absorb all the metal and space between them, would result readily in the columnar structure shown in Fig. 3, p. 5.

Still another form is shown in Fig. 38. These are thin sheets, apparently of the iron carbide Fe_3C, called cementite, shooting across a cavity or vug in an ingot of ferromanganese. These plates may reach a great size, as is shown in Fig. 39. Here the great facets of the block of ferromanganese seem to be due to the fact that, when the mass was broken open, rupture traveled

Fig. 38. Sheets Apparently of Cementite, Fe_3C, in Ferromanganese. The Author's Collection.

along the faces of certain of these great plates of cementite, which act as cleavage planes. Fig. 40, p. 92, again shows a micrograph of cast iron containing pronounced sheets of this cementite.

Definitions. — To facilitate the present discussion of the phenomena of progressive freezing, let us adopt provisionally the following terms.

The Frozen Continent means the part of the alloy which, at any given instant under consideration, has already frozen.

By the Shore Layers I mean those layers which have already in part solidified, and yet in part remain unfrozen, with poollets or estuaries of still molten matter, or in other words the layers in which freezing is actually going on.

By the Littoral Region I mean that part of the still unfrozen alloy immediately adjoining the shore layers; in other words, the layers which have not yet actually begun freezing but are about to.

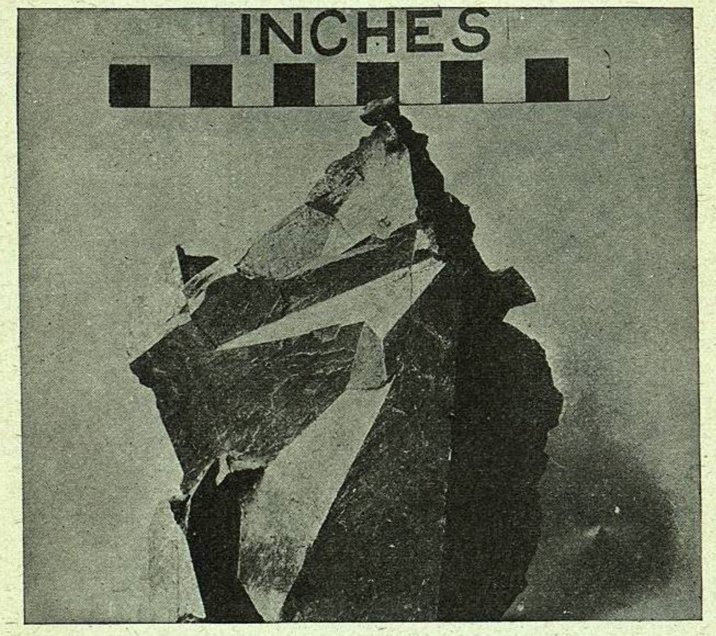

Fig. 39. Block of Ferromanganese with Large Facets Formed by Cementite Sheets. The Author's Collection.

The Open Sea means the still unfrozen mother-metal, beyond the littoral region.

Fig. 42, p. 96, may make the meaning of these terms clearer.

In the study of the growth of the frozen continent we may, to fix our ideas, confine our attention to some one of the many forms of growth. Let us select the broad armed pine-tree type shown in Fig. 42.

We will now further examine this pine-tree variety of the shoot-growth type of deposition as distinguished from the onion type shown in Fig. 34, p. 85, and we will note in particular two features which show that, great as is the apparent difference between the two modes, they really have much in common. These two features are, 1st, that although the deposition proceeds along certain spines chiefly, yet it is nevertheless a deposition in layers; 2nd, that though these spines enclose and as it were landlock part of the mother-metal remaining molten at the time when they shoot out, nevertheless much of it remains unlocked, and free to migrate, so that in fact much segregation occurs.

79. The Deposition is in Layers, though in Distorted Ones. — When we come to reflect upon the structure shown in

Fig. 40. Cast Iron Showing Plates of Cementite and Eutectic.
Section parallel to cooling surface.
(Tiemann, in the Author's Laboratory, *The Metallographist*, IV, p. 322.)

Fig. 36, p. 88, we infer that, though the deposition takes place chiefly along branches and spines, yet it is a deposition of successive layers on them. This is indicated in the space just below letter *A*, where the tint shades off very gradually. This, then, is a deposition by layers, differing from the layers of the onion type of Fig. 34 in the fact that, whereas the latter are smooth continuous concentric cube-surfaces, in the type shown in Fig. 36 these layers, while remaining parallel with each other, yet may collectively change direction abruptly, with sharp reëntering angles where they pass the crotch of a bough or spine, and salient ones where

they pass around an apex. They may be like the parallel though plicated sheets of a distorted bed of schist, or the pages of a crumpled pamphlet.

