Article: Super-heavy pyrite $(\delta^{34}S_{pyr} > \delta^{34}S_{CAS})$ in the terminal Proterozoic Nama Group, Southern Namibia: A consequence of low seawater sulfate at the dawn of animal life

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1. Methods

Sample collection and preparation

The most pristine-appearing, fine-gained, crystalline limestone samples, weighing approximately 500 g each, were obtained from outcrops at 6-20 m intervals throughout measured and previously described (Saylor et al., 1995) stratigraphic sections of the lower Nama Group in Southern Namibia. Calcrete and organic deposits were trimmed from the samples using a water-lubricated trim-saw. Trimmed samples were then rinsed in de-ionized water (DI) and submerged for approximately 10 minutes in 6N HCl to remove any remnant contaminants from the sample surface. Samples were then air-dried overnight and powdered using a *SPEX 8510 Shatterbox* with an alumina-ceramic container.

Sulfur extraction and isotopic analysis

Approximately 300 g of powder from each sample was soaked in DI for 24 hrs to remove water-soluble sulfates, including gypsum and oxidized sulfides. Carbonate associated sulfate (CAS) and pyrite sulfur were extracted from these samples.

CAS was extracted by completely dissolving the rinsed powder in roughly 600 mL of 6N HCl, which was added in 50 mL aliquots over a period of 2 hours, under continuous stirring and at room temperature. After complete dissolution of the calcium carbonate material, the solute was filtered under vacuum to remove any insoluble residue. An excess of 1M BaCl₂ solution was added to the filtrate to precipitate dissolved sulfate as BaSO₄. The concentration of sulfur from CAS (S_{CAS}) was obtained by dividing the mass of the precipitated S_{CAS} (calculated stoichiometrically from the mass of the precipitated BaSO₄) by the initial mass of the powdered rock sample.

Pyrite sulfur was extracted from the insoluble filter residue using a modified version of the chromium reduction method originally described by Canfield et al (1986). Approximately 2 g of insoluble residue from each sample was treated with 6N HCl and 0.4M reduced CrCl₂ solution. This reaction proceeded for 2 hrs at 90°C under N₂ gas. Sulfur from the liberated H₂S was precipitated as Ag₂S after bubbling through a 0.1M AgNO₃ trap. The concentration of sulfur from pyrite (S_{pyr}) was obtained by dividing the mass of the precipitated S_{pyr} (calculated stoichiometrically from the mass of the precipitated Ag₂S) by the initial weight of the powdered rock sample.

The BaSO₄ and Ag₂S precipitates were rinsed, filtered under vacuum, and dried overnight. The precipitates were then combined with an excess of V₂O₅ (~10x mass of precipitate) and analyzed for their sulfur isotopic composition (δ^{34} S) at Indiana University on a *Finnigan MAT 252* gas source mass spectrometer fitted with a peripheral elemental analyzer for on-line sample combustion (Studley et al., 2002). Sulfur isotope compositions are expressed in standard δ -notation as ‰-deviations from V-CDT. Samples values were calibrated using two international standards: NBS-127 (20.3‰) and S3 (-31.5‰); and four internal standards: ERE-Ag2S (-4.3‰); EMR-CP (0.9‰); BB4-18 (39.5‰); and PQB (38.0‰). Analytical error of <0.5‰ was obtained from replicate analyses of samples and laboratory standards.

Carbon and oxygen isotope analysis

Approximately 1 g of calcium carbonate material was drilled with a masonry bit from the purest limestone laminates available in each sample. Carbonate carbon (δ^{13} C) and carbonate oxygen (δ^{18} O) isotopes of this material were then quantified at the Woods Hole Oceanographic Institution using the methods of Ostermann and Curry (2000).

Elemental analysis

Approximately 0.5 g of powdered whole-rock material was digested for two hours in aqua regia at 95°C. The solution was then diluted and analyzed for relative concentrations of Sr, Mn, and Al by ICP-MS. International certified reference materials USGS GXR-1, GXR-2, GXR-4, and GXR-6 were analyzed at the beginning and end of each sample batch. Internal control standards and duplicate samples were analyzed after every ten samples.

