

Unravelling the Temporal and Chemical Evolution of a Mineralizing Fluid in Karst-Hosted Deposits: A Record from Goethite in the High Atlas Foreland (Morocco)

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Table S1. Summary of information and performed analyses of Imini goethite.

Sample number	Description	Location		Elevation (m)	XRD	SEM	Geochemical analyses	Isotopic analyses	(U-Th)/He dating
		Lat (°N)	Long (°W)						
<u>Far West</u>									
18FAR02	massive botryoidal goethite	31°2'29"	7°27'57"	1711	x	x	x	x	x
18FAR02A	massive botryoidal goethite	31°2'29"	7°27'57"	1711	x	x	x	x	x
18FAR02B	massive botryoidal goethite	31°2'29"	7°27'57"	1711	x	x			
18FAR02C	powdery hematite and goethite	31°2'29"	7°27'57"	1711	x		x		
18FAR03	massive botryoidal goethite	31°2'29"	7°27'57"	1711	x	x			
18FAR07X	massive botryoidal goethite	31°1'12"	7°28'6"	1739	x	x	x		
18FAR15	massive botryoidal goethite	31°1'12"	7°28'6"	1739	x	x			
18FAR17	botryoidal goethite	31°1'12"	7°28'6"	1739	x	x			
18FAR18	botryoidal goethite	31°1'12"	7°28'6"	1739	x	x			
<u>Tifersine</u>									
18TIF01	massive botryoidal goethite	31°2'45"	7°27'21"	1674	x	x	x	x	x
18TIF05	thin botryoidal goethite vein	31°2'45"	7°27'21"	1674	x	x	x		
18TIF12	mixed Mn oxides and goethite	31°2'27"	7°27'18"	1654	x				
18TIF16	brechified goethite	31°2'27"	7°27'18"	1654	x				
18TIF20	thin botryoidal goethite vein	31°2'27"	7°27'18"	1654	x	x	x	x	x
<u>Plateaux</u>									
15PL02	massive botryoidal goethite	31°1'35"	7°29'31"	1763	x	x	x	x	x
18PL02A	powdery hematite and goethite	31°1'27"	7°29'3"	1766	x				
18PL02B	thin botryoidal goethite vein	31°1'27"	7°29'3"	1766	x	x	x	x	x
18PL07	massive botryoidal goethite	31°1'27"	7°29'3"	1766	x	x	x	x	x
18PL07B	massive botryoidal goethite	31°1'27"	7°29'3"	1766	x	x			
18PL20	thin botryoidal goethite vein	31°1'27"	7°29'3"	1766	x	x			
18PL25	thin botryoidal goethite vein	31°1'27"	7°29'3"	1766	x	x	x	x	x
18PL27	massive botryoidal goethite	31°1'27"	7°29'3"	1766	x	x	x		

Note: All samples are associated to Mn ores, and are hosted by Cenomanian-Turonian dolostones.

Table S2. Results of geochemical analyses for major elements (in wt.%).

Sample number	FeO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI	Total
D.L.	0.1	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01		
<u>Far West</u>													
18FAR02	<0.1	2.67	0.15	84.55	0.350	0.76	0.13	0.02	<0.01	<0.001	0.14	11.24	100.0
18FAR02A	<0.1	3.05	0.16	82.79	0.413	0.78	0.14	0.03	<0.01	0.001	0.16	11.63	99.2
18FAR02C	<0.1	2.69	0.37	87.02	0.526	0.38	0.16	0.02	0.01	0.001	0.11	7.50	98.8
18FAR07X	<0.1	2.99	0.18	82.73	0.381	0.80	0.13	0.03	<0.01	<0.001	0.20	11.65	99.1
<u>Tifersine</u>													
18TIF01	<0.1	3.02	0.19	83.09	0.778	0.77	0.19	0.03	0.01	0.002	0.18	11.56	99.8
18TIF20	<0.1	3.09	0.47	80.13	1.205	0.95	0.49	0.04	0.01	0.003	0.36	11.84	98.6
18TIF05	<0.1	2.36	0.05	84.97	0.386	0.78	0.40	0.03	<0.01	<0.001	0.24	11.52	100.7
<u>Plateaux</u>													
15PL02	<0.1	2.45	0.09	83.07	0.229	0.77	0.55	0.03	<0.01	<0.001	0.19	11.74	99.2
18PL02B	<0.1	2.72	0.44	83.36	0.335	0.93	0.17	0.04	<0.01	0.002	0.28	11.86	100.1
18PL07	<0.1	2.24	<0.01	84.80	0.276	0.71	0.26	0.04	<0.01	<0.001	0.19	11.69	100.2
18PL25	<0.1	1.87	<0.01	85.32	0.079	0.70	0.29	0.05	<0.01	<0.001	0.11	10.82	99.3
18PL27	<0.1	2.18	<0.01	85.26	0.176	0.71	0.17	0.02	<0.01	<0.001	0.08	11.48	100.1

Table S3. Results of geochemical analyses for rare earth elements (in ppm).

