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IONIC MIGRATION AND WEATHERING IN FROZEN ANTARCTIC SOILS

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16. Abstract

Soils of continental Antarctica are forming in one of the most severe terrestrial environments. Continuously low temperatures and the scarcity of water in the liquid state result in the development of desert-type soils. In an earlier experiment to determine the degree to which radioactive $NaCl^{36}$ would migrate from a shallow point source in permafrost, movement was observed. To confirm this result, a similar experiment involving Na^{22} Cl has been conducted. Significantly less movement of the Na^{22} ion was observed. Ionic movement in the unfrozen interfacial films at mineral surfaces in frozen ground is held to be important in chemical weathering in Antarctic soils.

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IONIC MIGRATION AND WEATHERING IN FROZEN ANTARCTIC SOILS

By

Fiorenzo C. Ugolini and Duwayne M. Anderson

Soils of continental Antarctica are developing in one of the most severe terrestrial climates. The persistently low temperatures and the paucity of liquid water have lead to soils that are dry, devoid of organic matter, and generally coarse in texture with poorly developed horizons. Salts are usually present and desert pavement is found in the place of the organic layer, characteristic of most temperate and arctic soils. Exceptions to these generalizations are few, but do exist. Organic matter is sometimes encountered as sparse and sporadic algal or moss mats, and near Molodezhnaya on the west coast where conditions are milder, clay migration leading to the development of a recognizable B horizon has been reported (1).

With age, Antarctic soils develop a yellowish-red hue and acquire finer textures. Because of the extremely dry conditions, even though ground temperatures are well below 0°C, the soils remain loose and unconsolidated. Summer thaw, which always is shallow, seldom results in the appearance of liquid water. Technically that portion of the soil profile below the zone of summer thaw (the active layer) is called permafrost. In many cases, especially on younger terrain, ice is encountered at a depth of one to several decimeters. The term ice-cemented permafrost was introduced by one of us to distinguish this situation (2).

Antarctic soils are classified as Ahumic, cold desert soils by Tedrow and Ugolini (3) and as Frigic soils by Campbell and Claridge (4). Agreement on the desertic features is unanimous among all who have investigated these soils (2,5,6,7). But differences of opinion exist on the type of weathering and soil-forming processes. In the polar regions emphasis has been placed on the prevalence of physical versus chemical weathering, and in Antarctica the results of the thorough study of Kelly and Zumberge (8) would seem to preclude any possibility of chemical weathering of significance today. Glazovskaia (9), however, advanced evidence that mineral alteration and clay formation is occurring presently at Mirny. This finding has been confirmed in the ice-free areas of southern Victoria Land (7,10,11). These studies, however, necessarily involve glacial debris in glaciated terrain. For this reason, however, it is not possible to fully refute a contention that the mineral alteration and the clay minerals formation observed might have taken place at different localities and under conditions different from the cold, arid climate that now prevails. In this circumstance, direct evidence of (i) ionic transport and (ii) liquid films bathing mineral surfaces seemed essential.

A preliminary experiment conducted during the austral summer of 1968 indicated that Cl^{36} ion moved upward in the dry, cold soils of the lower Wright Valley, Antarctica (12), during a period of 25 days. To confirm these results and to gain additional insight into the migration process, during austral summer of 1969, 20 μc of $Na^{22}Cl$ were placed at the top of the ice-cemented permafrost at three sites. The area chosen for this experiment was in the lower Wright Valley on the morainic complex of the Trilogy glaciation near the earlier Cl^{36} site (Fig. 1). These soils are younger than 7,000 years. Since, according to Nichols (13), the full-bodied stage of the Trilogy glaciation occurred at least 7,000 years ago. The following considerations governed the choice of sites and tracer:

1. to contrast ionic migration in a slightly saline, coarse textured and shallow depth to the ice-cemented permafrost soil, with that in a saline, fine textured and deeper soil;

2. an experiment duration of two years or more;

3. to compare and contrast the movement of the positive (Na^{22}) ion with that of (Cl^{36}) observed in the preceding study.

The Na^{22} installations were made on November 1-4, 1969. Of the three sites prepared for the experiment, only sites 1 and 3 subsequently were sampled. Site 2, intermediate in age and soil conditions, because of limited time available in the field, was excluded. Sampling was accomplished on October 28-29, 1971.

