Elastic Properties of Polycrystalline Magnesium, Iron, and Manganese Carbonates to 10 Kilobars

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Compressional- and shear-wave velocities to 10 kb and the chemistry for naturally occurring polycrystalline aggregates of magnesite $MgCO_3$, siderite $FeCO_3$, and rhodochrosite $MnCO_3$ are reported. Velocity-density relationships for the magnesite-siderite series show a dependence on mean atomic weight similar to that observed for the olivine series. Iron substitution for magnesium in carbonates decreases the shear modulus and increases Poisson's ratio. The bulk modulus, however, changes relatively little with iron substitution. Manganese substitution in carbonates affects the velocities and elastic parameters in much the same way as iron.

An important source of information on the composition of the earth's interior is derived from measurements of elastic-wave velocities in rocks and minerals. *Birch* [1961*a*] has shown that, to a first approximation, compressional-wave velocities are related to density and mean atomic weight. This relationship has been used to obtain mantle compositions by estimating velocities in olivine aggregates with varying iron content [e.g., *Birch,* 1961*b*, 1969; *Christensen,* 1968]. Recently, new experimental data on the elastic properties of the olivine series have become available from single-crystal studies [*Graham and Barsch,* 1969; *Kumazawa and Anderson,* 1969] and from measurements of hot pressed synthetic aggregates [*Chung,* 1970; *Mizutani et al.,* 1970] and naturally occurring dunites [*Mao et al.,* 1970; *Christensen and Ramananantoandro,* 1971]. The results of these studies agree well with compressional-wave-density relationships predicted by *Birch* [1961*a*] and show that shear-wave velocities in olivine also decrease with increasing iron content.

Many minerals are undoubtedly present in the upper mantle, and it is important to establish how variations in composition within different mineral groups affect elastic-wave velocities and moduli. *Birch* [1961*a*] observed that, in addition to the olivine series, an isostructural line connecting spinel to magnetite on a velocity-density plot was approximately at right angles to lines of constant mean atomic weight. Recently, *Liebermann* [1970] has shown that the substitutions of 3*d* transition elements for magnesium and aluminum in the spinel and corundum lattices have similar effects on velocity-density relationships.

In this paper velocities and elastic moduli are presented for three carbonate end members: magnesite, siderite, and rhodochrosite. The changes in elastic properties with iron-magnesium substitution in carbonates are shown to be remarkably similar to the olivine series. The data for rhodochrosite are used to estimate the effect of manganese substitution on the elastic properties of minerals.

SAMPLES AND DATA

The samples are naturally occurring aggregates. Chemical analyses determined by atomic absorption and expressed in weight per cent are given in Table 1. X-ray diffraction patterns of the siderite and rhodochrosite show no additional minerals present in either sample. Thus the moderate amounts of calcium in the rhodochrosite and the moderate amounts of manganese and magnesium in the siderite are within the crystal lattices in solid solution. A small peak that was observed at a *d* value of 3.04 A for the magnesite sample suggests that some of the calcium in the chemical analysis of this specimen is present as calcite.

Velocities to 10 kb were measured for each sample in three mutually perpendicular directions from cores 1.9 cm in diameter and 4 to 5 cm in length by a pulse transmission technique similar to that described by *Birch* [1960]. These velocities and the bulk densities of each core

TABLE 1. Chemical Analyses
(Values in weight per cent.)

	Magnesite	Siderite	Rhodochrosite
$FeCO_3$	0.61	86.9	0.97
$MgCO_3$	92.6	6.68	3.05
$CaCO_3$	6.82	1.10	7.75
$MnCO_3$	0.18	5.14	87.2
$ZnCO_3$			0.06
$PbCO_3$		0.32	
Total	100.21	100.14	99.03

are given in Table 2. Barium titanate transducers of 2 MHz frequencies and ac cut quartz transducers of 1 MHz frequencies were used to generate and receive the compressional and shear waves, respectively. The data in Table 2 are uncorrected for length changes at elevated pressures, which would lower the 10-kb compressional- and shear-wave velocities by approximately 0.02 and 0.01 km/sec, respectively. Elastic constants calculated at various pressures from the mean velocities and the densities are given in Table 3. Velocities and densities used for the calculations were corrected for dimension changes with an iterative routine and the dynamically determined compressibilities.