2. Detailed Stratigraphic Description of the Nama Group Carbonates

The Nama Group was deposited in a foreland basin of the Kalahari Craton that developed during convergence along the bordering Damara and Gariep compressional belts (Grotzinger and Miller, 2008; Gresse and Germs, 1993; Germs, 1995, 1974). The Nama basin was divided by a basement arch into northern and southern sub-basins during the deposition of the lower Nama Group (Fig. 1; Grotzinger and Miller, 2008; Germs, 1983; Saylor et al., 1998). The Proterozoic portion of the Nama Group, which is the focus of the present study, comprises the Kuibis and most of the overlying Schwarzrand subgroups. These subgroups were deposited in shore-associated settings ranging from upper shoreline/tidal flats to below-wave-base lower shoreface (Grotzinger and Miller, 2008; Saylor et al., 1995, 1998; Germs, 1995).

Carbonate units in the Kuibis subgroup are mostly contained within the lower and upper Omkyk and Hoogland members and are recognized across the northern sub-basin (Fig. 1;

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Grotzinger and Miller, 2008; Saylor et al., 1995, 1998; Germs, 1995). The Omkyk members consist of ten-meter-scale upward-coarsening middle-to-upper shoreface successions of hummocky-cross stratified calcisiltites, heterolithic interbeds, crossstratified grainstones, and stromatolites. The Hoogland member consists primarily of middle shoreface heterolithic interbeds that record a transgressive-regressive depositional succession. Lower carbonate beds fine upwards into interbedded shales and limestones, while upper carbonate beds coarsen upwards into heterolithic interbeds with crossstratification and coarse-grained ripples

Carbonate units in the Schwarzrand subgroup are mostly contained within the Huns and Spitzkopf members and are recognized across the southern sub-basin (Fig.1; Grotzinger and Miller, 2008; Saylor et al., 1995, 1998; Germs, 1995). The Huns member consists largely of meter-scale upward coarsening cycles of calcisiltites, calcarenites, pellet/intraclast grainstones, and stromatolites. It is capped by pinnacle reefs, indicative of a flooding surface, which are enveloped in the green siltstones and shales of the roughly 70 m thick non-carbonate Feldschuhhorn member (Saylor et al., 1995; Saylor and Grotzinger, 1996). The Spitzkopf member comprises fine-grained, thinly-bedded calcisiltites with locally developed thrombolites and stromatolites, indicative of low-energy deep-ramp deposition (Grotzinger and Miller, 2008; Saylor et al., 1995, 1998).

The studied sections of the Nama Group are highly fossiliferous, containing Ediacarantype fossils (Narbonne et al., 1997; Germs, 1972b; Jensen et al., 2000), Vendotaenids (Germs et al., 1986), *Cloudina* (Germs, 1972a; Grant et al., 1991), *Namacalathus* (Grotzinger et al., 2000), *Namapoikia* (Wood et al., 2002), and other calcified fossils (Grotzinger and Miller, 2008; Germs, 1995; Germs et al., 1986; Grotzinger et al., 1995).

3. Age constraint

The age of the Nama Group is relatively well-constrained from the U-Pb dating of three ash beds within the group (Fig. 1; Grotzinger et al., 1995): 549 ± 1 Ma in the Hoogland member (Kuibis subgroup, northern sub-basin); and 545 ± 1 Ma and 543 ± 1 Ma in the Spitzkopf member (Schwarzrand subgroup, southern sub-basin). The Proterozoic-

Cambrian boundary is represented by a regionally extensive erosional unconformity near the top of the Schwarzrand subgroup in the southern sub-basin (Germs, 1983; Saylor and Grotzinger, 1996; Narbonne et al., 1997; Grotzinger et al., 1995), which is overlain by incised-valley fill dated (U-Pb, ashbed) at 539 ± 1 Ma (Grotzinger et al., 1995). Therefore, assuming constant rates of sedimentation above and below the dated ash beds, the Nama Group section investigated here spans approximately 10 Myr and extends to within 1 Myr of the Proterozoic-Cambrian transition (Saylor et al., 1998).

