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Detrital goldmanite from the Palaeocene of the North Sea

GOLDMANITE [$Ca_3(V,Al,Cr,Fe^{3+})_2(SiO_4)_3$], the vanadium analogue of andradite garnet, is of rare occurrence. Moench and Meyrowitz (1964) first reported a calcium-rich garnet with vanadium as a major constituent (V_2O_3 18.3%), to which the name goldmanite was given. In this case the vanadium-rich garnets occur as dark green to brownish green crystals in a small uranium–vanadium deposit in sandstone close to the base of a thick diabase sill near Laguna, New Mexico. Subsequently goldmanite has been described from a number of different localities and parageneses. Goldmanite with V_2O_3 of 21.87% was reported from magnetite-bearing skarn deposits in Western Siberia (Shepel' and Karpenko, 1970). Filippovskaya *et al.* (1972) described a vanadian grossular with 15.2% V_2O_3 in a metamorphosed Cambrian silica- and organic-rich shale from Northern Kazakhstan. In China similar rocks have provided the purest goldmanite specimen previously described, which was reported by Wang *et al.* (1974) to contain 26.33% V_2O_5, equivalent to 24.38% V_2O_3. The first record of goldmanite in Europe was recently made by Benkerrou and Fonteilles (1989), who described garnets with up to 21.31% V_2O_3 from thermally metamorphosed calcareous metapelites and skarns in Brittany.

This paper documents the second record of this mineral in Europe, and is unusual on two counts. Firstly, electron microprobe analysis of the material has shown it to be the most vanadium-rich garnet ever described (V_2O_3 28.66%). Secondly, the goldmanite was found as a detrital grain in a sandstone of Palaeocene age. It was found in a sidewall core from the Amoco oil exploration well 9/27-1 in the UK sector of the North Sea, at a depth of 6240 ft (1902 m), within the Palaeocene Montrose Group interval. Previously described occurrences of goldmanite are typically *in situ*, from metamorphosed vanadium-bearing sediments.

The goldmanite grain was discovered during routine heavy mineral analysis of the Palaeocene Montrose Group sandstone sample. Separation of heavy minerals from the 63–125 μm grain size fraction was achieved by gravity-settling in bromoform (s.g. 2.8), following disaggregation with a pestle and mortar and ultrasonic cleaning to remove any adhering clays or other matter. The goldmanite grain, which was subrounded and clearly detrital in origin, was hand-picked from the dry heavy mineral suite under the optical microscope during separation of the garnet suite for a provenance study based on variations in the garnet geochemistry as described by Morton (1985). The grain was picked for analysis because of its isotropic character and because it was considered to have an unusual compositon in view of its grass-green colour under transmitted light. Because of its colour, it was initially suspected to be the zinc spinel gahnite, which had previously been identified in Palaeocene heavy mineral suites from this region. The grain was mounted on double sided adhesive tape on a glass slide. After coating with carbon its composition was determined using a Link Systems AN 10/55 energy-dispersive X-ray analyser attached to a microscan V electron microprobe. The count time was 100 seconds and the results were processed using a Link Systems ZAF 4-FLS matrix correction programme (Table 1). The standards used for calibration of the analysed element set are Fe, Ti, Cr, V and Mn metals, Mg and Al oxides, and wollastonite for Si and Ca.

The average analysis reveals that the grain has V_2O_3 28.66%. Thus, the grain contains 96.3 mol.% of the goldmanite end-member, and is therefore the purest goldmanite analysed to date. The goldmanite grain also contains small amounts (2.9 mol.%) of the chromium end-member uvarovite: previous analyses of goldmanite have shown that this is a common association, with varying amounts of the uvarovite component commonly found in goldmanite (see Table 1, analysis 4). As Table 1 shows, the analytical total is slightly less than 100%. This may be because the grain was not polished prior to analysis, although the possibility that the grain is slightly hydrated can not be dismissed. However, the results are in good

