analytical data of a bone should be considered because of inconsistencies, as pointed out by Oakley (*11*). Based on these data, the bones are arranged in order of their relative age. Where there is a sufficiently large bone sample with enough collagen, the radiocarbon age is determined. This then will yield an age scale with a number of fixed points to which the analytical data of a small amount of bone sample, say from the skull of *Homo rhodesiensis*, is compared. With prudent interpolation one may arrive in this manner at its age.

Besides collagen, dentin—the organic matter in teeth—can also be utilized for dating except that modern dentin has inherently only approximately two-thirds of the collagen content of bone. But the possibility of dating ivory, such as tusks from mammoths, and so forth, is indicated.

Radiocarbon laboratories have reported many shell dates from the carbonate of the shell as the sample. Recently several papers have appeared that point to the unreliability of data from river shells (*12*) and land snail shells (*13*) because of the varying and unknown amounts of "dead" carbonate from limestone that are incorporated by the living organism.

This problem is not encountered with marine shells. But when they are dead and buried they may be subjected—like bones—to various groundwater environments (*14*). Usually investigators have attempted to circumvent possible errors arising from carbonate exchange by removing the outer layer of shells with hydrochloric acid and using only the central portion for dating.

Similar to bones, shells also contain an organic protein constituent, conchiolin, which is present in 1- to 2-percent amounts in modern shells. The two major inorganic components of shells are calcium carbonate in the form of calcite and harder aragonite, which are arranged like bricks in a wall with the conchiolin being the mortar. In contrast to collagen, conchiolin contains mostly glycine, alanine, aspartic acid, and serine (*15*). Its solubility characteristics are similar to those of collagen.

Thus conchiolin can be prepared for dating in a manner analogous to the treatment of collagen in bones. Usually kilogram amounts of raw material of shells are required in contrast to decagrams for bones.

Shells suffer destruction in time mainly from boring organisms which are smaller shells or sponges. These organisms excrete from their accessory boring organ a fluid which dissolves carbonate and eases the mechanical work of the borer. After general loosening of the carbonate layers ground-water erosion can act more destructively than before. In the absence of organisms, even in a moist environment only moderate changes occur in the protein of shells which affect its solubility. After about 10^4 to 10^5 years, only about 1 to 5 percent of the peptide bonds are broken, and the protein fragments are leached out of a shell (*16*).

It is interesting to note that while bones have an initially higher collagen content, after 8000 to 10,000 years or much more, shells can have comparable amounts of conchiolin left, indicating a faster decay rate of the more loosely assembled bones in contrast to the much tighter structure of shells.

Several abalone shells (*Haliotis*) from Santa Rosa Island, California, were dated. One set of shells gave an age of 7120 ± 120 years for the outer carbonate layers (UCLA–663) and 7230 ± 120 years for the inner layers (UCLA–663). The organic portion ($\sim$ 0.4 percent) yielded a corrected date of 7210 ± 400 years (UCLA–663). Similar results were obtained from a sample about 1000 years younger (UCLA–659). The correction (*17*) used (250 ± 50 years) takes into account the threshold which atmospheric carbon dioxide experiences before it enters the ocean and the upwelling characteristics of the ocean currents on the Southern California coast.

Besides such large shells as abalone, smaller shells commonly associated with Central American burials may be dated. For example, a Lunarca-type shell of 2700 ± 90 years (UCLA–687–1) still had a conchiolin content of 0.15 percent which is sufficient for conchiolin-based dating provided kilogram amounts of sample are available.