4. Evaluating Diagenesis

Smooth and consistent variation in δ^{13} C values throughout the sampled sections that parallels δ^{13} C variations of contemporaneous terminal Neoproterozoic sections (Fig. DR1) from China (Condon et al., 2005; Jiang et al., 2003), Australia (Calver, 2000; Calver, 1995), and Oman (Fike et al., 2006) suggests that the sampled Nama Group sections are a near-primary record of oceanic δ^{13} C and that the Nama subbasins were connected to the global ocean over this interval (Saylor et al., 1998; Grotzinger et al., 1995).

High-quality preservation (Narbonne et al., 1994) of the Nama Group carbonates is also evidenced by their relatively heavy δ^{18} O values (87% of samples > -10‰; Fig. DR2a), low Mn/Sr ratios (99% of samples < 2; Fig DR2b), and extremely high [Sr] [range: 115 – 3940 ppm; AVG (±SE) = 1805 ±176 ppm; 40% of samples > 2000 ppm]. Furthermore, there was no significant (p < 0.05) correlation between either δ^{34} S_{pyr} and δ^{18} O (Fig. DR2a; p =0.12; R² = 0.03; n = 89) or δ^{34} S_{CAS} and Mn/Sr (Fig. DR2d; p = 0.60; R² = 0.01; n = 84). δ^{34} S_{pyr} and Mn/Sr were significantly (p < 0.05) negatively correlated (Fig. DR2b; p = 0.03; R² = 0.05; n = 91), indicating that the better preserved samples (lower Mn/Sr) exhibit higher δ^{34} S_{pyr}. Likewise, δ^{34} S_{CAS} and δ^{18} O were significantly (p < 0.05) negatively correlated (Fig. DR2c; p = 0.02; R² = 0.06; n = 100), indicating that the better preserved samples (heavier δ^{18} O) exhibit lower δ^{34} S_{CAS}.

 $\delta^{34}S_{pyr}$ also tends to exhibit extreme resilience to thermal alteration (Baumgartner and Valley, 2001). Sulfidic black shales subjected to a metamorphic gradient ranging from chlorite to sillimanite grade, spanning temperatures from 300 to 600°C, exhibited only a

weak, inverse relationship between metamorphic grade and $\delta^{34}S_{pyr}$ (Oliver et al., 1992). It is therefore unlikely that meteoric or thermal diagenesis was responsible for the ³⁴Senriched pyrite observed in the Nama Group carbonates. In fact, diagenesis appears to have imparted the opposite effects, i.e., pyrite that is depleted in ³⁴S, relative to CAS (Fig. DR 2b,c).

5. Supplementary Information for Manuscript Fig. 2 (Compilation of Published $\delta^{34}S_{CAS}$ and $\delta^{34}S_{pyr}$)

Prior reports of anomalously ³⁴S-enriched pyrite (numbers correspond to those in Fig. 2):

(1) Random Fm, Canada, ~538 Ma, $\delta^{34}S_{pyr} = 23.4\%$, n = 2 (Strauss et al., 1992);

