

Cassagnaite, a new, V-bearing silicate mineral from the Cassagna mine, northern Apennines, Italy

RICCARDO BASSO^{1,*}, CRISTINA CARBONE¹ and ANDREA PALENZONA²

¹ Dipartimento per lo Studio del Territorio e delle sue Risorse, Università di Genova, Corso Europa 26, 16132 Genova, Italy

*Corresponding author, e-mail: mineral@dipteris.unige.it

² Dipartimento di Chimica e Chimica Industriale, Università di Genova, via Dodecaneso 31, 16146 Genova, Italy

Abstract: Cassagnaite occurs at the Cassagna manganese mine (Eastern Liguria, Italy), filling fractures in braunite + quartz layered mineralizations together with piemontite. It occurs as very rare isolated prismatic to tabular {001} crystals, usually elongated along [100], and as entangled aggregates of a few crystals. Few aggregates consist of very small cassagnaite crystals (maximum size up to 0.05 mm) closely associated with much larger piemontite, quartz, and braunite crystals. The crystals are generally very small, with a maximum size up to 0.1 mm, golden brown in colour, transparent with vitreous lustre. The crystal structure, refined in the space group *Cmcm* with cell parameters $a = 6.066(1)$ Å, $b = 8.908(1)$ Å, $c = 18.995(2)$ Å and $Z = 2$, may be described as a layer stacking along [001] of a fundamental building block of composition $[M1_2(OH)_2(SiO_4)_2]^{4-}$ that alternates with intersheets, randomly occurring in a ratio ideally 1:1, of type 1 $[(Ca, Mn^{2+})_2SiO_2]^{4+}$ and of type 2 $(Ca, Mn^{2+})_2M2_2(OH)_2O_2]^{4+}$, where Fe^{3+} and Mn^{3+} populate 3/4 of the M1 site and Al the remaining 1/4, while V^{3+} , Mg and Al occupy in nearly equal proportions the M2 site. The simplified formula, inferred from chemical analyses, structure refinement and crystal-chemical considerations, may be written as $(Ca, Mn^{2+})_4(Fe^{3+}, Mn^{3+}, Al)_4(OH)_4(V^{3+}, Mg, Al)_2(O, OH)_4(SiO_4)_2(Si_3O_{10})$. From the composition of the “dominant” end-member of the complex solid-solution the end-member formula $Ca_4Fe^{3+}(OH)_4V_2^{3+}O_2(OH)_2(SiO_4)_2(Si_3O_{10})$ may be proposed for cassagnaite. So, cassagnaite may be classified as sorosilicate with insular and triple tetrahedral groups and belongs to the ardennite group in Dana’s classification.

Key-words: cassagnaite, new mineral, chemical data, X-ray powder pattern, crystal structure, vanadium, ardennite group.

Introduction

In the Val Graveglia (Northern Apennines, Liguria, Italy) rare and new minerals are widespread in manganese ore deposits and in silicified woods associated to metacherts (“Diaspri di M. Alpe” Formation) that occur at Molinello, Gambatesa, Statale, and Cassagna mines (Cortesogno & Galli, 1974; Cortesogno *et al.*, 1979; Cabella *et al.*, 1998). In particular, in the Cassagna mine some of these rare minerals (such as medaite, palenzonaite, strontio piemontite, sursasite, tinzenite, and tiragalloite) were found. In this paper we report the occurrence of cassagnaite, a new mineral species, (approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association, Ref. 2006 – 19a), whose name derives from the Cassagna mine where the mineral has been found. The holotype sample is deposited in the collection of the Dipartimento per lo Studio del Territorio e delle sue Risorse (Dip.Te.Ris), Università di Genova, Italy.