These similes, indeed, suggest that the rate of deposition is the same on the spines and twigs as on the boughs of our pine-tree structure, which may or may not be the case. It is more probable that the rate of deposition along certain surfaces is more rapid than along others, as if the boughs of a pine-tree were to increase in thickness rapidly, while the increase in thickness of the twigs was much slower, and that of the spines very much slower still. Such a condition of affairs seems to exist in the space just below the letter *A* in Fig. 36; for while the tint shades off very gradually, downwards from the upper side of this space, and upwards from the lower side, we do not find such shading from the right and left sides; as if the growth had taken place from the top and bottom of this space and not from the sides.

80. Landlocking Type of Deposition. — If we were to push to its logical conclusion this idea of growth by shoots instead of by concentric hollow-cube layers, we might conceive that such a cubical mass of molten alloy as is shown in Fig. 34 was, by such shoot-growth, cut up in the beginning of the freezing into a series of cubelets, each completely insulated from its neighbors by these shoots. Such a condition of affairs is shown diagrammatically in Fig. 41, p. 95, the whole mass being thus cut up into twenty-seven insulated landlocked cubelets, of which nine appear in our section. It is not to be supposed that in any actual case such complete subdivision and insulation could thus occur at the very beginning of the freezing as here sketched. If it occurred it should be later, when through the gradual thickening of such shoots they had come to insulate certain still molten parts from the main mass of the still molten interior, and as it were to "landlock" certain pools of the molten alloy, insulating them from what we may call the still molten open sea — open in the sense that in the interior of the cube beneath its frozen top it extends from frozen shore to frozen shore. We may call it open in spite of the fact that it is supposed to be frozen over at its upper surface quite as much as at its bottom and sides.

Nevertheless, the condition shown in Fig. 41 may be taken as the extreme type towards which this landlocking mode of freezing tends, and for convenience we may call it the "landlocking type" to distinguish it from the other extreme, the "onion type."

Assuming that, once this landlocking has taken place the freezing henceforth occurs in parallel layers, after the whole has frozen each cubelet will present the same series of regions that the cube in Fig. 34 shows, (1) the outer unsaturated layers; (2) the saturated ones; and (3) the eutectic.

Of course, the causes which led to this subdivision of the whole cube into these twenty-seven cubelets, should in fact be expected to lead to the further subdivision of these in turn into still smaller ones, and of these again into still smaller, until at last the mass is thus divided up into the microscopic enclosures which Fig. 36, p. 88, shows us.

Now in each of these microscopic enclosures the same series of events should happen which would take place if freezing occurred as shown in Fig. 34. In each microscopic cube we should find the same series of deposits, (1) the first deposited unsaturated layers, (2) the saturated layers, and (3) the eutectic. This differentiation of our microscopic cubelet thus should yield what we may call microscopic segregation, such as we see not only in Fig. 36, but also in Figs. 17, 18, 20 and 21 to 23. In each of these we find this microscopic segregation. In all except Fig. 36 we see the segregation of the eutectic as a microscopic mass, surrounded by the earlier frozen excess-substance. In Fig. 36 we do not recognize the eutectic structure, but we find clearly marked the unsaturated layers, still showing the remains of their initial heterogeneousness. For instance, in the space just below letter *A* the dark and white parts shade off by imperceptible gradations into each other, as already pointed out.

81. Segregation is both Microscopic and Macroscopic. — Up to this point we have imagined two distinct types of freezing. In the first or "onion" type, shown in Fig. 34, the mass in freezing acts as one whole, so that the mother-metal is neither crossed nor intruded into by any shoots as freezing proceeds, but remains throughout a single open, smooth-shored and smooth-bottomed sea, the shores, sides and bottom of which form a single cube, at each instant concentric with the walls of the ingot-mould. Here each layer as it deposits is the surface of a continuous cube extending completely around the shores, sides and bottom of this open sea, which is thus gradually silted up by the deposition of this

series of layers, each concentric with the initial shape of the sea itself. Thus our sea retains not only its initial shape but its initial centre, until by complete silting up it finally disappears.