- (2) Mazowze Fm, Poland, ~540 Ma, $\delta^{34}S_{pyr} = 23.6\%$, n = 11 (Bottomley et al., 1992);
- (3) Włodowa Fm, Poland, ~545 Ma, $\delta^{34}S_{pyr} = 27.6\%$, n = 11 (Bottomley et al., 1992);
- (4) Lublin Fm, Poland, ~549 Ma, $\delta^{34}S_{pyr} = 28.8\%$, n = 19 (Bottomley et al., 1992);
- (5) Tapley Hill Fm (Australia), ~662 Ma, $\delta^{34}S_{CaSO4} = 26.3\%$, n = 5; $\delta^{34}S_{pyr} = 29.9\%$, n =
- 43 (Gorjan et al., 2000);
- (6) Twitya Fm (Canada), ~665 Ma, δ^{34} S_{pyr} = 30.4‰, n = 4 (Hayes et al., 1992);
- (7) Aralka Fm (Australia), ~668 Ma, δ^{34} S_{pvr} = 47.3‰, n = 9 (Hayes et al., 1992);
- (8) Datangpo Fm, China, ~670 Ma, δ^{34} S_{pvr} = 43.9‰, n = 10 (Xu et al., 1990);
- (9) Luoquan Fm, China, ~700 Ma, δ^{34} S_{pyr} = 23‰, n = 1 (Hayes et al., 1992);
- (10) Minle Fm, China, ~704 Ma, δ^{34} S_{pyr} = 43.3‰, n = 21 (Li et al., 1999);
- (11) Liantuo Fm, China, ~748 Ma, $\delta^{34}S_{pyr} = 39\%$, n = 17 (Tie-bing et al., 2006);
- (12) Newland Fm, Montana (USA), ~1440 Ma, $\delta^{34}S_{pyr} = 19.3\%$, n = 7 (Hayes et al., 1992);
- (13) Reward Fm, Australia, ~1640 Ma, $\delta^{34}S_{pyr} = 21.7\%$, n = 9 (Shen et al., 2002);
- (14) Urquhart Fm, Australia, ~1670 Ma, $\delta^{34}S_{pyr} = 28.5\%$, n = 3 (Hayes et al., 1992);
- (15) Onwatin Fm, Canada, ~1850 Ma, δ^{34} S_{pyr} = 15.9‰, n = 6 (Thode et al., 1962);

(16) Zhamoketi Fm, China, ~636 Ma, $\delta^{34}S_{CAS} = 13.4\%$, n = 63; $\delta^{34}S_{pyr} = 16.4\%$, n = 40 (Shen et al., 2008).

Additional data were obtained from compilations by Claypool et al (1980), Hayes et al (1992), Kampschulte and Strauss (2004), Strauss (1993), Goldberg et al (2005), Schroder et al (2004), Lyons et al (2006) and Canfield (1998).

<u>6. Terms and formulae used in the Rayleigh fractionation model (Fig. 4 of</u> <u>manuscript)</u>

Terms: $f_{SO4} = \text{fraction of initial H}_2 \text{S oxidized to SO}_4^{2-}$ (independent variable) $\delta^{34}\text{S}_{SO4(c)} = \text{cumulative } \delta^{34}\text{S}_{SO4}$ $\delta^{34}\text{S}_{SO4(i)} = \text{instantaneous } \delta^{34}\text{S}_{SO4}$ $\delta^{34}\text{S}_{H2S} = \text{cumulative } \delta^{34}\text{S}_{H2S}$ $\delta^{34}\text{S}_{H2S(o)} = \text{initial } \delta^{34}\text{S}_{H2S} = 27.2\%$ $\xi = \text{instantaneous oxidative isotope fractionation } (\delta^{34}\text{S}_{SO4} - \delta^{34}\text{S}_{H2S}) = -4 \text{ and } -5$

Formulae: $\delta^{34}S_{H2S} = \{ [\delta^{34}S_{H2S(0)}/(f_{SO4})] - \xi/(1 - \xi/1000) \} / [1/(1 - \xi/1000) + (1 - f_{SO4})/f_{SO4}]$ $\delta^{34}S_{SO4(i)} = \delta^{34}S_{H2S} + \xi$ $\delta^{34}S_{SO4(c)} = [\delta^{34}S_{H2S(0)} - (\delta^{34}S_{H2S})(1 - f_{SO4})]/f_{SO4}$

7. Seawater [SO₄²⁻] at the Terminal Proterozoic

Nama-Ara Group comparison (cont'd)

Although it is possible that the Nama (Namibia) and Ara Group (Oman) carbonates were deposited in semi-isolated basins (of substantially differing sulfate concentrations), their similar δ^{13} C profiles argue against this. Nonetheless, if sulfate concentrations were low enough to make the residence time of seawater sulfate less than the mixing time of the oceans, then regional differences in [SO₄²⁻] would be compatible with globally synchronized δ^{13} C. Indeed, the recent report showing wide variations in Fe_{HR}/Fe_T amongst coeval late Neoproterozoic shales (Canfield et al., 2008) suggests that the oxidation state of the ocean, and its associated concentrations of dissolved Fe(II) and sulfate, may have exhibited significant spatial heterogeneity throughout this period.