Occurrence and physical properties

In the Val Graveglia mines the Mn-ores occur as braunite-bearing layered mineralizations, massive lenses

and boudins near the stratigraphic base of the cherts of the “Diaspri di M. Alpe” Formation, overlying the ophiolitic basement (Marescotti & Cabella, 1996; Cabella *et al.*, 1998). The mineralizations are characterized by braunite + quartz association equilibrated under prehnite-pumpellyite facies conditions (Cortesogno *et al.*, 1979; Lucchetti *et al.*, 1990) during the tectono-metamorphic evolution that affected both ophiolites and cherts. Hydrothermal fluid circulation, along later extensional fractures under decreasing P-T metamorphic conditions, induced the concentration of commonly dispersed elements that were involved into the genesis of As, Ba, Cu, Sr, and V-rich mineral assemblages. While at the Gambatesa and Molinello mines some vanadium minerals were discovered for the first time, representing new mineral species (such as cavoite, medaite, palenzonaite, reppiaite, saneroite, tiragalloite, vanadiocarpholite, and vanadomalayaite), cassagnaite represents the first new V-rich mineral found at the Cassagna mine as type locality. Cassagnaite occurs filling fractures in braunite + quartz layered mineralizations together with piemontite. It appears as very rare isolated prismatic to tabular {001} crystals, usually elongated along [100] (Fig. 1) and as entangled aggregates of a few crystals. The crystals are generally very small, with a maximum size of 0.06 mm. Only two crystals with higher dimensions (up

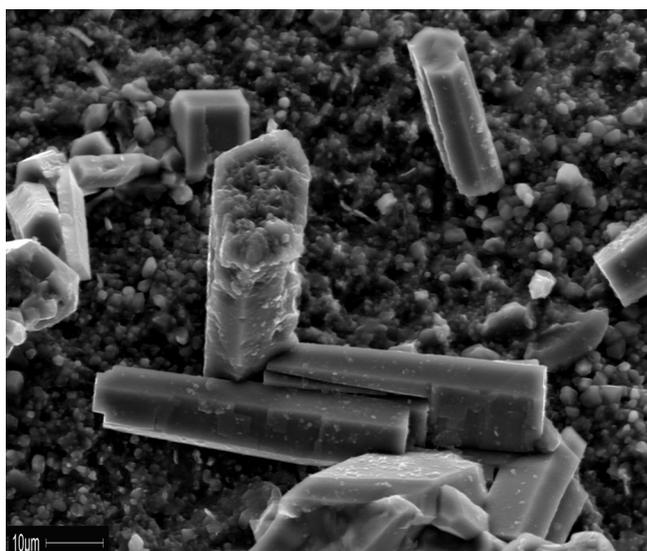


Fig. 1. SEM image of [100] elongated prismatic and {001} tabular crystals of cassagnaite.

to $0.04 \times 0.06 \times 0.1$ mm) have been found, one of which was used for X-ray analyses and the other was unfortunately lost. Few aggregates, one of which is up to 1 mm in diameter, consist of very small cassagnaite crystals (maximum size up to 0.05 mm) closely associated with much larger piemontite, quartz, and braunite crystals.

Cassagnaite is transparent with vitreous lustre, golden brown in colour and the streak is nearly white. The morphology of the crystals is generally constituted by the prism {011} and the pinacoids {001} and {100}. It is brittle and exhibits {001} cleavage (or parting). Due to the unusual scarcity of available material and to the reduced size of the crystals, the determinations of physical and optical properties are not complete. The calculated density is 3.22 g/cm^3 . The mineral does not fluoresce under short- and long-wave ultraviolet light. Optically, cassagnaite is biaxial and some optical measurements were performed on the largest face, likely parallel to the {001} cleavage, of a prismatic crystal elongated along [100], with dimensions $0.01 \times 0.02 \times 0.04$ mm. The observed section shows parallel extinction, positive elongation and low interference colours. The refractive index values are N (parallel to a): $1.810 (\pm 0.005)$ and n : $1.800 (\pm 0.005)$, measured by Cargille's liquids at 25°C ($\lambda = 589 \text{ nm}$). The pleochroism is very weak: $N =$ golden yellow-brown and $n =$ pale golden yellow-brown.

Chemical composition

Quantitative analyses (seven points on two crystals) were performed by means of an electron microprobe (PHILIPS SEM 515 electron microscope equipped with EDAX PV9100 spectrometer) in energy-dispersion mode, with an accelerating voltage of 15 kV and a beam current of about 2 nA. Pargasite (Mg, Al, Si, Ca), metallic vanadium (V), rhodonite (Mn), and fayalite (Fe) were used as reference

Table 1. Chemical composition for cassagnaite.

