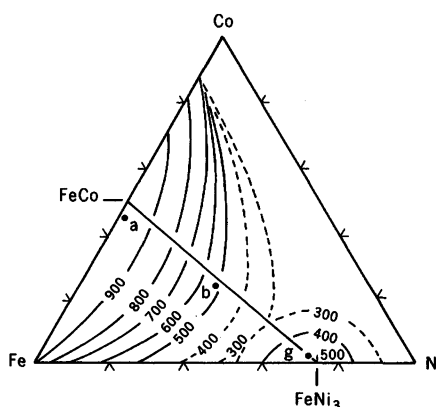


Fig. 3 (left). Ternary phase diagram of the Fe-Ni-Co system. Points *a*, *g*, and *b* represent the compositions of the α phase, the γ phase, and the bulk composition, respectively. The solid contour lines mark the upper surfaces of the two-phase regions, $\alpha + \gamma$ and γ and γ' , as determined experimentally (3, 4); the dashed contour lines mark the extent of the two-phase regions at 400° and 300°C , as proposed by us. Fig. 4 (right). Temperature-composition section along the solid line between FeCo and FeNi_3 in Fig. 3.

of the lamellae (see Fig. 2). Because of their very small size, the exact composition and crystal structure of the grains has not yet been determined.

Josephinite specimens show evidence of extensive alteration. Serpentine veins crosscut most of the specimens, and serpentine rinds surround nearly all of the specimens. Magnetite occurs as rims around metal grains within specimens and is abundant in the rinds. Iron-nickel metal, apparently secondary, also occurs as veins that crosscut specimens, including those that contain interior Widmanstaetten patterns. The α phases commonly have inclusions of iron cobalt chloride (lawrencite?) that might be an alteration phase. The Widmanstaetten patterns are well preserved only in the central portions of specimens within the rind of serpentine and magnetite, where they were not obliterated by the encroaching metamorphism.

Regardless of the range of temperature or the mechanism of exsolution for the formation of Widmanstaetten pattern described here, the bulk composition requires the homogeneous γ phase from which the phases exsolved to have been above 500°C. These observations are inconsistent with an origin by reduction of sulfides, silicates, or oxides during serpentinization (6). It is more plausible to us that josephinite was derived from the earth's interior and accompanied the peridotite during obduction of the ophiolite (1, 7) and that the alteration features described above were produced at the time of serpentinization of the Josephine Peridotite.

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Evidence of Acidification of Headwater Streams in the New Jersey Pinelands

Abstract. Seventeen years of stream pH data indicate a trend of acidification in two small streams in the New Jersey Pine Barrens which drain relatively undisturbed areas. The decline in pH has amounted to approximately 0.4 unit, with an estimated increase in H^+ concentration of about 50 microequivalents per liter. The data collected to date are consistent with the postulation of an atmospheric source for the increased H^+ .

Acidification of aquatic ecosystems has been observed in the northeastern United States, Scandinavia, and Canada (1-3) and has been linked to acid rain. Recently, concern has been expressed regarding the balance of aquatic communities subject to acidification, particularly with respect to increased concentrations of dissolved aluminum caused by acid precipitation (3). Decreasing stream pH has been reported in Scandinavia, and there appear to have been reversals in that trend from time to time (1); in addition, substantial but ephemeral decreases in stream pH due to snowmelt events have been reported (2). Data which indicate chronic stream-water acidification are rare, however. In most areas of North America where terrestrial and aquatic effects of acid precipitation have been studied, the landscape has been glaciated and is rather young geologically. Reaction with exchangeable cations in the soil and weathering of minerals in the regolith or underlying bedrock tend to neutralize most of the H^+ ;

as a result, the pH of stream water is usually greater than 5 (4) whereas the pH of precipitation is approximately 4 (3).

The Pinelands region, which encompasses approximately 2500 km² of southern New Jersey, is underlain by siliceous sands of Miocene, Pliocene, and Pleistocene age. Soils are mostly Hapludults and Quartzipsamments, which are acid (pH 3.4 to 4.6) and have a very low cation-exchange capacity (0 to 4 meq per 100 g) and percent base saturation (0 to 20 percent) (5). Below the leached A2 horizon, iron oxides coat the mineral grains. There is relatively little neutralization by ion exchange or mineral weathering as precipitation moves through the soil. This low amount of neutralization is evidenced by the low pH of shallow groundwater, which averaged 4.3 for 78 samples collected at McDonalds Branch in 1978 through 1979 (6). This report summarizes data from McDonalds Branch (39°50'N, 74°30'W) and Oyster Creek (39°48'N, 74°15'W), the headwater streams in the Pinelands,

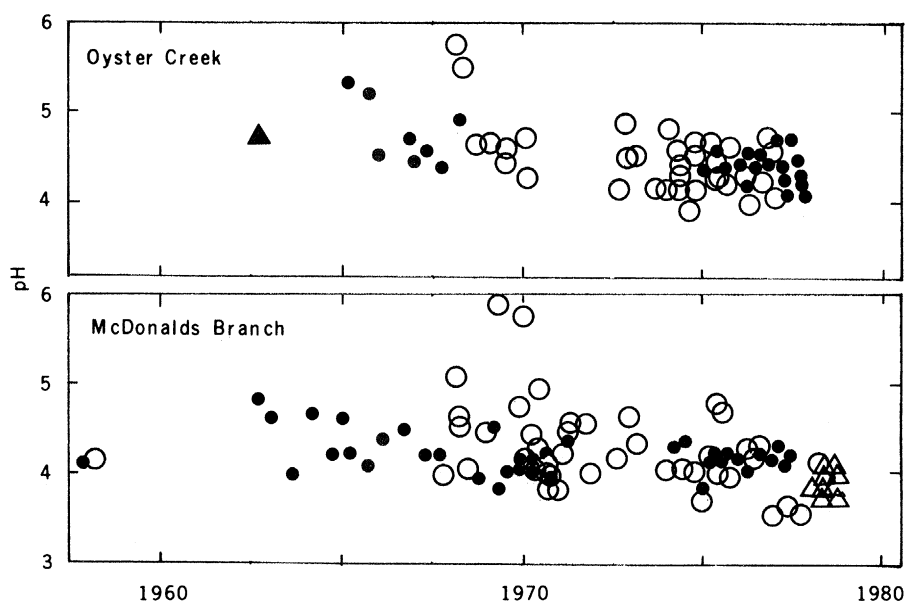


Fig. 1. Stream pH, 1958 through 1979. Closed circles represent samples in which anion and cation equivalents balanced and calculated and measured specific conductances were equal. Open circles are samples for which the chemical analyses were incomplete or for which discrepancies in anion and cation and conductivity balances could not be attributed to errors in pH. The closed triangle represents the average pH determined in a branch of Oyster Creek in a 1963 study (17). Open triangles are monthly means of pH data collected weekly from May 1978 to January 1979 during a University of Pennsylvania trace metal study.