Estimates from fluid inclusions

Measurements of fluid inclusions obtained from the Ara Group suggest that seawater $[SO_4^{2^-}]$ in the basin was much higher $(20.5 \pm 4.5 \text{ mM}, \text{Lowenstein et al., } 2003; \ge 23 \text{ mM},$ Horita et al., 2002) than values inferred from the Ara Group sulfur isotope data (Fike et al., 2006). However, less than one-third (~6.5 mM) of the $[SO_4^{2^-}]$ reported for these fluid inclusions was measured directly; the balance (~14 mM) was inferred to have been lost via precipitation of CaSO₄ during early-mid stage evaporation of the brine (Lowenstein et al., 2003). Given these assumptions, there is substantial uncertainty associated with the fluid inclusion-based estimates of seawater $[SO_4^{2^-}]$ at the terminal Proterozoic.

8. Figure Captions for Supplementary Figures DR1 and DR2

Figure DR1. Calcium carbonate δ^{13} C record of contemporary terminal Neoproterozoic sections from China (Condon et al., 2005; Jiang et al., 2003), Australia (Calver, 2000; Calver, 1995), Oman (Fike et al., 2006), and Namibia (this study; Saylor et al., 1998; Workman et al., 2002). Synchroneity between Nama Group δ^{13} C and δ^{13} C from contemporaneous formations from other continents suggests that the Nama Group carbonates are well-preserved and were deposited in a basin connected to the global ocean. Ages of the Nama Group are estimated from U-Pb lead dates obtained from volcanic ash beds within the group (Grotzinger et al., 1995), assuming a constant rate of sedimentation between these ashbeds. Ages of the other sections were estimated using methods similar to those described in Fike et al (2006).

Figure DR2. Evaluation of $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ diagenesis: (a) $\delta^{18}O_{CaCO3}$ vs. $\delta^{34}S_{pyr}$; (b) Mn/Sr vs. $\delta^{34}S_{pyr}$; (c) $\delta^{18}O_{CaCO3}$ vs. $\delta^{34}S_{CAS}$; and (d) Mn/Sr vs. $\delta^{34}S_{CAS}$. Statistically significant correlations (p < 0.05) are marked with an asterisk. Lack of significant positive correlation between the anomalously enriched $\delta^{34}S_{pyr}$ or depleted $\delta^{34}S_{CAS}$ and either of the conventional geochemical indicators of diagenesis (light $\delta^{18}O$ or elevated Mn/Sr) suggests that diagenesis was not responsible for the anomalous trends observed in the Nama Group carbonates.