DISCUSSION

Simmons [1964*a*, *b*] reported mean compressional and shear-wave velocities at 10 kb of 7.45 and 4.29 km/sec, respectively, for pure magnesite. Compressional-wave velocities were given in two directions and shear-wave velocities were given for three cores. These values are substantially lower than the mean velocities in Table 2 and are evidently due to high porosity. *Simmons* [1964*b*] reported a mean bulk density of 2.848 g/cm³ for his sample, which is considerably lower than the 2.98 g/cm³ density for pure magnesite [*Deer et al.*, 1962]. No velocities have been reported for siderite or rhodochrosite.

TABLE 2. Velocities in Kilometers per Second

Rock	Density, g/cm³	Propagation Direction	Mode	Pressure, kb 0.4	2.0	4.0	6.0	8.0	10.0
Magnesite	2.972	A	V_p	7.90	8.15	8.27	8.34	8.39	8.43
Chewelah, Wash.	2.968	B	V_p	7.89	8.12	8.24	8.32	8.37	8.42
	2.966	C	V_p	7.68	8.08	8.21	8.28	8.34	8.37
	2.969*		V_p	7.82	8.12	8.24	8.31	8.37	8.41
	2.972	A	V_s	4.55	4.62	4.67	4.70	4.72	4.73
	2.968	B	V_s	4.40	4.54	4.60	4.64	4.66	4.68
	2.966	C	V_s	4.50	4.60	4.66	4.69	4.71	4.72
	2.969*		V_s	4.48	4.59	4.64	4.68	4.70	4.71
Siderite	3.752	A	V_p	6.74	6.97	7.08	7.13	7.17	7.20
Roxbury, Conn.	3.753	B	V_p	6.61	6.89	6.99	7.03	7.06	7.08
	3.756	C	V_p	6.61	6.93	7.04	7.10	7.14	7.16
	3.754*		V_p	6.65	6.93	7.04	7.09	7.12	7.15
	3.752	A	V_s	3.59	3.67	3.73	3.76	3.78	3.80
	3.753	B	V_s	3.46	3.55	3.60	3.63	3.65	3.67
	3.756	C	V_s	3.43	3.51	3.56	3.59	3.60	3.61
	3.754*		V_s	3.49	3.58	3.63	3.66	3.68	3.69
Rhodochrosite	3.569	A	V_p	6.90	7.04	7.10	7.13	7.15	7.17
Catamarea Province,	3.563	B	V_p	6.99	7.13	7.24	7.32	7.37	7.40
Argentina	3.568	C	V_p	6.70	6.85	6.93	6.98	7.01	7.04
	3.567*		V_p	6.86	7.01	7.09	7.14	7.17	7.20
	3.569	A	V_s	3.07	3.28	3.37	3.42	3.46	3.48
	3.563	B	V_s	3.46	3.49	3.53	3.56	3.59	3.61
	3.568	C	V_s	3.33	3.44	3.51	3.55	3.57	3.59
	3.567*		V_s	3.29	3.40	3.47	3.51	3.54	3.56

* Mean of three preceding measurements.

TABLE 3. Elastic Properties of Magnesite, Siderite, and Rhodochrosite

Pressure, kb	K_s, mb	μ, mb	V_p/V_s	σ_s	ϕ, (km/sec)^2
		Magnesite			
2.0	1.12	0.62	1.77	0.27	37.8
6.0	1.19	0.65	1.78	0.27	39.8
10.0	1.22	0.66	1.79	0.27	40.9
		Siderite			
2.0	1.16	0.48	1.94	0.32	31.0
6.0	1.22	0.50	1.94	0.32	32.2
10.0	1.24	0.51	1.94	0.32	32.8
		Rhodochrosite			
2.0	1.20	0.41	2.05	0.34	33.6
6.0	1.24	0.44	2.04	0.34	34.5
10.0	1.25	0.45	2.02	0.34	34.8

Because of their relative purity, carbonates offer an excellent opportunity to examine the effect of iron, magnesium, and manganese substitution on the elastic moduli and wave velocities in minerals. In Figures 1 and 2 the data of *Chung* [1970] for the olivine series are compared with velocities of magnesite and siderite at 10 kb. Velocity-density relations for the magnesite-siderite series appear to be remarkably similar to those for the olivine series. The agreement between the two series suggests that velocity measurements for additional carbonates may provide important information about the relationships between various cation substitutions and elastic properties, which can be applied to silicates.