Site 1 (Fig. 1) is located about 1 km from the Wright Lower glacier, a distributary lobe of the Wilson Piedmont glacier blocking the lower Wright valley. The soil surface is covered by a desert pavement with scattered ventifacts (Fig. 2). The depth to the ice-cemented permafrost varied locally from 29 cm to 39 cm (November 2, 1969). The soil is sandy and light brownish gray (2.5Y6/2) in color (14). On November 2, 1969, the soil temperature at the top of the ice-cemented permafrost was constant at -17.0°C. The surface temperature varied from -3°C to -13°C. Soil moisture (after drying the soil at 110°C) showed the distributions given in Table 2.

Site 2 (Fig. 1) is located about 2 km from the Wright Lower glacier. The desert pavement contains numerous ventifacts, and boulders appear cavernously weathered. The depth to ice-cemented permafrost varied from 49 cm to 54 cm (November 1, 1969). The soil is sandy and grayish brown (2.5Y5/2) in color. Soil temperature of the top of the permafrost was constant at -20°C. Soil surface temperatures oscillated between -5°C and -14°C (November 2, 1969). Soil moisture (after drying the soil at 110°C) showed the distribution given in Table 2.

The sites were revisited between 27-31 October, 1971. Two hundred cm^3 (*ca.*) samples were collected at selected vertical increments from the point source to the soil surface (Table 1)(15). Duplicate samples were taken for soil moisture determination, and for chemical and physical analyses. At the time of retrieval, the temperature at the top of the ice-cemented permafrost was -20°C and the soil surface temperature fluctuated between -6°C and -16°C.

The samples were counted with a 5-inch NaI (Tl) crystal and phototube with a 400 channel Packard Model 116 Pulse Height Analyzer. The crystals were placed inside a lead castle shielding 4 inches thick. Background samples were also counted. All the samples were counted for 100 minutes. With the exception of the samples next to the source, no activity (after correction for background) was recorded at any depth down to within 5-10 cm of the initial location of the radioactive NaCl introduced. Because of the sampling increments employed, (see Table 1), it is possible that the Na^{22} had moved 5 cm, (from 35 to 30 cm) and 10 cm (from 50 to 40 cm) in profiles 5 and 7 (sites 1 and 3), respectively. The sandy nature of the soils, the extreme dryness, and the lack of structure had made it impossible to use more closely spaced sampling increments. The results, however, are sufficient for the purpose of a rough comparison of the migration of the positively charged ion (Na^{22}) with the negatively charged (Cl^{36}). At site 1, Cl^{36} was detected 7 cm above the point of injection after only 25 days. At comparable sites, Na^{22} had a maximum migration a distance of 5 cm in 2 years.

Although it is difficult to establish with certainty that migration of these two ions occurred under similar moisture content and temperature regimes, data collected over the years show that the hydrothermal regime for the month of November for the years 1962, 1968, 1969, and 1971 are similar. However, field evidence gathered during 1971 indicate that the summers of 1969 and 1970 must have experienced more snow and warmer temperatures than previous years. In the morainic complex of the lower Wright Valley during the austral summers of 1962, 1968, and 1969, a number of dry kettles containing salt efflorescences were observed, but in the austral summer of 1971, the bottoms of these kettles were covered with 1 m to 1.5 m of ice, clear evidence of melting and runoff during 1969 and 1970.

The physical and chemical parameters of profiles 5 and 7 (Table 1) have characteristics typical of soils in the lower Wright valley (2). Textures generally are sandy; however, profile 7, chronologically older than profile 5, contains more silt and clay. The fines tend to accumulate near the surface, a feature common to the Antarctic, Arctic, and alpine soils. Salt concentration is higher in the old soil, profile 7, but the salt distribution shows a similar trend.

Inasmuch as prevailing temperatures at these sites are below 0°C for most if not all of the year, the migration of ions and solutes within the soil profile must occur by diffusive movement in thin films of unfrozen water that separate the mineral surfaces from ice, and in thin films of adsorbed water in those regions devoid of ice. Much is now known about the water-ice phase composition of frozen soils (16,17). It is of interest to compute the unfrozen water phase composition for profiles 5 and 7 in order to estimate the extent of the liquid phase through which diffusion must occur. The calculation is made possible by a recently devised prediction equation requiring only an estimate of the specific surface area (18). This equation gives the maximum amount of liquid phase present as a function of temperature in degrees below freezing (0°C) (all water present in excess of this amount exists as ice; at water contents lower than the predicted value, the water present exists as a semi-liquid adsorbed phase and no ice can be present). This equation, however, is restricted to nonsaline soils and when applied to these saline soils, the unfrozen water content is underestimated. Order of magnitude estimates that are useful in the present context can be obtained, however. Values of the specific surface area, S, and values for W_u at -1°C and -10°C calculated from the particle size distribution data of Table 1, and equations 1 and 2 are listed in Table 2.