<u>Unit</u>	<u>Est.</u> <u>Age</u> (Ma)	<u>δ13C</u>	<u>δ180</u>	<u>δ34S</u> (CAS)	<u>δ34S</u> (pyr)	<u>∆34S</u>	[<u>S_{CAS}]</u> (ppm)	<u>[S_{РҮR}]</u> (ppm)	<u>[Sr]</u> (ppm)	<u>[Mn]</u> (ppm)	[Mn]/[Sr]
L. Omkyk	552.0	-6.8		20.9			46				
L. Omkyk	552.0	-5.7	-5.6	15.5			81				
L. Omkyk	551.9	-5.7	-8.6	26.0	28.1	-2.1	14	106	245	443	1.81
L. Omkyk	551.8	-5.1	-8.1	23.1			9				
L. Omkyk	551.7	-0.1	-8.3	15.9	35.4	-19.6	23	33	395	58	0.15
L. Omkyk	551.6	0.2	-7.0	21.3			10				
L. Omkyk	551.6	1.0	-7.1	13.5			15	45	502	51	0.10
L. Omkyk	551.5	1.8	-7.0	19.1			10				
L. Omkyk	551.4	1.4		14.2			30	11	515	515	1.00
L. Omkyk	551.4	1.8	-6.7	13.7			12				
L. Omkyk	551.3	1.9	-5.8	16.7	31.5	-14.8	22	40	586	136	0.23
L. Omkyk	551.2	1.5	-7.1	16.6			14				
L. Omkyk	551.1	1.7	-5.9	15.9	25.0	-9.0	9	11	917	112	0.12
L. Omkyk	551.1	1.6	-6.6	20.2			4				
L. Omkyk	551.0		-6.9	14.0	26.6	-12.6	24	19	591	36	0.06
L. Omkyk	550.9	1.3	-7.7	14.4			22				
L. Omkyk	550.8	2.9	-9.3	13.7	33.9	-20.2	7	9	1570	49	0.03
L. Omkyk	550.8	2.5	-7.3	22.9			<1				
L. Omkyk	550.7	1.1	-6.6	16.8			50	<1	417	111	0.27
L. Omkyk	550.6	2.3	-8.2	20.4			34				
L. Omkyk	550.5	0.7	-6.0	17.4	26.6	-9.1	3	21	991	45	0.05
L. Omkyk	550.5	0.9	-6.2	16.7			13				
L. Omkyk	550.4	2.0	-6.8				16				
L. Omkyk	550.3	2.0	-5.3		27.7		16	34	792	23	0.03
U. Omkyk	550.7						20				
U. Omkyk	550.6				23.9			212	573	452	0.79
U. Omkyk	550.5	-0.2	-7.9	29.5			16				
U. Omkyk	550.5	1.8	-8.6		26.4		6	44	756	162	0.22
U. Omkyk	550.4	2.4	-8.7	24.7			7				
U. Omkyk	550.3	2.3	-8.8	29.9	23.9	5.9	26	36	595	270	0.45
U. Omkyk	550.2	2.5	-8.6	27.5			8				
U. Omkyk	550.2	3.3	-7.7	25.4	26.6	-1.2	16	27	824	61	0.07
U. Omkyk	550.1	4.0	-9.1	29.7			10				
U. Omkyk	550.0	2.9	-9.9	37.4	31.6	5.9	28	40	637	70	0.11
U. Omkyk	549.9	4.7	-7.5	35.3			18				
U. Omkyk	549.9	2.9	-9.7	35.2	33.8	1.4	54	26	846	462	0.55
U. Omkyk	549.8	3.2	-8.4	33.5			63				
U. Omkyk	549.7		-7.2	32.2	39.6	-7.5	13	27	880	107	0.12
U. Omkyk	549.6	4.3	-9.0	33.2			10	44	771	67	0.09
U. Omkyk	549.5		-6.8								
U. Omkyk	549.5	4.4	-8.1	35.1			20	109	405	74	0.18
U. Omkyk	549.4	6.0	-9.3	38.5			17				
U. Omkyk	549.3	6.1	-5.6	39.0	34.6	4.4	13	81	695	103	0.15
U. Omkyk	549.2	5.2	-10.5	40.0			5				

<u>9. Table DR1: Geochemical Data from the Nama Group (blanks = no data obtained).</u>