Table 1. Goldmanite Analyses

	1	2	3	4	5
SiO_2	35.52	35.64	35.58	34.90	36.6
TiO_2	-	-	-	0.66	-
Al_2O_3	-	-	-	2.58	4.9
Cr_2O_3	1.07	0.70	0.88	3.39	-
V_2O_3	28.41	28.92	28.66	19.60	18.3
Fe_2O_3	-		0.24	0.15	5.4
FeO	-	0.22	-	-	-
MnO	-	-	-	-	0.3
MgO	-	-	-	-	0.7
CaO	33.15	32.98	33.06	32.73	33.3
Total	98.15	98.46	98.42	94.01	99.5
Andradite			0.8	0.5	16.7
Goldmanite			96.3	73.0	59.4
Grossular			-	14.1	20.4
Pyrope			-	-	2.8
Uvarovite			2.9	12.4	-
Yamatoite			-	-	0.7

1 and 2: Detrital grass-green vanadian garnet, Palaeocene sandstone, Well 9/27-1, UK sector, North Sea (electron microprobe single spot analyses).

3. Average of 1 and 2, with all Fe calculated as Fe_2O_3.

4: Dark green vanadian garnet, metamorphosed organic-rich shale, Ishimskaya Luka, northern Kazakhstan (Filippovskaya et al., 1972).

5. Dark green to brownish-green goldmanite, metamorphosed uranium-vanadium deposit in sandstone, Laguna ore district, New Mexico, USA (Moench and Meyrowitz, 1964).

Yamatoite (column 5) is the manganese analogue of goldmanite (Deer et al. 1982, p. 469).

agreement with published analyses of type goldmanite (Deer *et al.*, 1982).

After EPMA the grain was immersed in a suitable X-ray transparent medium, crushed into numerous tiny fragments, rolled into a sphere and mounted on a fibre. The resulting X-ray powder photograph, utilizing a 114.6 mm diameter Debye-Scherrer asymmetric (Straumanis) powder camera, produced a measurable, though not ideal, pattern. To minimise errors, the *d*10.40 and 10.42 lines (~90° 2θ) and *d*14.42 line were used to determine the cell edge. This was calculated to be 12.06 Å, which is in good agreement with the 12.07 Å value obtained by Strens (1965) for end-member synthetic goldmanite.

As noted above, the slightly low total indicates either minor hydration or quality of surface finish. In order to examine the former possibility the d_{420} line, which is a measure of hydration in the grossular–hydrogrossular series, was examined. Kobayashi and Shoji (1984) demonstrated a line shift with $SiO_4 \rightleftharpoons (O_4H_4)$ and minor andradite content. The measured d_{420} for the North Sea goldmanite is 2.699 Å, which is identical to that calculated for the synthetic compound (Strens, 1965). Shepel' and Karpenko 1970) reported a d_{420} value of 2.693 Å for a Siberian goldmanite containing 21.87% V_2O_3, 2.48% Fe_2O_3 and 37.49% SiO_2. Pure goldmanite theoretically contains 36.16% SiO_2 and 30.07% V_2O_3, and Moench and Meyrowitz (1964) report d_{420} 2.688 Å for the type goldmanite, which contains 36.6% SiO_2 and 5.4% Fe_2O_3. The data given by

Kobayashi and Shoji (1984) indicate d_{420} changes from 2.65 Å–2.71 Å over the range $3SiO_2$ to $2SiO_2$. From the limited amount of data available the d_{420} value reported by Moench and Meyrowitz (1964) for a low iron goldmanite does not reflect a replacement of SiO_2 by (O_4H_4), and likewise the North Sea goldmanite is also deemed anhydrous.