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References and Notes

1. K. P. Oakley, *Science* **140**, 488 (1963).
2. S. F. Cook and R. F. Heizer, *Southwestern J. Anthropol.* **9**, 231 (1953).
3. R. F. Sognnaes, School of Dentistry, University of California, Los Angeles, private communication.
4. J. F. Woods and G. Nichols, Jr., *Science* **142**, 386 (1963).
5. Courtesy of P. C. Orr, Museum of Natural History, Santa Barbara, Calif.
6. Courtesy of G. L. Jepsen, Department of Geology, Princeton University.
7. Courtesy of D. Lal, Department of Geophysics, Tata Institute, Bombay, India.
8. Courtesy of O. H. Prufer, Department of Anthropology, Case Institute, Cleveland.
9. A. S. Woodward, *Nature* **108**, 371 (1921).
10. Courtesy of J. D. Clark, Department of Anthropology, University of California, Berkeley, and K. P. Oakley, Sub-Department of Anthropology, British Museum, London.
11. K. P. Oakley, *Science* **141**, 1172 (1963).
12. M. L. Keith and G. M. Anderson, *ibid.*, p. 634; W. S. Broecker, *ibid.* **143**, 596 (1964).
13. M. Rubin, R. C. Litkins, E. G. Berry, *J. Geol.* **71**, 84 (1963).
14. E. A. Olson and W. S. Broecker, *Radiocarbon* **3**, 141 (1961).
15. P. E. Hare, *Science* **139**, 216 (1963).
16. P. H. Abelson, *Carnegie Institution of Washington Yearbook* (1954–55), p. 107.
17. J. R. Arnold and E. C. Anderson, *Tellus* **9**, 28 (1957); H. Craig, *ibid.*, p. 1; G. J. Fergusson and T. A. Rafter, *Proc. Intern. Conf. Peaceful Uses Atomic Energy* **18**, 526 (1958); R. Revelle and H. E. Suess, *Tellus* **9**, 18 (1957).
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Site of Preference Energy and Selective Uptake of Transition-Metal Ions from a Magma

Abstract. *Results of absorption spectra measurements on silicate glasses of various compositions indicate that ions of the first transition-metal series are present in tetrahedral and octahedral sites in silicate melts (glasses). The fractionation patterns observed for transition-metal ions between magmas and silicate minerals can be interpreted according to crystal field theory in terms of octahedral "site preference energies" of transition ions in crystal lattices.*

Numerous explanations have been offered for the distribution of trace elements during magmatic crystallization (*1, 2*). Most of the proposals are modifications and extensions of the classical Goldschmidt criteria (*3*) of ion size and charge, but all of the explanations lack generality, particularly in regard to ions of the transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu). Furthermore, all such interpretations must fail for a solid solution series with a minimum melting point (*4*). One recent explanation is that offered by Williams (*5*), which accounts rather successfully for the order of deposition of transition ions in a basic magma by crystal-field theory (*6*). We wish to amplify Williams' ideas and to show that crystal-field theory appears to provide a general explanation for the fractionation of transition-metal ions (oxidation states II and III) between magmas and silicate minerals which have crystallized from silicate melts.

The energy of transition-metal ions is a function of the symmetry and position of anions of ligands which surround an ion in liquids and solids. In such an electrostatic field the five '3*d*' orbitals are no longer degenerate, and some ions are stabilized relative to others. The field-induced separation of '3*d*' orbitals, Δ, is greater for octahedral symmetry than for tetrahedral and, for a given value of Δ and symmetry, it is possible to estimate crystal-field stabilization energies.