U. Omkyk	549.2	3.1	-8.9	29.0	22.7	6.2	4	37	504	57	0.11
U. Omkvk	549.1	3.5	-7.9	18.5			15			-	
U. Omkvk	549.0	3.4	-7.1	22.5			5	3	263	138	0.52
Hoogland	549.0	2.8	-8.1	32.3	34.3	-2.0	12	47	671	112	0.17
Hoogland	549.0		-9.2	31.2	27.8	3.4	35	22	761	310	0.41
Hoogland	548.9	2.8	-9.8	28.3			52	17	699	1300	1.86
Hoogland	548.9	2.9	-9.6	37.0	32.0	5.0	118	48	2440	546	0.22
Hoogland	548.8	3.0	-9.8	38.8	27.6	11.2	7	6	724	475	0.66
Hoogland	548.8	3.0	-8.9	41.4	37.1	4.3	69	10	1850	335	0.18
Hoogland	548.7	4.2	-8.6		32.0			60	941	330	0.35
Hoogland	548.7	2.7	-8.3	28.2	29.4	-1.2	26	3	712	429	0.60
Hoogland	548.7	2.6	-6.2	39.0	28.7	10.3	4	34	1330	193	0.15
Hoogland	548.6	2.4	-6.9	33.4			32	20	1220	251	0.21
Hoogland	548.6	2.8	-6.8	36.7	33.0	3.6	20	10	1230	216	0.18
Hoogland	548.5	3.5	-6.7	37.9			12	26	1370	175	0.13
Hoogland	548.5	2.7	-6.0	47.0	37.9	9.2	85	70	2310	69	0.03
Hoogland	548.4	3.1	-7.3		39.8		52	19	1560	197	0.13
Hoogland	548.4	1.6	-6.2		41.5		24	38	1270	60	0.05
Hoogland	548.3	2.4	-9.3		45.7			88	2040	31	0.02
Hoogland	548.3	1.8	-8.1	38.8	40.0	-1.2	2	17	1930	41	0.02
Hoogland	548.2	3.5	-10.4	35.2	34.9	0.2	17	78	3250	99	0.03
Hoogland	548.2	2.6	-7.3		33.5		44	30	2020	185	0.09
Hoogland	548.1	2.8	-8.9	40.8	46.9	-6.1	33	41	2770	135	0.05
Hoogland	548.0	1.9	-8.4	50.3	55.1	-4.8	17	29	3160	298	0.09
Hoogland	547.9		-9.4	47.9	57.3	-9.4	11	30	2790	277	0.10
Hoogland	547.9	1.8	-8.6	32.9	61.9	-29.0	33	25	3460	240	0.07
Hoogland	547.8	1.8	-6.5	30.5	39.4	-8.8	13	36	2380	364	0.15
Hoogland	547.7	1.7	-7.7	44.7							
Hoogland	547.7	1.5	-9.3	47.3	35.3	12.0	10	47	1880	452	0.24
Hoogland	547.6	1.7	-9.8	64.2	65.4	-1.2	17	7	3050	462	0.15
Hoogland	547.5	2.2	-10.7	54.0	80.2	-26.2	4	15	3940	397	0.10
Hoogland	547.5	2.0	-7.6								
Hoogland	547.4	1.8	-8.1	39.2	44.6	-5.4	32	75	2260	204	0.09
Hoogland	547.3	1.9	-8.2	34.6	51.1	-16.5	16	29	3190	480	0.15
Hoogland	547.2	1.7	-9.6	30.3	27.7	2.6	43	67	2670	1030	0.39
Hoogland	547.1	2.3	-8.7	32.5	23.5	9.0	10	26	2650	734	0.28
Hoogland	547.0	1.8	-5.2	45.4	37.3	8.1	32	70	2260	335	0.15
Hoogland	546.9	1.6	-6.6	41.0	38.5	2.6	57	77	1810	301	0.17
Hoogland	546.9		-7.5	17.0	48.1	-31.1		2	897	224	0.25
Huns	546.7	1.2	-9.9		65.8			33	1330	502	0.38
Huns	546.7	2.4	-10.8		34.4			61	2590	88	0.03
Huns	546.6	2.7	-10.3	19.0	39.4	-20.4	61	37	1200	333	0.28
Huns	546.5	2.1	-8.8	20.5	36.0	-15.4	20	45	3060	42	0.01
Huns	546.4		-7.3	17.3	26.2	-8.8	15	130	756	991	1.31
Huns	546.3	1.2	-7.1	17.9	36.4	-18.5	6	8	2020	62	0.03
Huns	546.2	1.9	-6.3	24.2	32.4	-8.2	21	34	2700	20	0.01
Huns	546.2	1.8	-10.9	25.0	39.3	-14.3	16	10	3070	12	0.00
Huns	546.1	1.6	-10.0		42.2			42	1270	151	0.12