On the basis of 24 oxygen atoms the average analysis may be empirically expressed as $Ca_{5.97}(V_{3.87}\,Cr_{0.12}\,Fe^{3+}_{0.02})_{\Sigma 4.01}\,Si_{6.00}\,O_{24}$. On this basis, the density is calculated as 3.77 gm/cm^3, which compares closely with the calculated density of 3.765 gm/cm^3 for the pure synthetic goldmanite (Strens, 1965). Utilising the Gladstone–Dale factors of Mandarino (1981) leads to a calculated refractive index which is either too high or too low, whereas derivation of a factor for V_2O_3 (0.255) from the goldmanite analysis of Filippovskaya *et al.* (1972) results in an R.I. of 1.828, which is in good agreement with the R.I. of 1.834 determined for the synthetic goldmanite by Strens (1965).

The molecular content of North Sea goldmanite is 96.3% goldmanite, 2.9% uvarovite and 0.8% andradite (Table 1). With such a high vanadium content it seems highly likely that full vanadium substitution in the $M_2{}^{3+}$ site may occur in natural material, analogous to the pure andradite reported by Fuchs (1971) and others.

The discovery of goldmanite is of particular interest owing to its rarity; furthermore this is the first discovery of goldmanite as a detrital mineral rather than as a component of a metamorphosed sediment. In view of its rarity, the identification of the mineral would have been an accurate provenance indicator. had a local *in situ* occurrence been documented. To date, however, this is not the case. Nevertheless, the occurrence of detrital goldmanite in the North Sea sedimentary basin indicates that there must be an *in situ* locality of goldmanite within the hinterland that supplied the sediment to the basin. The presence of vanadium-rich garnet as a detrital mineral in the North Sea Palaeocene has recently been substantiated by the discovery of another green isotropic garnet. This grain, which was also clearly detrital in orgin, was found in a Montrose Group sandstone cuttings sample at 2620 m from the Norwegian well 25/4-3 (Heimdal oilfield). EPMA revealed that this garnet contains 10.3% V_2O_3, and is therefore less vanadium-rich than the grain from Well 9/27-1.

The goldmanite was discovered during a provenance study of Palaeocene Montrose Group sands, the source of which has been broadly constrained by sedimentological and seismic evidence to the East Shetland Platform (Rochow, 1981; Morton, 1982; Mudge and Bliss, 1983). The heavy mineral data acquired from this sample further constrains the source rocks to an area around the Shetland Isles, as the presence of chloritoid in the heavy mineral suite is characteristic of the metamorphic rocks on Shetland. A number of occurrences of green garnets have been documented from Shetland, but to date analyses have shown these to be chrome-rich grossulars without significant vanadium contents (Macpherson and Livingstone, 1982). In the light of this new evidence it would seem to be time to re-examine all such occurrences on Shetland.

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References

Benkerrou, C. and Fonteilles, M. (1989) Vanadian garnets in calcareous metapelites and skarns at Coat-an-Noz, Belle-Isle-en-Terre (Cotes du Nord), France. *Am. Mineral.*, **74**, 852–8.

Deer, W. A., Howie, R. A., and Zussman, J. (1982) *Rock-forming minerals*, **1A**, *Orthosilicates*. Longman, London.

Filippovskaya, T. B., Shevnin, A. N. and Dubakina, L. S. (1972) Vanadium garnets and hydrogarnets from Lower Paleozoic carbon- and silica-bearing metasediments of Ishimskaya Luka, northern Kazakhstan. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.*, **203**, 137–41.

Fuchs, L. H. (1971) Occurrence of wollastonite, rhonite, and andradite in the Allende meteorite. *Am. Mineral.*, **56**, 2053–68.

Kobayashi, S. and Shoji, T. (1984) Infrared analysis of the grossular–hydrogrossular series with a small amount of the andradite molecule. *Mineral. J.*, **12**, 122–36.

Macpherson, H. G. and Livingstone A. (1982) Glossary of Scottish Mineral Species. *Scott. J. Geol.*, **18**, 1–47.

Mandarino, J. A. (1981) The Gladstone-Dale relationship: part IV. The compatibility concept and its application. *Can. Mineral.*, **19**, 441–50.