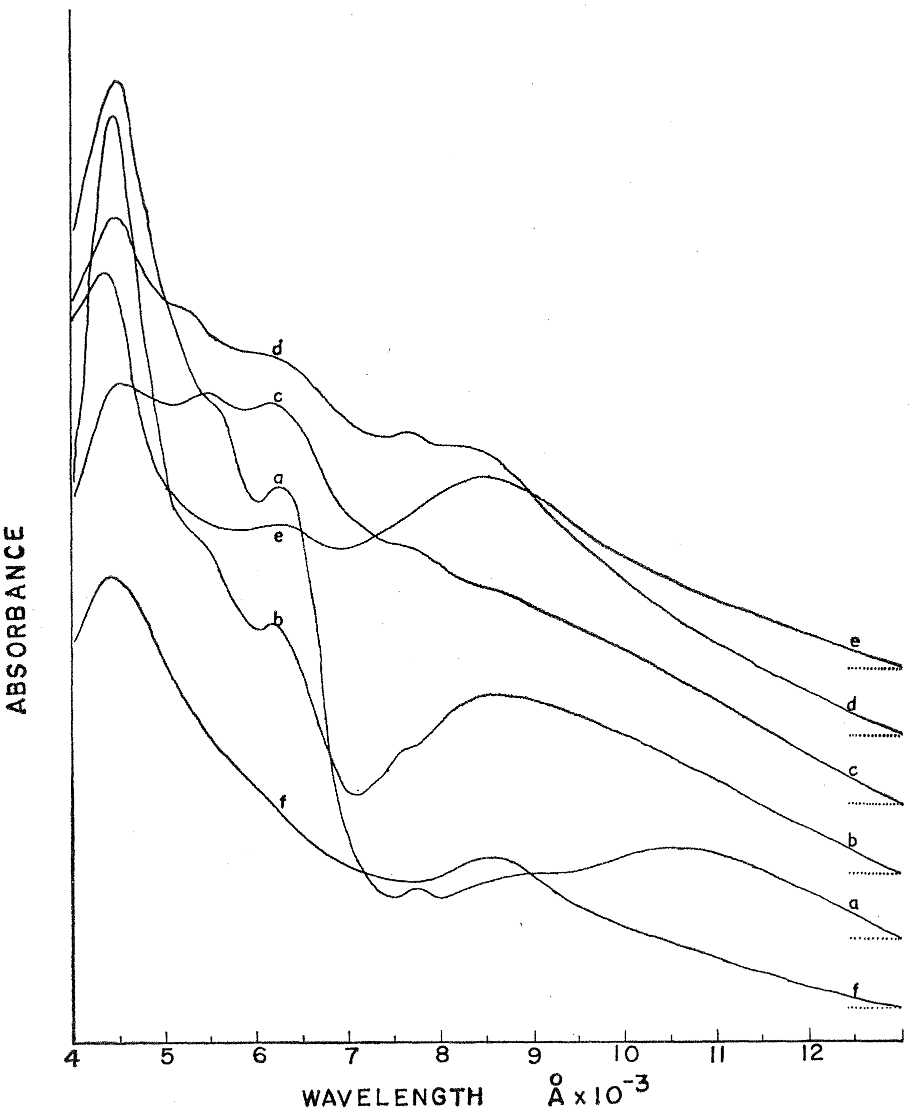

Fig. 1. Absorption spectra of various silicate glasses containing 5 percent NiO by weight. All measurements were made with a Cary model-14 recording spectrophotometer. Compositions are given in percentage by weight. (Curve *a*) Soda-alumina-silica eutectic. Composition: Na_2O, 21.0; Al_2O_3, 4.5; SiO_2, 74.5. (Curve *b*) Albite glass ($NaAlSi_3O_8$). (Curve *c*) Diopside-albite glass. Composition: diopside, 30; albite, 70. (Curve *d*) "Granite." Composition: SiO_2, 75.0; Al_2O_3, 12.5; Na_2O, 3.5; K_2O, 3.5; CaO, 0.5; NiO, 5.0. (Curve *e*) "Tholeiite." Composition: SiO_2, 50.0; Al_2O_3, 19.0; MgO, 12.0; CaO, 11.0; Na_2O, 3.0; NiO, 5.0. (Curve *f*) Diopside glass ($CaMgSi_2O_6$). The absorption maxima at the approximate wavelengths 4500, 5400, 6300, 7800, and 10500 Å are indicative of Ni^{2+} in tetrahedral coordination, whereas the bands at 4300 and 8500 Å are characteristic of Ni^{2+} in octahedral sites. With increasing proportions of Na^+ ions and SiO_2, and decreasing Al_2O_3, the absorption peak at 4300 Å intensifies and migrates to longer wavelengths, while the band at 8500 Å disappears and those at 5400 and 7800 Å increase in intensity. These results are in accord with those of Moore and Winkelmann (*10*).

The structure of a liquid is quasi-crystalline; there are indications that transition-metal ions in solids and their derived liquids occur in similar configurations and are therefore stabilized in both environments. For example, the absorption spectra of $Ni(H_2O)_6{}^{2+}{}_{aq}$ and crystalline $NiSO_4 \cdot 6H_2O$ are almost identical (*7*). In general, one anticipates slightly larger interatomic distances and less regular coordination in liquids than in solids. However, these differences are generally small, as the comparable heats of fusion of compounds of transition elements and other metals would indicate. But when ions are dissolved in polycomponent liquids where configurations of several types are present, a distribution of ions between the different sites will occur if thermal energies are comparable with site-energy differences. In silicate melts tetrahedral and octahedral sites predominate and transition ions may enter either site. However, transition-metal ions are rarely found in tetrahedral sites in crystals which separate from a silicate liquid.