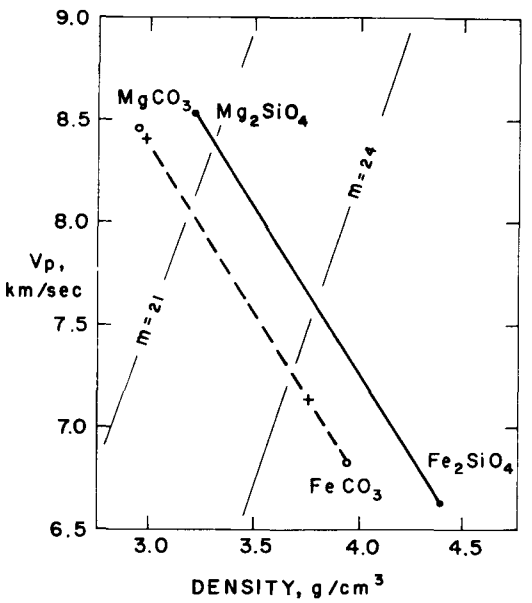

Fig. 1. Compressional-wave velocity-density relations for the olivine series Mg_2SiO_4-Fe_2SiO_4 [*Chung*, 1970] and the siderite-magnesite series $FeCO_3$-$MgCO_3$ (between the plus signs). The extended velocity-density lines to the densities of pure $MgCO_3$ and $FeCO_3$ are also shown.

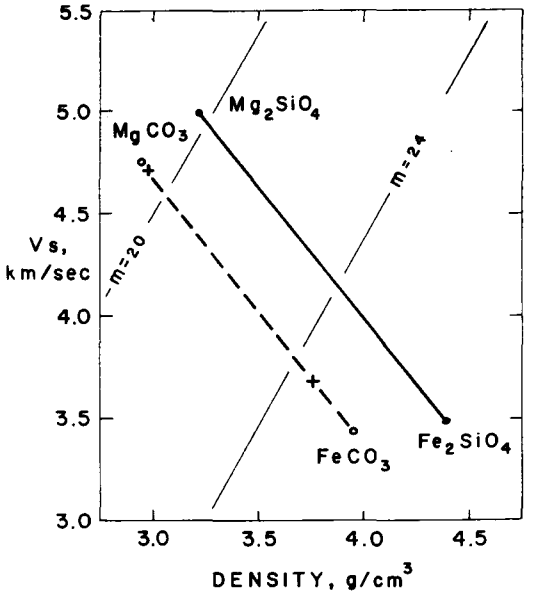

Fig. 2. Shear-wave velocity-density relations for the olivine series Mg_2SiO_4-Fe_2SiO_4 [*Chung*, 1970] and the siderite-magnesite series $FeCO_3$-$MgCO_3$ (between the plus signs). The extended velocity-density lines to the densities of pure $MgCO_3$ and $FeCO_3$ are also shown.

The bulk moduli K_s and shear moduli μ for the pure end members $MgCO_3$ and $FeCO_3$, estimated by extending the velocity-density lines of Figures 1 and 2 to the densities of pure $MgCO_3$ and $FeCO_3$, show changes with iron substitution of -0.02% and -29.9%, respectively. A similar relation between K_s and iron substitution in the olivine lattice has been noted by *Mao et al.* [1970] and *Chung* [1970]. The small decreases in K_s for both magnesite-siderite and olivine are presumably related to the similar unit cell volumes for the end member of each series. For corundum Al_2O_3 to hematite Fe_2O_3, however $\Delta K_s = -20\%$, which is comparable to the volume increase of 23% [*Liebermann*, 1970].

The behavior of μ with iron substitution in the magnesite-siderite and olivine series does not show so simple a relationship with cell volume as K_s.

The data for rhodochrosite in Table 2 indicate that the effect of manganese substitution in carbonates on elastic properties is quite similar to that of iron. A similar conclusion was noted by *Liebermann* [1970] for the spinel and corundum lattices, in which substitution of any 3*d* transition element appeared to have about the same effect on velocities and elastic moduli. Because of the relatively high anisotropy of the rhodochrosite specimen (Table 2) and the significant amounts of calcium in the rhodochrosite analysis (Table 1), the similarities in the elastic properties of $MnCO_3$ and $FeCO_3$ may be even greater than is indicated in Table 3.

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