In the second or "landlocking" type, shown diagrammatically in Fig. 41 and illustrated by Fig. 36, this sea is broken up at the very beginning of freezing into a number of pools, each completely landlocked by the growth from shore to shore of dividing barriers, and each pool is thus completely isolated from its neighbors. In each of these pools freezing proceeds as in the first type, and

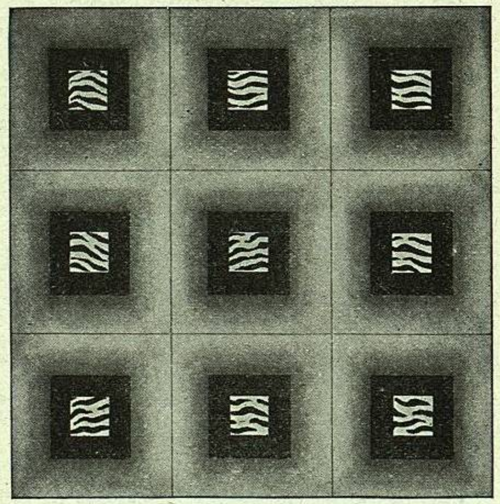

Fig. 41. The "Landlocking" Type of Freezing.

from the subdivision of these pools into microscopic poollets, microscopic segregation results.

Let us now recognize that freezing actually is of both these types simultaneously. There is the gradual silting up of our sea by the deposition of concentric layers, and there is also landlocking, due to the fact that these concentric layers are themselves not smooth sheets but mossy strata. The silting up of our sea is not by the deposition of impalpable mud in thin smooth layers on sides and bottom, but by the growth of a moss-like or peat-like mass, a thin forest of minute pine-trees. At any given instant the mass as a whole consists (1) of the already frozen outer continent, (2) of the shore layers now in the act of depositing, and (3) of the still open central sea including the littoral region. But the shore layer is itself composite somewhat as shown in Fig. 42. At its inner face the summits *A* of its little pine-trees project out into the still open central sea; at its outer face their thickened trunks and branches mat themselves close together, completely filling up the interstices; the mass is solid, as at *B*. Between summit and base is a series first of bays *C*, then of well-protected

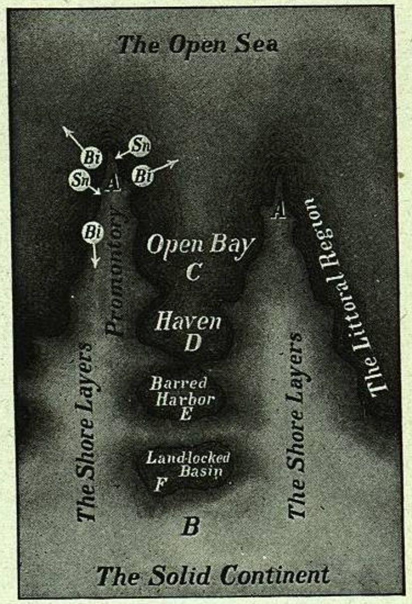

Fig. 42. The Shore Layers and the Littoral Region.

havens *D*, then of harbors *E*, the mouths of which are badly obstructed by bars, and finally of completely landlocked basins *F*.

In each of these landlocked basins freezing proceeds selectively as in other cases. First layers are deposited poorer in bismuth* than this mother-basin or pool from which they freeze, the pool of which they form the progressively encroaching shores. As freezing progresses the successive layers of shore deposited are

* We are still considering the case of bismuth-bearing tin.

richer and richer in bismuth, till at the final disappearance of the pool the last frozen particle is richer than the pool was at the moment when it became landlocked. Thus the drying up or rather freezing up of each of these landlocked pools gives rise to microscopic segregation.

But at the same time macroscopic segregation is going on for exactly the same reason as in the onion type. The only differences between the two cases are (1) that the shore layer is serrated in our present case though smooth in Fig. 34; and (2) that this landlocking takes place. But neither of these differences can prevent the progressive enrichment of the mother-metal, the open sea. The enrichment takes place quite in the same way, whether the layers which freeze out are smooth in outline, or serrated.

Consider for a moment the growth of a single pine-tree *A*, Fig. 42. A very thin layer of metal is deposited upon it; this layer is richer in tin and poorer in bismuth than the open sea from which it freezes; hence by its freezing the immediately adjoining layer of sea is enriched in bismuth; this excess of bismuth diffuses outwards into the open sea, which thus becomes progressively enriched. We may attempt to indicate this by the arrows in Fig. 42. But the enrichment of the open sea which took place through the deposition of this layer will take place with the deposition of each succeeding layer; and thus the open sea or mother-metal becomes gradually enriched as its shores gradually draw together, as its tide slowly falls; and with its enrichment comes the corresponding enrichment of the successively deposited layers, the successively emerging curved lines of the seashore. Manifestly this is just what is shown in Fig. 34, substituting serrated for smooth contours, and substituting layers microscopically segregated and thus each heterogeneous, for layers each homogeneous, though each different from its neighbors, each richer in bismuth than the next older one.