Therefore, if significant proportions of transition-metal ions are in tetrahedral sites in a silicate liquid, there will be substantial incorporation of these ions into octahedral sites in crystals. In effect, the ΔH of extraction of these ions from the liquid will become progressively more negative as the proportion of tetrahedral sites increases and distribution coefficients will progressively favor incorporation of the ions in the solid. Such systems will show highly nonideal behavior of certain transition-metal ions. It must be emphasized, however, that these energy terms may not be apparent from thermodynamics of melting of the pure transition-metal compounds, where the variety of potential sites in the fused state is limited. Williams (*5*) has correlated the order of uptake of trace amounts of transition-metal ions in minerals which crystallized from the Skaergaard intrusion with the order of crystal-field stabilization energies of transition ions in a crystal field of anions of octahedral symmetry. We consider that the patterns observed cannot be explained in terms of octahedral

Table 1. Crystal-field stabilization energies (CFSE) for transition ions in octahedral and tetrahedral lattice sites in oxides. The data are from Dunitz and Orgel (*12*); the figures in parentheses are from McClure (*8*).

No. of *d*-electrons	Ion		CFSE		Octahedral "site preference energy" (kcal mole^{-1})
	2+	3+	Octahedral (kcal mole^{-1})	Tetrahedral (kcal mole^{-1})	
0	Ca^{2+}		0	0	0
		Sc^{3+}	0	0	0
1		Ti^{3+}	20.9 (23.1)	14.0 (15.4)	6.9 (7.7)
2		V^{3+}	38.3 (30.7)	25.5 (28.7)	12.8 (2.3)
3	V^{2+}		— (40.2)	— (8.7)	— (31.5)
		Cr^{3+}	53.7 (60.0)	16.0 (13.3)	37.7 (46.7)
4	Cr^{2+}		— (24.0)	— (7.0)	— (17.0)
		Mn^{3+}	32.4 (35.9)	9.6 (10.6)	22.8 (25.3)
5	Mn^{2+}		0 (0)	0 (0)	0 (0)
		Fe^{3+}	0 (0)	0 (0)	0 (0)
6	Fe^{2+}		11.9 (11.4)	7.9 (7.5)	4.0 (3.9)
		Co^{3+}	— (45.0)	— (26.0)	— (19.0)
7	Co^{2+}		22.2 (17.1)	14.8 (15.0)	7.4 (2.1)
8	Ni^{2+}		29.2 (29.3)	8.6 (6.5)	20.6 (22.8)
9	Cu^{2+}		21.6 (22.2)	6.4 (6.6)	15.2 (15.6)
10	Zn^{2+}		0	0	0

fields alone, and that consideration of tetrahedral coordination is critical. Thus, the magnitude of the octahedral "site preference energy" (*8*) determines the order in which ions of the transition metals are incorporated into minerals which crystallize from a magma with octahedral and tetrahedral sites.

Absorption spectra measurements of transition-metal ions in silicate glasses (representing supercooled silicate liquids) and minerals by us (Fig. 1) and by other workers (*8–11*), indicate that transition-metal ions occur in tetrahedral and octahedral coordination in silicate melts but occupy octahedral sites in minerals (olivine, pyroxenes) which crystallized from a magma.

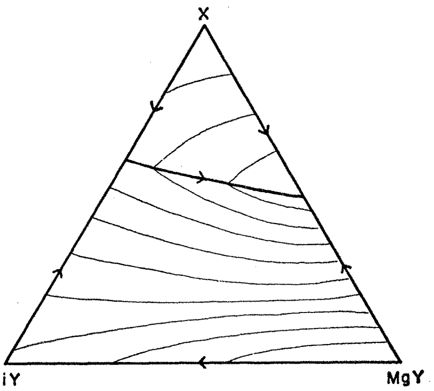

Fig. 2. Predicted phase diagram for the ternary system: *X*-Ni*Y*-Mg*Y*. Component *X* is a compound which forms a liquid with a high proportion of tetrahedral sites. Binary system: Ni*Y*-Mg*Y* is a solid solution series. An "inversion" of liquid-solid relations in the projected binary solid-solution series is postulated in melts possessing a high proportion of component *X*. As a result, Ni*Y* (for example, Ni_2SiO_4) becomes the high melting constituent.

