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- [Manuscript received 3 May 1965]

Instability of the garnet $Ca_3Mn^{III}Si_3O_{12}$, and the substitution $Mn^{III} \rightleftharpoons Al$

OF the first six elements (Sc, Ti, V, Cr, Mn, Fe) of the first transition series, Sc is heavily enriched in garnet relative to host rock (Oliver, 1956, 1961 records 40 ppm in host rock, and up to 2000 ppm in garnet), indicating that a scandium garnet is probably stable. Titanium (III) garnets are not definitely known to exist, but they would form only at very low P_{O_2} . Vanadium, chromium, and iron (III) garnets of the type $Ca_3M^{III}Si_3O_{12}$ are stable, but no garnet has yet been described in which Mn^{III} definitely replaces Al in the (a) sites of space group $Ia\bar{3}d$. Since higher manganese oxides and minerals such as viridine and piemontite (the latter often associated with garnet containing little or no 'Mn₂O₃') are moderately common in metamorphic rocks, the absence of Mn (III) garnets cannot be explained by postulating that P_{O_2} was outside the stability field of Mn^{III} . Since the ionic radius of Mn^{III} is close to that of

Fe^{III} , it would be expected to replace Al whenever the latter is replaced by Fe^{III} . This is certainly not the case with most garnets, amphiboles, and micas. We therefore require an explanation of the instability of CaMn(III) garnet, and of the reluctance of Mn^{III} to replace Al.

Experimental evidence. Synthesis of garnets of the $\text{Ca}_3M_2^{III}\text{Si}_3\text{O}_{12}$ type, with $M^{III} = \text{V, Cr, Mn, and Fe}$ was attempted with two types of starting material, namely glass or mixtures of Ca(OH)_2 , $M_2\text{O}_3$, and silica gel. These were sealed with water in silver capsules with appropriate external buffers, and were then held at 530–600° C, 2–3 kilobars for 30 days.

TABLE I. Experimental data on garnet stability

M^{III}	P	T	Time	Products	Buffer
V	3.0 kb	530° C	30 days	V-Gt + Qz + P	$\text{Fe}_2\text{O}_3 : \text{Fe}_3\text{O}_4$
Cr	3.0	600	30	Cr-Gt + Qz + P	$\text{Fe}_2\text{O}_3 : \text{Fe}_3\text{O}_4$
Mn	2.0	585	30	Wo + Mn_2O_3 + Qz	$\text{Mn}_2\text{O}_3 : \text{MnO}_2$
	3.0	600	30	same	same
Fe	3.0	600	30	Fe-Gt + Qz + P	$\text{Mn}_3\text{O}_4 : \text{Mn}_2\text{O}_3$

P, partially reacted or unreacted $M_2\text{O}_3$, wollastonite, &c.; Wo, wollastonite; Gt, garnet; Qz, quartz. Andradite run was seeded.

Excess silica was present to suppress substitution of $(\text{OH})_4^-$ for SiO_4^{4-} . High yields of garnet were obtained from the Ca–V, Ca–Cr and Ca–Fe garnet mixtures, but the Ca–Mn runs reacted to wollastonite, Mn_2O_3 , and quartz, indicating that CaMn(III) garnet is unstable under these (P, T) conditions.

Mineralogical evidence. Small amounts of ' Mn_2O_3 ' have been recorded in garnet analyses, e.g. Magnusson (1930) found 0.17% ' Mn_2O_3 ' in a garnet from Långban, and Sastri (1963) noted a purplish coloration of the $\text{HF-H}_2\text{SO}_4$ solution of a spessartine from Andhra Pradesh, indicating the presence of a higher manganese oxide. In the latter mineral, $(\text{Al, Fe})^{III}$ is low (1.927) and (Ca, Mn) is high (3.194), so that a case can be made for assigning up to 0.073 Mn as Mn^{III} to the (Al, Fe) group. These analytical data do not rule out substitutions of the type 2Mn^{III} for $\text{Ca} + \text{Si}$, $\text{Mn}^{III} + \text{Mn}^{\text{IV}}$ for 2Al , or Mn^{IV} for Si , which would not violate the symmetry principles discussed below.