Oxide	range (wt%)	mean (wt%)	recalculated to obtain Ca+Mn ²⁺ = 4 (wt%)
CaO	17.85–18.93	18.42	18.42
MnO	14.61–15.20	14.98	5.20
Mn ₂ O ₃			10.88
Fe ₂ O ₃	12.37–13.02	12.61	12.61
Al ₂ O ₃	6.71–8.49	7.55	7.55
MgO	2.07–2.61	2.36	2.36
V ₂ O ₃	5.04–5.84	5.42	5.42
SiO ₂	29.25–33.75	31.69	31.69
H ₂ O by difference			5.87
Total			100.00

standards for the elements in brackets. Raw data were reduced using the ZAF algorithm and the standard software of the EDAX PV9100. Spot analyses show neither significant variations of composition nor compositional zoning in individual crystals. Other elements are below detection limits. The mean chemical composition is reported in Table 1 along with an indication of variability. H₂O content could not be directly determined because of the lack of material but a micro-Raman analysis has been carried out with a Renishaw 2000 Ramascope equipment using a laser operating at 633 nm; the large band in the range $3500\text{--}3000 \text{ cm}^{-1}$ of the Raman shift shows the presence of (OH)⁻ ions in the structure of cassagnaite.

The empirical formula, based on 26 oxygen atoms *pfu* taking into account crystal-chemical considerations and the indications of the structure refinement later discussed, is $\text{Ca}_{3.3}\text{Mn}_{0.7}^{2+}\text{Fe}_{1.6}^{3+}\text{Mn}_{1.4}^{3+}\text{Al}_{1.5}\text{V}_{0.7}^{3+}\text{Mg}_{0.6}\text{Si}_{5.2}\text{O}_{26}\text{H}_{6.5}$.

X-ray powder-diffraction analysis

The X-ray powder-diffraction pattern was obtained by a Gandolfi camera (diameter 114.6 mm), using a V-filtered CrK α radiation. Relative intensities were visually estimated and the reflections were indexed on the basis of the pattern calculated by means of the LAZY PULVERIX program (Yvon *et al.*, 1977), using the structural model resulting from the refinement as input data. A comparison between these patterns is reported in Table 2. The unit-cell parameters refined from the measured powder data are $a = 6.07(1) \text{ \AA}$, $b = 8.89(1) \text{ \AA}$ and $c = 18.96(2) \text{ \AA}$.

X-ray structure analysis

Severe difficulties were encountered to find a single crystal suitable for the X-ray analysis. All the checked crystals exhibit very poor reflection quality, almost all a large quantity of streaked reflections, likely related to a high degree of structural disorder, and generally weak reflections likely due to the small size. Finally, the data collection was performed on a prismatic crystal, with dimensions $0.04 \times 0.04 \times 0.10$ mm, by means of an

Table 2. X-ray powder-diffraction data for cassagnaite (d in Å).

$h k l$	Measured		Calculated		$h k l$	Measured		Calculated	
	d	I	d	I		d	I	d	I
0 0 2	9.52	100	9.498	100	2 2 3}			2.331	16
1 1 0	4.98	45	5.014	53	1 3 4}	2.32	40	2.325	21
1 1 1	4.85	50	4.848	54	2 2 4}			2.217	17
0 0 4	4.76	25	4.749	23	0 4 1}	2.21	20	2.212	20
0 2 0	4.42	10	4.454	15	0 4 3}			2.101	10
0 2 2	4.03	40	4.033	46	0 2 8}	2.093	40	2.095	12
0 2 4	3.25	35	3.249	37	2 2 5}			2.092	27
1 1 5	3.02	60	3.028	58	2 0 8	1.868	15	1.870	18
0 2 5}			2.890	7	2 4 4}			1.679	27
2 0 2}	2.88	20	2.889	9	3 1 6}	1.675	35	1.674	4
1 1 6}			2.677	44	3 3 0}			1.671	13
1 3 0}	2.66	70	2.667	36	2 4 5	1.623	25	1.623	24
0 2 6	2.57	30	2.580	56	0 0 12	1.579	15	1.583	17
2 0 4	2.54	65	2.556	70	2 4 6	1.558	20	1.561	20
2 2 0	2.50	20	2.507	20	4 0 0}			1.516	31
2 2 2	2.42	30	2.424	33	2 2 10}	1.515	25	1.514	29
1 1 7	2.37	15	2.387	13					