McClure (*8*) and Dunitz and Orgel (*12*) have accounted for the distribution of transition-metal ions in spinels from a consideration of the octahedral "site preference energy" of an ion. This parameter represents the difference in crystal-field stabilization produced by oxygen ions in octahedral coordination and in tetrahedral coordination about a transition ion (Table 1). Data from absorption spectra measurements indicate that crystal-field stabilization energies by oxygen ions are almost identical in oxide and silicate lattices (*8, 11*). The orders of octahedral "site preference energy" listed in Table 1, namely,

$$\mathrm{Ni} > \mathrm{Cu} > \mathrm{Co} > \mathrm{Fe} > \mathrm{Mn} \geqq \mathrm{Ca},\ \mathrm{Zn}$$

for M^{II} ions, and

$$\mathrm{Cr} > \mathrm{Mn} > \mathrm{V} > \mathrm{Ti} > \mathrm{Fe} \geqq \mathrm{Sc}$$

for M^{III} ions,

are almost identical to the orders observed for the selective uptake of trace amounts of transition-metal ions in minerals which crystallize from a basic magma (*5, 13*).

We conclude, therefore, that because of added stability available to most transition-metal ions in octahedral sites in minerals, it is energetically more favorable for these ions to be removed from tetrahedral coordination in a magma and to enter into octahedral sites in minerals crystallizing from the magma. Furthermore, the spectra illustrated in Fig. 1 indicate that the proportion of tetrahedral sites in silicate melts (glasses) increases with increasing amounts of alkali ions and silica, and decreasing amounts of alumina (*10*). One would predict from this that distribution coefficients of transition-metal ions with large octahedral "site preference energies" between mineral and magma would be greater for granitic magmas than for silicate melts of basaltic composition.

In conclusion, we predict that a large octahedral "site preference energy" value for certain transition-metal ions could lead to interesting and unexpected phase relationships. It is possible that in a three component system of the type: *X*-Mg*Y*-Ni*Y*, where *Y* is an anion (SiO_4^{4-}, O^{2-}, and so forth) and component *X* is a compound which forms a liquid with a high proportion of tetrahedral sites—for example, alkali silicates (*10*)—an "inversion" of solid solution relations as observed in the binary system: Mg*Y*-Ni*Y*, might take place in melts containing large proportions of component *X*. Hence, within the ternary system, projection of liquid-solid relations in the binary solid series would show Ni*Y* as the high-melting constituent (Fig. 2). The existence of such a phenomenon would account for the dilemma discussed by Ringwood (*1*) concerning the enrichment of Ni^{2+} in magnesium olivines which crsytallized at an early stage from a magma.

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References and Notes

1. A. E. Ringwood, *Geochim. Cosmochim. Acta* **7**, 189, 242, (1955).
2. B. Mason, *Principles of Geochemistry* (Wiley, New York, 1958), p. 129.
3. V. M. Goldschmidt, *J. Chem. Soc. London* **1937**, 655 (1937).
4. D. M. Shaw, *J. Geol.* **61**, 142 (1953).
5. R. J. P. Williams, *Nature* **184**, 44 (1959).
6. L. E. Orgel, *An Introduction to Transition-Metal Chemistry: Ligand-Field Theory* (Methuen, London, 1960).
7. C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes* (Pergamon, London, 1962), p. 296.
8. D. S. McClure, *J. Phys. Chem. Solids* **3**, 311, (1957).
9. W. A. Weyl, *Coloured Glasses* (Soc. Glass Technology, Sheffield, 1951); H. L. Smith and A. J. Cohen, *Phys. Chem. Glasses* **4**, 173, (1963).
10. H. Moore and H. Winkelmann, *J. Soc. Glass Technol.* **39**, 215, 250, 289 (1955).
11. O. Schmitz-DuMont, H. Gossling, H. Brokopf, *Z. Anorg. Allgem. Chem.* **300**, 159 (1959); S. P. Clark, Jr., *Am. Mineralogist* **42**, 732 (1957); R. G. Burns, R. H. Clark, W. S. Fyfe, Proceedings of the Vernadsky Centennial Symposium, *Chemistry of the Earth's Crust* (Moscow, 1964).
12. J. D. Dunitz and L. E. Orgel, *J. Phys. Chem. Solids* **3**, 317 (1957).
13. L. R. Wager and R. L. Mitchell, *Geochim. Cosmochim. Acta* **1**, 129 (1951).
14. Supported by a grant from the NSF. One of us (R.G.B.) acknowledges scholarship support from the Royal Commission for the Exhibition of 1851, London; and from the University of California.

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