$$S = \sum_{n_i}^{n=1} K\frac{6}{\rho} \frac{[Pi - (Pi - 1)]}{\sqrt{Di\ Di - 1}} \qquad (1)$$

and

$$\mathrm{Ln}W_u = 0.2618 + 0.5519 \ln S - 1.449 S^{-0.264} \ln\theta \qquad (2)$$

In equations 1 and 2

S = specific surface area (m^2/g)

ρ = particle density, here taken to be 2.75 g/cm^2

K = correction factor for nonspherical grains taken to be 4.9 (determined by matching S calculated from the grain size distribution of powdered basalt and equation 1 with that actually measured by ethylene glycol retention.)

Pi = proportion of grains finer than the diameter Di

Di = equivalent spherical diameter

W_u = unfrozen water content (gH_2O/g)

θ = degrees below 0°C (°C)

Complete phase composition curves calculated from equations 1 and 2 for the nine sampled depths are shown in Fig. 3. From the curves of Fig. 3. and the values of W_u given in Table 2, it is clear that at temperatures below about -5°C, the amount of unfrozen water present through which diffusion could occur is extremely small; hence, the diffusion path must be extremely long and tortuous and the transmissibility of the liquid films virtually insignificant. Only at temperatures of -1°C and higher do the calculated values of W_u become large enough to constitute effective conductance channels for ionic movement; but at these temperatures, the values calculated for W_u exceed, and therefore must be limited to, the total measured water contents. Even making allowances for an increase in W_u due to the high salt content, for example, raising them by a factor of 10, the values below -5°C are less than 0.003 g H_2O/g clay; at -1°C, they are limited by the total water content in the soil to values of 0.025 g H_2O/g or less. Thus, it is evident that the very slight movement of Na^{22} observed is most likely accounted for by the dryness of the soil and the very small surface areas available for solute migration.

In comparing what seems like a rapid migration of Cl^{36} observed in the earlier investigation to the results reported here, two possibilities exist: either the soil moisture-temperature regime was significantly different, or the Cl^- anion is more mobile than the Na^+ cation under these circumstances.

Let us examine the second possibility. The labeled Na added in the NaCl form might be adsorbed on the exchangeable sites or it might remain in the interparticle spaces as a free salt. Wherever the Na^{22} is located, on the exchangeable sites or in solution, because of the extremely dry and below freezing conditions, the migration of these ions is limited to movement in the thin films of unfrozen water. At the temperature and moisture experienced by the soils of the lower Wright Valley, the thickness of this film is very small, on the order of 6Å (two molecular diameters). The ions within this film are not completely free from the charged surfaces of the silicates and, therefore, not fully available for migration. The activation energy for movement that the Na ions have to surmount is further increased by the silica-alumina complexes and gels that coat most soil particles (19,20,21). Fripiat et al. (22) have shown that the dissociation of water next to the surface of silicate is of the order of one 10^6 times greater than the bulk water. This high concentration of H^+ ion leads to release of silica due to acid attack of the silicate surfaces. It has been established that this process takes place under neutral or even alkaline conditions (19). Detailed analyses of profiles 5 and 7 (Table 3) have shown considerable quantities of amorphous silica and lesser amounts of alumina. Furthermore, alumina-silica complexes display positive or negative charges depending whether they are above or below the isoelectric pH. At the pH of 8, the natural pH of the soil, negative charges prevail; hence, sodium migration is further restrained. The work of Smith (23) and others (24,25) are in agreement with our results and interpretations. In leaching experiments using $CaCl_2$, Smith (23) found that chloride moved through the soil 1.04 to 1.67 times faster than it would if it had been associated uniformly with all the soil water.

This behavior is explained as the result of Cl^- exclusion due to electrical repulsion effects in the vicinity of negatively charged soil particles. In addition, if the colloidal fraction of the soil, though small, had an exchange capacity large compared to the quantity of Na^{22} introduced, only a few labeled Na ions would be expected to hydrolyze from the exchangeable sites and be available for migration, even though the presence of free salts in profiles 5 and 7 (see Table 1) offsets this and would tend to allow the Na^{22} ions to pass in solution due to the mass action principle.