ENRAF-NONIUS MACH-3 automatic diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation. The cell parameters were determined and refined using 25 reflections, measured in the $12^\circ < \theta < 19^\circ$ range. A semi-empirical absorption correction was applied using the ψ scan method (North *et al.*, 1968). The crystal structure was refined in the space group $Cmcm$ (no forbidden reflections were detected) using as starting values the positional parameters of the orientite structure refined by Moore *et al.* (1985), as suggested by the similar stoichiometry of chemical composition and unit cell. The refinement was carried out by a modified version of the ORFLS program (Busing *et al.*, 1962), using the scattering factors for neutral atoms taken from Ibers & Hamilton (1974). The numbering of cations and oxygens was assumed according to those reported for orientite in the data base ICSD 201629. M1 and M2 refer to the atom sites populated by Mn^{3+} and Mn^{2+} , respectively, in the structure refinement of orientite reported by Moore *et al.* (1985). According to these authors, the multiplicity of the sites M2 and Si1 was reduced to a half. The structure refinement of cassagnaite required a half multiplicity also for the O6 oxygen. Scale factor, occupancies of Ca/Mn on the Ca site, Fe/Al on the M1 site and V/Mg on the M2 site, positional and thermal parameters were simultaneously derived, except for the O6 atom, whose temperature factor was fixed to a value of 1 \AA^2 . Tables 3–5 summarize experimental details and results of the crystal structure refinement.

In consideration of the complicated scheme of solid solution and site ordering, the cationic populations of the Ca, M1, and M2 sites were inferred following this method:

- a fraction of the total manganese as Mn^{2+} to fill up the Ca site ($\text{Ca} + \text{Mn}^{2+} = 4 \text{ pfu}$);
- full occupancy of the M1 site with trivalent cations ($\Sigma = 4 \text{ pfu}$), taking into account the composition resulting from the empirical formula and the crystal-chemical

characters of the minerals with analogous $6 \times 9 \text{ \AA}$ sheet structures emphasized by Moore *et al.* (1985);

- the remaining cations used to fill the M2 site, on the basis of the stoichiometry of the empirical formula, to obtain ideally $\Sigma = 2 \text{ pfu}$;
- best agreement for each of the Ca, M1, and M2 sites among the electron numbers and the mean polyhedral distances derived from the structure refinement and those calculated from the cationic population, respectively.

The resulting cationic populations of the Ca, M1, and M2 sites may be expressed as $(\text{Ca}_{3.3}\text{Mn}_{0.7}^{2+})$, $(\text{Fe}_{1.6}^{3+}\text{Mn}_{1.4}^{3+}\text{Al}_{1.0})$, and $(\text{V}_{0.7}^{3+}\text{Mg}_{0.6}\text{Al}_{0.5}) \text{ pfu}$, respectively. Final refinement occupancies of the Ca (Ca/Mn = 0.88/0.12), M1 (Fe/Al = 0.68/0.32) and M2 (V/Mg = 0.44/0.56) sites correspond to 20.6, 21.8, and 16.8 electrons, respectively, in agreement with the electron numbers (20.9, 22.4, and 16.6) required from the above cationic distribution. Also the mean polyhedral distances from refinement (Table 5) agree with those required from the above cationic distribution. If a linear contribution by each fraction of cation is supposed for the calculus of the mean polyhedral distances and the single cation-oxygen is reproduced by sum of both cation and oxygen effective ionic radii (Shannon, 1976), the following calculated distances are obtained: $\langle \text{Ca} - \text{Mn} - \text{O} \rangle = 2.41 \text{ \AA}$, $\langle \text{M1} - \text{O} \rangle = 2.00 \text{ \AA}$, and $\langle \text{M2} - \text{O} \rangle = 2.02 \text{ \AA}$.