Let us recognize clearly this double heterogeneousness, this double segregation, macroscopic and microscopic; this progressive enrichment of the whole mass as we pass from outside to centre, and also this enrichment, in each individual thin layer, of those parts which were the central regions of the landlocked pools.

82. Progressive Variation in the Microscopic Segregation. — That as we pass from without inwards the character of

the microscopic segregations should change really follows from what has been said; but a further word of explanation may not be amiss.

We have seen how, with the gradual thickening of the walls of the solid continent which forms the already frozen part of the ingot, the remaining open sea is gradually enriched in bismuth, the dissolved metal. Now at any given moment the composition of each bay shown in Fig. 42 should be very closely that of the open sea; and the composition of the havens and of the partly barred harbors should also follow closely, though not quite so closely, the composition of the open sea. At least their composition should shift with that of the open sea, and in the same direction, though, thanks to the ever increasing barriers, not necessarily at exactly the same rate. Ignoring for the present this difference in rate, the composition of each landlocked basin, at the moment when its last communication with the open sea is frozen across, should be closely that of the open sea; so that the composition of the successive landlocked basins formed in successive layers should, at this moment of the completion of their isolation, vary progressively from layer to layer. Each basin at the moment of its insulation, should be richer in bismuth than the earlier formed basins were at the moment of their insulation.

But it is chiefly the composition of any given basin at this moment of its insulation that will determine in what kind of layers it will deposit as it in turn freezes up. Each basin will hereafter act independently of the rest; it is as if we started with a different initial composition for each. And, just as we saw in § 60, p. 68 that the series of alloys of two metals of limited reciprocal solubility should be eutectiferous in its middle but not at its ends, so of the local segregations arising from the freezing of these basins, some may be eutectiferous, and some not.

Thus, the basins formed in the outer crust of the ingot, early in the freezing, when hardly any enrichment of the open sea has taken place, might have so little of the dissolved metal that the enrichment of the successive layers during freezing would not reach the saturation-point. Such ponds would yield only unsaturated layers. Others, formed somewhat later, when the enrichment of the open sea had gone farther, might at the moment of their insulation contain so much of the dissolved metal that the enrichment of the successively formed layers would pass the saturation-point; in which case, exactly as in § 64, p. 72, not only saturated layers but also some eutectic should form. Still others, later formed, and with a still larger proportion of the dissolved metal, would yield a larger proportion of eutectic; *etc.*

83. Approach Towards One or the Other of These Types. —While freezing is doubtless always between these two extreme types, the onion and the landlocking, yet we may recognize certain features which should bring it nearer to one type or the other. The earlier the out-shooting pine-trees meet in the centre, the closer should the conditions approach to the extreme landlocking type of Fig. 41, which completely prevents all axial or macroscopic segregation; and the less pronounced should therefore be the axial segregation. And in general the narrower the open sea, *i. e.*, the narrower the mould in which the metal is cast, the earlier will this meeting take place. Further, the farther the arborescent promontories shoot out into the open sea, the earlier will they meet. While we may not forecast fully what kinds of metal will form far-shooting promontories, yet we may expect that those with great thermal conductivity will as a whole shoot out farther than those which conduct heat but slowly; and the viscous ones should shoot out farther than the more mobile, because the convection currents are less in the former, and convection currents may be expected to oppose the shooting out of long-trunked pine-trees by tending to break off their trunks, or to wash them off. It is in still ponds that ice, in forming, shoots out long spines.

Thus we may expect macroscopic segregation to be less (1) in narrow ingots, (2) in viscous metals and in those of high thermal conductivity, than under the opposite conditions.

83*A*. Conditions Affecting the Degree of Residual Segregation. — In §§ 84 to 93 we shall consider how the rate of freezing and of cooling from the freezing-point downwards may be expected to influence the degree to which segregation will exist in the cold alloy. This discussion is in the nature of a forecast. A series of investigations has been planned and begun, to test the conclusions reached in this discussion. While it is greatly regretted that these experiments cannot be completed in time to permit the use of their results in the present work, it has been thought best to retain this discussion here, both as a mental exercise for the student, tending to familiarize him with at least cer-