It is possible that the method of implacing the radioisotopes had some influence. In the case of the Cl^{36}, a better contact might have been achieved between the solid bead, formed at once when the NaCl solution was poured, and the surrounding soil matrix than was obtained in the Na^{22} placement. Although such possibilities do exist, it is considered unlikely that the Na^{22} implantations were sufficiently different to explain the discrepancy of migration between the Cl^{36} and the Na^{22}. However, the more copious snowfall during 1969 and the relatively warmer 1970 (26,27) may have produced some melting accompanied by some leaching due to downward percolation surface water; this could have offset the upward migration of the Na^{22}. We conclude that our observations are best explained on the basis of a combination of the two initially suggested possibilities: a warmer and wetter regimen and the different electrical charges of Na and Cl.

Recent work of Cary and Mayland (28) on salt and water movement in unsaturated frozen soil has shown that the liquid phase movement takes place along the water films adsorbed to the soil particles. Soluble salts also move with the liquid phase and both salt and water move from the warm to the cold front. The soils of the lower Wright Valley have at depth an ice-cemented permafrost and contain thus a permanent cold front. From March through September, however, the surface soil experiences temperatures lower than the ice-cemented permafrost (27) and a reversible temperature gradient may ensue in the soil. However, during these months, the soil temperature averages between -25°C and -30°C. At these temperatures, the films of unfrozen water are extremely thin (Table 2) and movement of water and ions very slow. The ice-cemented permafrost remains the cold front only during the time the soil surfaces experience warmer temperatures. Field evidences have shown (2,29,30) that the ice-cemented permafrost tends to receed with time, and furthermore, salt in Antarctica soils concentrates near the surface rather than at the ice-cemented permafrost boundary. This reasoning leads to the conclusion that the temperature gradient during seven months of winter, imposes a driving force that causes the ascension of moisture and solutes which is not fully counterbalanced by the same gradient in the reverse direction during the remaining five months. Movement toward the surface caused by soil water evaporation generates a water gradient. This is possible at all times, but is enhanced during summer months. Thus, the net effect is the result of the interplay of a number of factors which is not yet predictable. The results of numerous experiments conducted at USA-CRREL to investigate the mobility of ions (31,32,33) have shown that, although ion diffusion is considerably lower in frozen soil than in unfrozen soil, the diffusion coefficients in the temperature range of 0°C-15°C are relatively high--in the order of $1 \times 10^{-7} cm^2 s^{-1}$ for silt soil at -3°C. Under saturated conditions and in a closed system, the diffusion coefficient (D) of an ion is virtually independent of total water content and thermal gradients, but determined by the temperature that controls the quantity of unfrozen water (32,33,34). Using the diffusion coefficient for Na, as calculated by Murrmann and Hoekstra (31) for saturated frozen Barrow silt, the distance of migration of Na in the soils of the lower Wright Valley can be estimated. A distance of 3.11 cm per year and a distance of 1.5 cm per year were obtained respectively for temperatures of -3°C and -6°C. A migration of 3.0 to 2.0 cm per year probably should be considered a realistic estimate; this corresponds to the rate we measured in the field. Although the migration in the Antarctic soils may occur, at least for part of the year, at temperatures considerably lower than -6°C, it has been found that the diffusion coefficient decreases only slightly below this temperature (31). The effective path length for Na ion diffusion in the Antarctic coarse soils is longer than in the silt of Barrow. The increased tortuosity tends to decrease the diffusion coefficient; however, this effect is compensated by the free salts present in the Antarctic soils.

We now briefly consider the phenomena of chemical weathering of soil minerals in the Antarctic climate. It is our belief that the weathering observed and commented upon (7,10,11) could be explained as a present and continuing phenomena and not a relict condition. Although the rate of weathering may be slow, the presence of liquid water films of high ionic strength bathing the mineral grains makes mineral dissolution and alteration virtually inevitable. It is significant that mineral weathering in Antarctica follows the same sequence as observed in temperate regions; hornblende, chlorite, plagioclase, and biotite are more susceptible to weathering than muscovite, K-feldspar and quartz (10,11). In Antarctica as in the other regions, muscovite tends to hydrate, and montmorillonite is found in soils with high pH's and an abundance of calcium (7). Thus, it seems that the major differences between weathering in the Antarctic and the weathering of temperate regions centers on differences in the rate and the redistribution of the products of weathering. In Antarctica, judging from the very immature soils observed on moraines of about 7,000 years in age, the rate of weathering is very slow. In all probability, this can be explained by the unfrozen water phase composition-soil temperature relationships illustrated in Fig. 3. Moreover, the weathering processes may be intermittent; snowfalls and melting vary from year to year. Some years melting occurs and in other times sublimation occurs. The replenishing of soil moisture surely increases the thickness of the adsorbed water films at temperatures above about -2°C. The augmented unfrozen water increases the mobility of the ions and other solutes and facilitates chemical weathering processes.