The electrostatic valence balance, reported in Table 6, is simplified by using simple Pauling bond strengths obtained dividing the formal charge of cations by the coordination number and assigning coordination number 6.5 to Ca, owing the half multiplicity of O6 and formal charge 3 to M2, neglecting the fraction of Mg. The bond strength sums for oxygens, although roughly estimated, clearly indicate that O5 and O6 are oxygens pertaining to hydroxyl groups. This hypothesis agrees with possible hydrogen bonds owing to the too short O...O distances, between oxygen atoms not

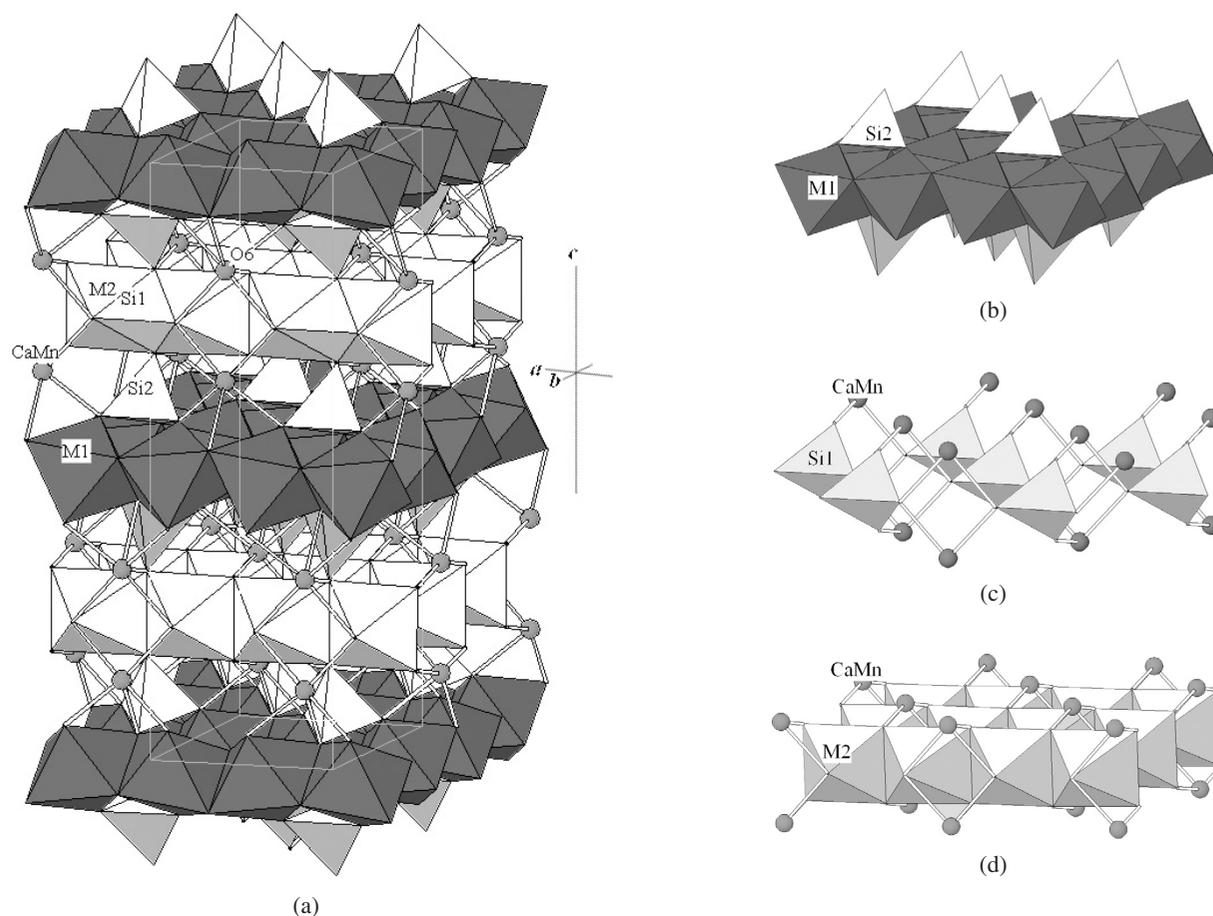


Fig. 2. Clinographic view of the crystal structure of cassagnaite: a) whole polyhedral framework where intersheets, inclusive of both the two randomly occurring types 1 and 2, are reported; b) fundamental building block; c) intersheet of type 1; d) intersheet of type 2.

Table 6. Electrostatic valence balance for cassagnaite.