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Hune	546.0	07	-00	21.2	36.3	-15 1	40	41	2540	288	0.11
Huns	545.9	17	-10.0	2112	25.8	13.1	25	13	2290	105	0.05
Huns	545.9	0.9	-73		23.0		38	32	1680	739	0.44
Huns	545.8	0.5	-5.0	16.6	24.9	-8.2	22	60	2120	583	0.27
Huns	545.7	1.4	-7.4	22.5	24.5	0.2	22	00	2120	505	0.27
Huns	545.6	1.4	-10.0	35.2			18				
Huns	545 5	1.8	-9.7	5512	58.8		12	21	2110	81	0.04
Huns	545 5	1.8	-10.3	30.5	47.0	-16 5	<1	19	2010	64	0.03
Huns	545.4	110	-12.2	5015	40.5	1015		4	227	129	0.57
Huns	545.4	0.7	-11.5		27.6			7	1180	33	0.03
Huns	545.3	1.5	-10.4		20.5			3	1220	31	0.03
Huns	545.2	0.5	-10.2	22.7	36.8	-14.1	11	33	1740	146	0.08
Huns	545.1	1.5	-9.5	37.0	53.5	-16.5	31	29	1820	22	0.01
Huns	545.1	1.6	-8.6	20.9	42.9	-22.0	12	7	1880	5	0.00
Huns	545.0	1.6	-9.4	2015	41.1			7	1470	17	0.01
Huns	544.9	2.0	-5.9		32.9			9	1230	32	0.03
Huns	544.8	2.0	-9.3	20.5	31.1	-10.6	49	15	1070	76	0.07
Huns	544.8	1.7	-9.9	28.4	35.6	-7.2	9	10	1140	44	0.04
Spitzkopf	544.8	2.1	-9.7	20.8	40.2	-19.4	9	59	3270	540	0.17
Spitzkopf	544.7	1.2	-11.6	22.6	33.8	-11.2	10	9	2320	528	0.23
Spitzkopf	544.7	1.3	-9.3	32.8	35.9	-3.0	60	10	1870	423	0.23
Spitzkopf	544.6	0.7	-9.0	28.1			51	6	1010	2840	2.81
Spitzkopf	544.6	1.0	-6.3	16.0			21	22	1690	1750	1.04
Spitzkopf	544.5	1.6	-8.2	16.1	32.5	-16.4	44	33	2440	1100	0.45
Spitzkopf	544.4	1.4	-6.0	17.4	36.4	-19.1	23	19	3710	52	0.01
Spitzkopf	544.3	1.2	-7.8	18.3			13	44	3650	127	0.03
Spitzkopf	544.3	1.5	-5.7	19.0	38.8	-19.8	6	13	2570	71	0.03
Spitzkopf	544.2	1.0	-6.4	18.7	42.1	-23.3	3	7	3080	27	0.01
Spitzkopf	544.2	1.4	-6.7		42.3			18	3830	28	0.01
Spitzkopf	544.1	1.1	-7.5	20.1			43	13	3350	106	0.03
Spitzkopf	544.1	1.2	-6.1		35.6			43	3770	140	0.04
Spitzkopf	544.0	1.5	-8.7	20.5	39.8	-19.3	26	34	3760	27	0.01
Spitzkopf	544.0	1.4	-9.3	21.2	39.8	-18.6	10	19	3650	80	0.02
Spitzkopf	543.9	1.3	-6.9	20.4	39.4	-19.0	23	31	2740	53	0.02
Spitzkopf	543.9	1.3	-9.7	18.9	35.0	-16.1	9	26	3220	95	0.03
Spitzkopf	543.8			18.8			16	2			
Spitzkopf	543.7	1.5		20.1	25.4	-5.3	14	56	3110	128	0.04
Spitzkopf	543.7	1.2	-8.0	17.9	36.8	-18.9	15	36	2270	57	0.02
Spitzkopf	543.6	1.3	-10.4	22.9	35.8	-12.9	6	14	2810	70	0.02
Spitzkopf	543.6	1.0	-11.4	24.0	31.5	-7.5	8	39	1820	130	0.07
Spitzkopf	543.5	1.3	-11.5	21.3	31.7	-10.3	7	26	1540	228	0.15
Spitzkopf	543.5	1.3	-11.3	20.2	32.7	-12.5	5	65	1560	121	0.08

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