In a broader context, the phenomena of chemical weathering in Antarctica are relevant to other planets, specifically to Mars. The Antarctic ice-free areas, because of their intense cold, negligible snow accumulation, extreme dryness and low biological pressure, are considered the best terrestrial analogs to Martian conditions (35,36). Considering that the atmosphere of Mars is known to contain water vapor, it is conceivable that similar processes of weathering are occurring in the Martian soils.

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15. Because of the pulverulent nature of the soils and the continuous wind in the Wright Valley, special precautions were taken to avoid the injection of the gamma emitting Na^{22}. Aspirators, and disposable outer garments were supplied by the Health Physics Officers of the Naval Nuclear Power Unit, Detachment (PM-3A). We thank Messrs. D. L. Erickson, HMC, and E. F. Jones, HMC, USN, for their support.

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Figure Legends

Figure 1. Lower Wright Valley, Southern Victoria Land, Antarctica.

Figure 2. Site 1, profile 5. Note the surficial desert pavement and the absence of distinct soil horizons. Despite the fact that the soil temperature is well below 0°C, the soil remains loose because there is not sufficient water to cement the particles together. The ruler is 15 cm long. 2 November 1969.

Figure 3. Unfrozen water. Phase composition curves calculated from equations 1 and 2 for the soils at sites 1 and 3.

Table 1. Chemical and physical parameters of soils from Sites 1 and 3, lower Wright Valley, Antarctica.

						Sand**						Silt**				Clay**
Site	Pro- file	Depth (cm.)	pH*	E.C.* (mmhos/ cm.)	Total Soluble Salt (pct.)	Very Coarse 2-1mm (pct.)	Coarse 1-.5mm (pct.)	Medium .5-.25mm (pct.)	Fine .25-.10mm (pct.)	Very Fine .10-.05mm (pct.)	Total (pct.)	Coarse 50-20μ (pct.)	Medium 20-5μ (pct.)	Fine 5-2μ (pct.)	Total (pct.)	Total <2μ (pct.)
1	5	0-10	8.8	0.33	0.35	31.3	34.8	18.3	12.3	3.3	94.4	2.2	0.9	2.5	5.6	N.D.
		10-20	8.5	1.50	0.11	26.8	34.4	20.0	14.6	4.2	91.5	3.5	2.4	1.3	7.2	1.3
		20-30	8.0	0.02	0.06	33.9	54.3	10.3	1.4	0.1	100.0	N.D.	N.D.	N.D.	N.D.	N.D.
		30-35	7.8	0.01	N.D.	28.9	53.2	14.5	3.1	0.3	100.0	N.D.	N.D.	N.D.	N.D.	N.D.
3	7	0-10	7.5	3.85	1.30	29.4	25.9	15.4	21.1	8.2	76.6	4.0	5.6	6.3	15.9	7.5
		10-20	7.4	1.70	1.21	24.5	26.9	17.2	22.8	8.6	79.2	4.0	6.3	5.5	15.8	5.0
		20-30	7.8	1.10	0.54	28.4	25.1	14.2	22.6	9.7	85.6	5.5	3.8	2.6	11.9	2.5
		30-40	7.7	0.70	0.01	31.8	29.0	14.8	18.7	5.8	94.9	3.1	1.7	0.3	5.1	N.D.
		40-50	8.0	0.70	0.11	21.4	28.3	15.4	24.2	10.7	88.9	4.5	4.1	1.2	9.8	1.3

*1:5 soil:water ratio

**Particle-size analysis according to P. R. Day, Methods of Soil Analysis, Agron. 9, Part I, Am. Soc. Agron., Madison, Wis., 545 (1965).

N.D.= Not detected

Table 2. Moisture content distribution and "unfrozen water" phase composition of soils from sites 1 and 3, lower Wright Valley, Antarctica.

			Field moisture at sampling* dates:				
Site	Profile	Depth (cm.)	11/2/69 (pct.)	10/29/71 (pct.)	Specific Surface Area (m^2/g)	W_u at -1°C (gH_2O/g)	W_u at -10°C (gH_2O/g)
1	5	0-10	0.5	0.4	0.129	0.420	0.0014
		10-20	0.6	0.4	0.115	0.394	0.0011
		20-30	1.7	0.3	0.015	0.127	0.00001
		30-35	2.2	0.8	0.017	0.137	0.00001
3	7	0-10	2.5	1.1	0.346	0.723	0.0087
		10-20	1.2	0.9	0.322	0.695	0.0077
		20-30	1.6	2.2	0.195	0.527	0.0031
		30-40	1.4	2.3	0.071	0.302	0.0004
		40-50	1.4	1.7	0.146	0.449	0.0017

*Moisture was determined on oven-dry basis.