	Ca	M1	M2	Si1	Si2	Σ
O1	0.31		$1/2 \times 2 \times 0.5$	$1/2 \times 1.0$	1.0	2.31
O2	2×0.31		$1/2 \times 2 \times 0.5$	$1/2 \times 1.0$		1.62
O3	0.31	0.5			1.0	1.81
O4	0.31	2×0.5			1.0	2.31
O5		2×0.5				1.00
O6	0.31		2×0.5			1.31

linked to the same cation, O5-O3 = 2.96(3) Å and O6-O5 = 2.84(7) Å (Table 5) and with the hydration degree inferred from the chemical composition.

The refinement results and the above considerations give rise to a possible structural model for cassagnaite similar to that proposed by Moore *et al.* (1985) for orientite, in which may be recognized an analogous sheet, named “fundamental building block” (f.b.b.) of composition $[\text{M1}_2(\text{OH})_2(\text{SiO}_4)_2]^{4-}$, where M1 is populated by trivalent cations as Fe^{3+} , Mn^{3+} , and Al, that alternates along [001] with an “intersheet” of whole composition $[(\text{Ca}, \text{Mn}^{2+})_4\text{M2}_2(\text{OH})_2\text{SiO}_4]^{8+}$ per unit formula, where M2 is populated by cations, ideally trivalent, as V^{3+} , Mg, and Al. The half-occupied sites M2, Si1, and O6 ac-

count for a disordered stacking, ideally in the ratio 1:1, of intersheets of type 1 $[(\text{Ca}, \text{Mn}^{2+})_2\text{SiO}_2]^{4+}$, where only Si1 tetrahedra are present, and intersheets of type 2 $[(\text{Ca}, \text{Mn}^{2+})_2\text{M2}_2(\text{OH})_2\text{O}_2]^{4+}$, where only M2 octahedra are present, taking into account that the coexistence of the face-sharing M2 octahedra and Si1 tetrahedra is forbidden for the unacceptable too short distance M2-Si1 = 2.14(3) Å.

Conclusions

The above described structural model infers the presence of isolated (SiO_4) tetrahedra, pertaining to the f.b.b., when the intersheet is of the type 2 and the formation of $(\text{Si}_3\text{O}_{10})$ groups, linking adjacent f.b.b., when the intersheet is of the type 1 (Fig. 2).

To account for this crystal-chemical aspect, the unit formula has been doubled compared with that assigned to orientite by Moore *et al.* (1985). So the simplified formula of cassagnaite may be written as $(\text{Ca}, \text{Mn}^{2+})_4(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al})_4(\text{OH})_4(\text{V}^{3+}, \text{Mg}, \text{Al})_2(\text{O}, \text{OH})_4(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$, where the hydroxyl groups per formula unit account for the valence balance and are positioned next to the cations to which they are bonded with the highest strength.

A slight deviation from the simplified ratio 1:1 of inter-sheets of the two types may be expected taking into account the chemical composition of cassagnaite, as inferred from the empirical formula, which shows a small excess of the Si content as well as a small deficiency of cations to fill up the M2 site.

According to Hawthorne (2002), the appropriate composition for the “dominant” end-member of the complex solid-solution may be written as $\text{Ca}_4\text{Fe}_4^{3+}(\text{OH})_4\text{V}_2^{3+}\text{O}_2(\text{OH})_2(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$ and it may be assumed as the end-member formula of cassagnaite.

The poor quality of the X-ray single-crystal reflections and the too low number of observed reflections prevent any attempt to introduce anisotropic temperature factors in the refinement and to refine the structure of cassagnaite according to the model proposed for orientite by Mellini *et al.* (1986), which involves a great number of parameters to be derived. The proposed structure of cassagnaite represents at present an averaged model of a high disordered structure and attempts will be made to improve it.

On the basis of the structural characters, cassagnaite belongs to the group of minerals with $6 \times 9 \text{ \AA}$ sheet structure reported by Moore *et al.* (1985).

From the point of view of the mineral classification, cassagnaite may be ascribed to the Dana Class: 58.3.1.2 Sorosilicate insular, mixed, single, and larger tetrahedral groups – with insular single and triple groups ($n = 1, 3$) – ardenite group (ardenite and orientite), and to the Strunz and Nickel Class 9.BJ, Sorosilicates with Si_3O_{10} , Si_4O_{11} , etc. Anions; Cations in Octahedral [6] and/or Greater Coordination.

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