Moench, R. H. and Meyrowitz, R. (1964) Goldmanite, a vanadian garnet from Laguna, New Mexico. *Am. Mineral.*, **49**, 644–55.

Morton, A. C. (1982) Lower Tertiary sand development in Viking Graben, North Sea. *Bull. Am. Assoc. Petrol. Geol.*, **66**, 1542- 59.

——(1985) A new approach to provenance studies: electron microprobe analysis of detrital garnets from Middle Jurassic sandstones of the northern North Sea. *Sedimentology*, **32**, 553–66.

Mudge, D. C. and Bliss, G. M. (1983) Stratigraphy and sedimentation of the Palaeocene sands in the northern North Sea. In *Petroleum Geochemistry and Exploration of Europe* (Brooks, J., ed.). Geol. Soc. London, Spec. Publ. **12**, 95–111.

Rochow, K. A. (1981) Seismic stratigraphy of the North Sea 'Palaeocene' deposits. In *Petroleum Geology of the Continental Shelf of North-West Europe* (Illing, L. V. and Hobson, G. D., eds.). Heyden & Son, London, 255–66.

Shepel', A. B. and Karpenko, M. V. (1970) First find of goldmanite in the USSR. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.*, **193**, 150–2.

Strens, R. G. J. (1965) Synthesis and properties of calcium vanadium garnet (goldmanite). *Am. Mineral.*, **50**, 260.

Wang, P.-C., Yu, C.-A., and Chang, K.-L. (1974) A preliminary study of the composition of vanadium minerals and its mode of occurrence in the Lower Cambrian black shale in a region of China. *Acta Geol. Sinica*, 219–29 (Chinese with English abstract).

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British Geological Survey,
Keyworth,
Nottingham NG12 5GG
CLAIRE R. HALLSWORTH

Royal Museum of Scotland,
Chambers Street, Edinburgh EH1 1JF, UK
ALEC LIVINGSTONE

British Geological Survey,
Keyworth,
Nottingham NG12 5GG
ANDREW C. MORTON

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The preparation of double-polished fluid inclusion wafers from friable, water-sensitive material

IN a study of sediment diagenesis, polished wafers for fluid inclusion analysis must: 1, have a high optical quality; 2, be very thin (i.e. less than 100 μm); 3, be processed under low-temperature conditions to prevent inclusion stretching and leakage; 4, maintain coherency in order to differentiate between cements and detrital grains.

The tried and tested methods of wafer preparation (Shepherd *et al.*, 1985; Roedder, 1984, p. 155) are in general not suitable for the preparation of polished wafers from clastic sedimentary rocks, especially those with a friable and/or water soluble nature. In the case of sandstones where fluid-inclusion data are required on the diagenetic cements, very thin wafers (50 μm and less) are required to overcome the problems of darkening and 'clouding' caused by sample grain size and diagenetic crystal size. This is illustrated in Fig. 1, where it can be seen that very small grains and crystals have not come into contact with the wafer edges and have therefore not been polished. The surface characteristics of the grains are preserved, which makes the detection of all other features, including any cement and fluid inclusions, difficult.

In polishing to an extremely thin wafer size, it has been discovered that many sedimentary samples, even those with a diagenetic cement, are too friable and tend to disintegrate. The problem can be traced to the cement/wax that bonds the sample to the glass plate for polishing. Several cements were tested and a brand of 'superglue' (Bostik^{tm} Superglue 4) gave the desired product, i.e. thin, coherent wafers approximately 1–3 centimetres in size. Under magnification, some improvement in cement (and inclusion) observation was clearly achieved with increased thinning of the wafer (Fig. 2). The whole procedure, used at Imperial College for samples of Rotliegend Sandstone from the Southern North Sea, is described below. In these rocks some of the cements, e.g. halite and to a lesser extent, anhydrite, are regarded as water-soluble.

Impregnation and encapsulation

The required section is broken from the sample, or cut using an oil-lubricated diamond saw. A cut section must be cleaned thoroughly with