Table 3. "Free oxides" of soils from Sites 1 and 3, lower Wright Valley, Antarctica.

Sites	Profile	Depth (cm.)	Free Oxides SiO_2* (pct.)	 Al_2O_3* (pct.)	 Fe_2O_3** (pct.)
1	5	0 - 10	2.35	1.30	2.36
		10 - 20	8.56	1.63	2.10
		20 - 30	17.42	1.76	2.57
		30 - 35	17.12	1.15	--
3	7	0 - 10	4.50	1.51	1.57
		10 - 20	4.50	1.32	1.29
		20 - 30	4.45	1.51	1.43
		30 - 40	4.43	1.07	1.54
		40 - 50	4.47	0.79	1.50

*NaOH extractable

**Dithionite extractable

Extracts prepared according to Jackson, M. L., Methods of Soil Analysis, Agron. 9, Part 1, Am. Soc. Agron., Madison, Wis. 1965, 578.

Determinations done according to Jackson, M. L., Soil Chem. Analysis, Adv. Course, Madison, Wis., 1956, 57, 60.

Cover Legend

Morainic complex in front of the lower Wright Glacier, south Victoria Land, Antarctica. The pole with the wind-shredded flag indicates Site 1, Profile 5.

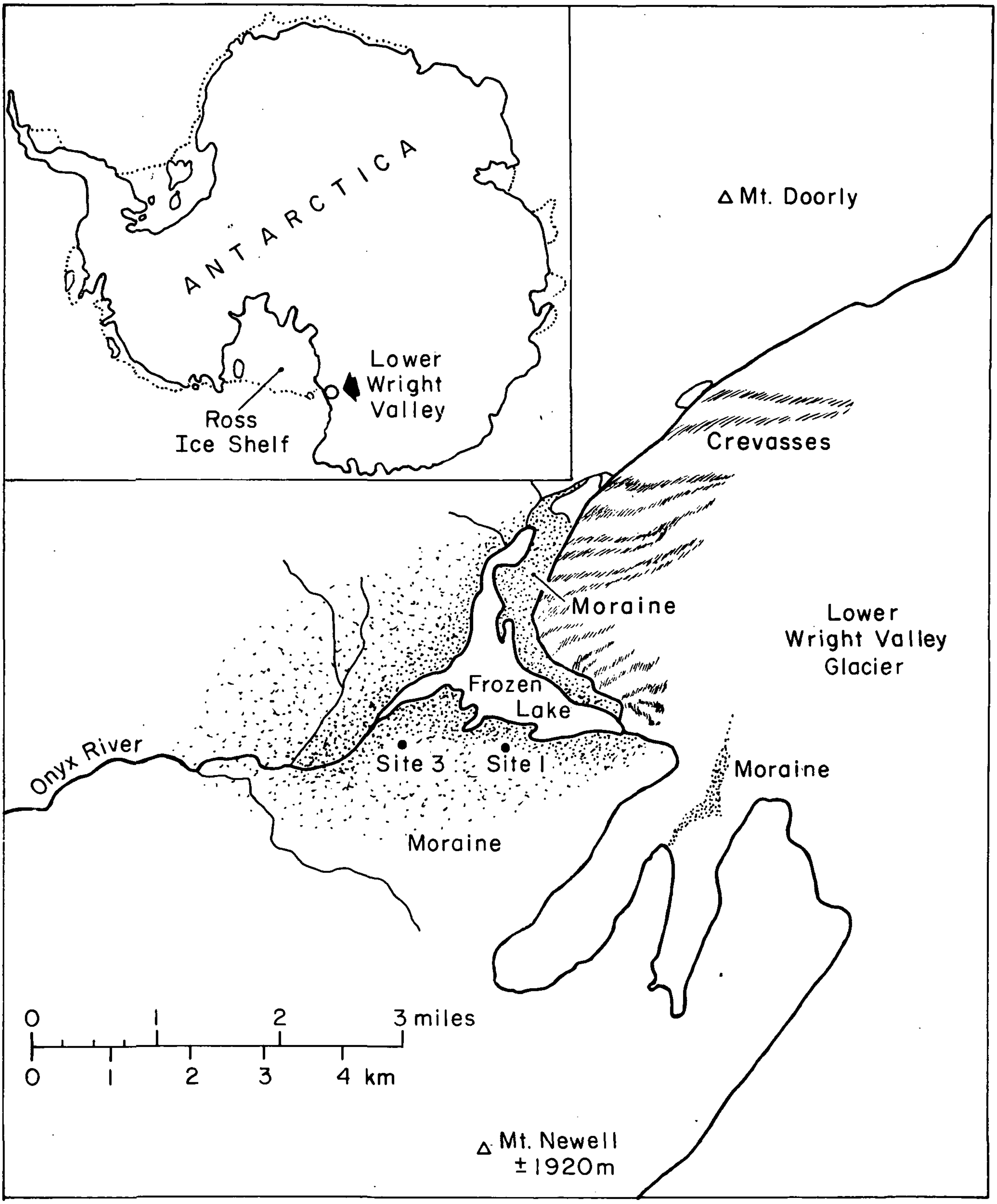

Figure 1. Lower Wright Valley, Southern Victoria Land, Antarctica

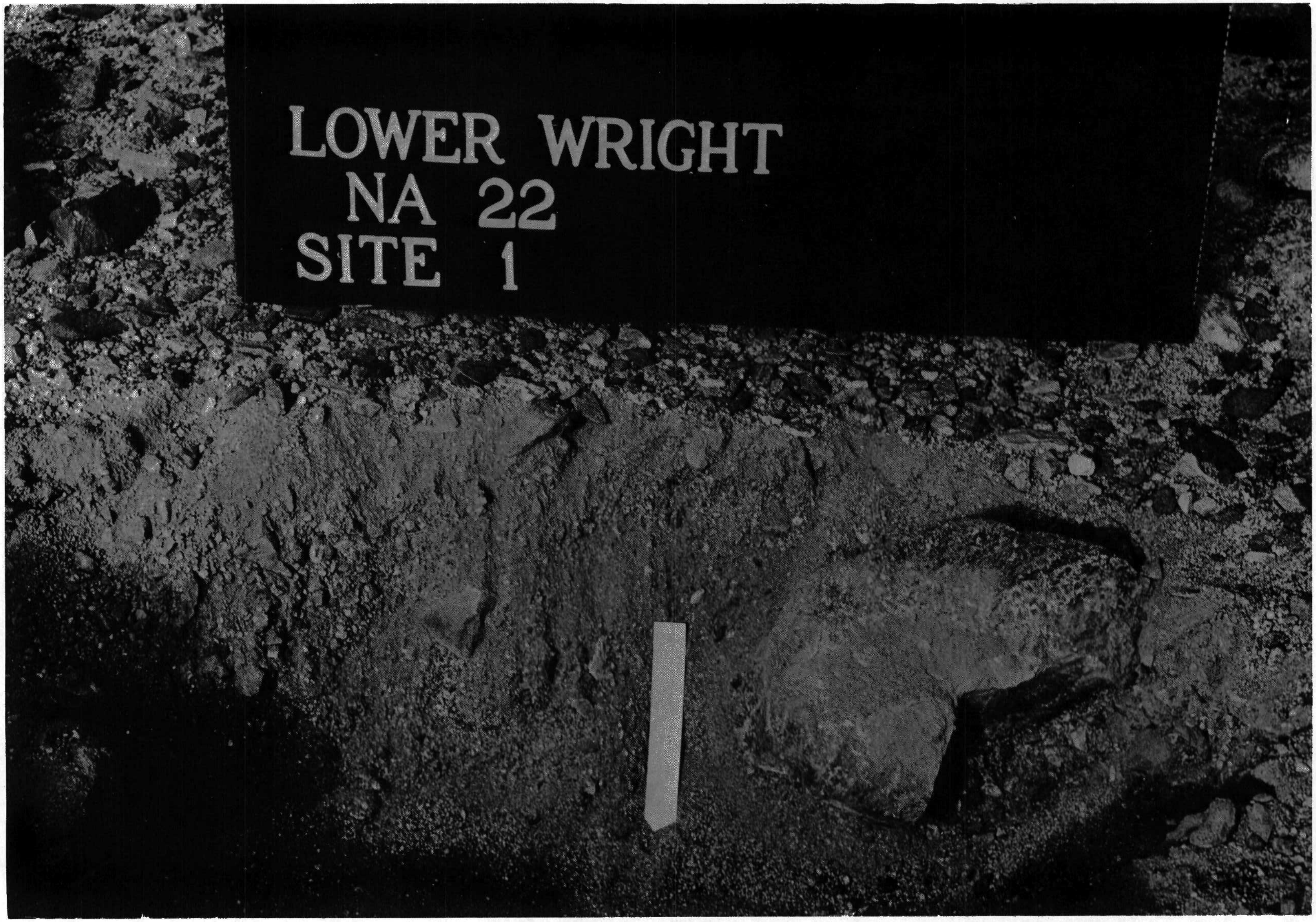

Figure 2. Site 1, profile 5.