Theoretical considerations. In field-free space, transition metal ions have five degenerate (equal energy) d -electron orbitals, which split under the influence of an octahedral ligand field into three low-energy (t_{2g}) and two high energy (e_g) orbitals (Orgel, 1960). The t_{2g} orbitals are directed along the diad axes of the octahedral site, i.e. between opposite pairs of (oxygen) ions, and the e_g orbitals are directed along the tetrad

axes, i.e. towards oxygen ions, and are thus more strongly repelled. In the trivalent ions of Ti, V, Cr, Mn, and Fe the *d*-orbitals are singly occupied. The theorem of Jahn and Teller (1934) requires that a regular octahedral site occupied by Mn^{III} shall suffer a tetragonal distortion. Two of the oxygen ions lying on one of the tetrad axes are thus brought closer ($c/a < 1$) to the cation, or removed further from it ($c/a > 1$) than in the undistorted site. In general, a ratio $c/a < 1$ corresponds to a more strongly ionic case than $c/a > 1$, but both types of distortion are known in silicate minerals (Burns and Strens, unpublished).

The Al site in the garnet structure has point group symmetry $\bar{3}$, and it is clear that distortion of the type that would be caused by Mn^{III} entering this site is incompatible with the symmetry requirements of the space group. Even if a compound $Ca_3Mn_2Si_3O_{12}$ exists, it will not crystallize with the garnet structure, and cannot therefore enter into extensive solid solution with garnet.

Even when no rigid symmetry barrier exists, the distortion produced by Mn^{III} may destabilize a structure sufficiently to cause a change of space group, or even complete instability of a compound. Conversely, substitution of Mn^{III} is favoured if a site has a pre-existing tetragonal distortion, for example Mn^{III} , but not Fe^{III} , enters the 'AlOH' site in epidote with c/a 0.95, and both Mn^{III} and Fe^{III} enter the epidote 'Al' site also with c/a 0.95, and the octahedral chain site in viridine with c/a 1.12 (Burns and Strens, unpublished).

Conclusions. Garnets with Mn^{III} replacing Al in the (*a*) sites of space group *Ia3d* are unstable, and the small amounts of ' Mn_2O_3 ' sometimes present in garnet are probably attributable to other types of substitution. Extensive replacement of Al by Mn^{III} will occur only when the Al-O octahedra are tetragonally distorted. Similar considerations apply to other ions which produce strong Jahn-Teller distortions, e.g. Cr^{II} and Cu^{II} , or which form certain types of hybrid bond, e.g. square planar dsp^2 bonds of Ni^{II} .

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[*Manuscript received 7 April 1965*]

*A three-axis universal clamp
for re-orientation of rocks in the laboratory*

MANY geologists have cause to collect rock specimens on which they make adequate markings to enable exact re-orientation in the laboratory. One of the more common methods for such re-positioning is to support the specimen on a block of modelling clay. This often becomes a tricky operation, especially with large specimens, which may cause sudden sagging of the clay and consequent loss of the desired position. Being exasperated with this technique the author designed a three-axis universal clamp, which can be quickly and accurately adjusted to hold a rock in any desired position. The device (fig. 1) can be cheaply and easily made, and by constructing it from wood and non-magnetic alloys a compass can be used near it for exact geographical re-orientation.

A hubless and spokeless aluminium alloy bicycle wheel, of 25 in. diameter and $\frac{7}{8}$ in. width, has been mounted in a composite wooden clamping block with dimensions $4\frac{1}{2} \times 5\frac{1}{4} \times 1\frac{1}{4}$ in. A hole drilled through the block and the rim of the wheel has a $\frac{1}{4}$ in. diameter bolt passing through it, about which the wheel can be rotated (A_3). Tightening of a wing nut on this bolt effectively locks the wheel to the large wooden baseplate (13×26 in.), which supports the whole device. The clamp consists of two wooden boards ($17 \times 2\frac{1}{4} \times \frac{3}{8}$ in.) attached to two location blocks and arms across a diameter of the wheel. At the extremities of the arms are two bearing housings connected by a plate that passes around one half of the wheel circumference and is supported by three anchor blocks. At each bearing housing and each anchor block this plate is spaced from the wheel by a single glass 'marble' of $\frac{1}{2}$ in. diameter that runs in the groove normally occupied by the tyre and the inner tube. The clamp can thus be rotated about an axis through the centre of the wheel corresponding to the position normally occupied by the axle (A_2). The $\frac{1}{2}$ in.-diameter arms supporting the clamp can rotate within the outer bearing housings and so provide the third axis of rotation (A_1). Rotation of the specimen about A_2 can be prevented by locking screws, one of which passes through each of the bearing housings and bears on to the side of the bicycle wheel, whilst rotation about A_1 is stopped by tightening a second pair of locking screws in the same housings.