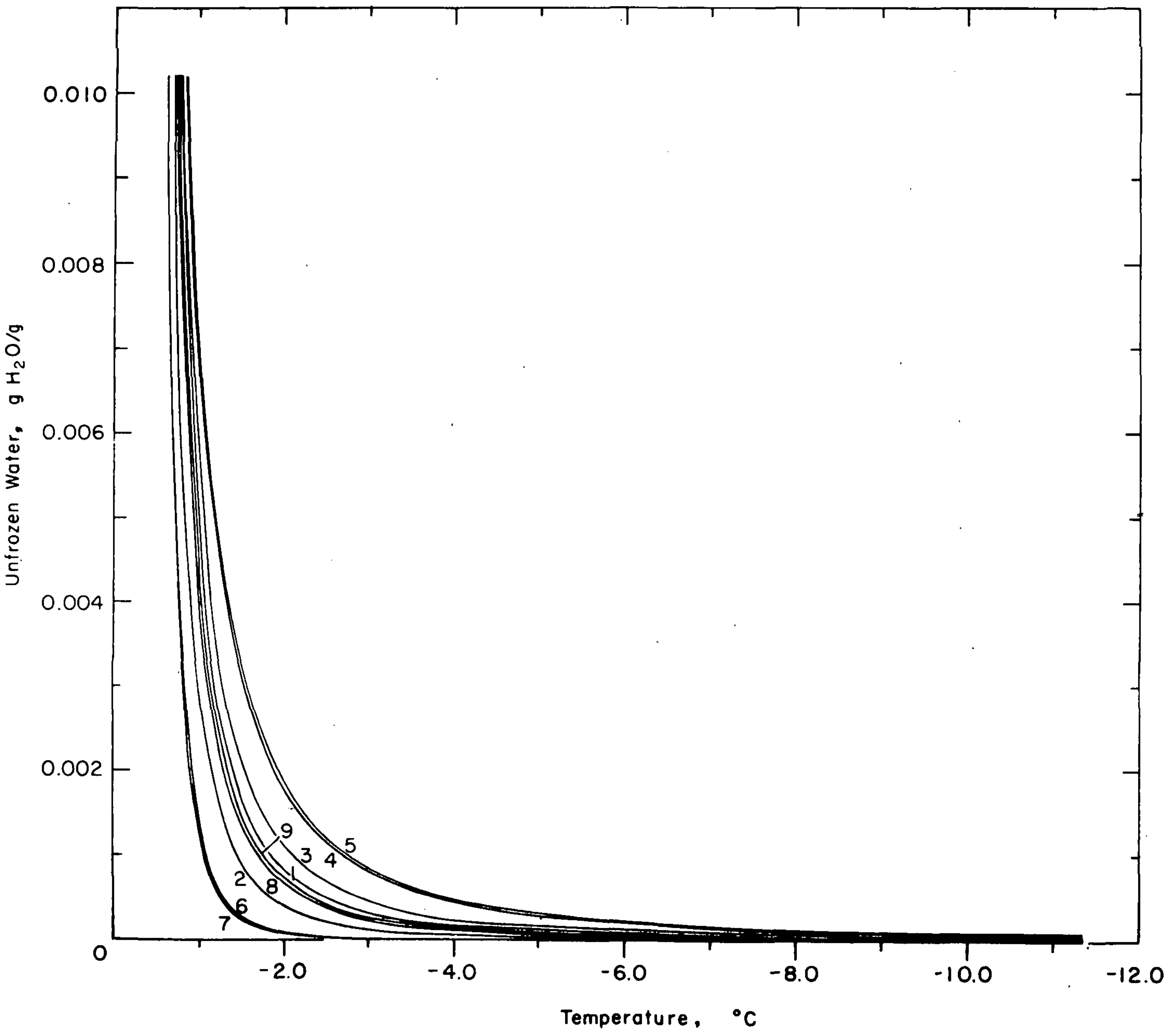

Figure 3. Unfrozen water.

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