Sample number	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
D.L.	0.05	0.05	0.01	0.05	0.01	0.005	0.01	0.01	0.01	0.01	0.01	0.005	0.01	0.002
<u>Far West</u>														
18FAR02	2.7	3.3	0.5	1.9	0.4	0.09	0.4	<0.1	0.3	<0.1	0.2	<0.01	0.1	0.02
18FAR02A	2.3	2.8	0.3	1.1	0.2	0.06	0.3	<0.1	0.3	<0.1	0.2	<0.01	0.2	0.02
18FAR02C	1.5	2.0	0.2	0.7	0.1	<0.01	0.1	<0.1	0.1	<0.1	<0.1	<0.01	<0.1	0.01
18FAR07X	2.6	3.0	0.3	1.2	0.2	0.05	0.3	<0.1	0.3	<0.1	0.2	<0.01	0.2	0.03
<u>Tifersine</u>														
18TIF01	2.2	2.4	0.3	1.1	0.2	0.05	0.2	<0.1	0.2	<0.1	0.1	<0.01	<0.1	0.01
18TIF20	6.7	6.3	0.9	3.0	0.5	0.13	0.6	0.1	0.6	0.1	0.4	0.07	0.5	0.08
18TIF05	1.6	2.1	0.3	1.1	0.2	0.06	0.3	<0.1	0.2	<0.1	0.1	<0.01	<0.1	0.01
<u>Plateaux</u>														
15PL02	1.3	2.0	0.2	1.0	0.2	0.05	0.3	<0.1	0.2	<0.1	0.1	<0.01	0.1	0.02
18PL02B	2.1	5.3	0.5	1.8	0.4	0.09	0.5	<0.1	0.4	<0.1	0.2	<0.01	0.2	0.04
18PL07	1.6	1.2	0.2	0.8	0.1	<0.01	0.2	<0.1	0.2	<0.1	<0.1	<0.01	<0.1	0.01
18PL25	0.5	0.5	0.1	0.3	<0.1	<0.01	<0.1	<0.1	<0.1	<0.1	<0.1	<0.01	<0.1	<0.01
18PL27	1.0	1.0	0.1	0.5	0.1	<0.01	0.1	<0.1	0.1	<0.1	<0.1	<0.01	<0.1	<0.01

Table S4. Results of geochemical analyses for minor elements (in ppm).

Sample number	Sr	Cs	Rb	Ba	U	Th	Ta	Nb	Y	Zr	Hf	Be	Sc	V	Cr	W	Mo	Sn	Bi	Tl	As	Sb	Ag	Pb	Zn	In	Cu	Co	Ni	Ga	Ge
D.L.	2	0.1	1	2	0.01	0.05	0.01	0.2	0.5	1	0.1	1	1	5	20	0.5	2	1	0.1	0.05	5	0.2	0.5	5	30	0.1	10	1	20	1	0.5
<u>Far West</u>																															
18FAR02	19	<0.1	<1	28	9.5	<0.05	<0.01	<0.2	<0.5	<1	<0.1	7	<1	391	<20	<0.5	140	<1	<0.1	0.3	859	1.5	<0.5	79	270	<0.1	300	26	<20	10	4
18FAR02A	21	<0.1	<1	68	12.2	<0.05	<0.01	<0.2	<0.5	<1	<0.1	7	<1	351	<20	<0.5	210	<1	<0.1	0.4	839	2.9	<0.5	49	270	<0.1	480	18	<20	8	7
18FAR02C	27	<0.1	<1	276	3.2	<0.05	<0.01	<0.2	<0.5	2	<0.1	3	<1	347	30	<0.5	130	<1	<0.1	0.7	767	4.0	<0.5	123	150	<0.1	130	19	<20	4	9
18FAR07X	21	<0.1	<1	86	16.5	<0.05	<0.01	<0.2	<0.5	<1	<0.1	9	<1	376	<20	<0.5	240	<1	<0.1	0.3	898	2.6	<0.5	67	250	<0.1	510	20	20	11	7
<u>Tifersine</u>																															
18TIF01	38	<0.1	<1	329	11.4	<0.05	<0.01	<0.2	<0.5	<1	<0.1	6	<1	403	<20	<0.5	130	<1	<0.1	0.9	936	3.4	<0.5	452	380	<0.1	520	24	<20	8	6
18TIF20	46	<0.1	<1	302	16.6	<0.05	<0.01	<0.2	<0.5	3	<0.1	8	1	684	80	<0.5	230	<1	<0.1	2.0	2600	4.0	<0.5	712	410	<0.1	660	41	20	12	6
18TIF05	20	<0.1	<1	71	11.7	<0.05	<0.01	<0.2	<0.5	<1	<0.1	8	<1	519	<20	<0.5	270	<1	<0.1	0.3	1060	2.5	<0.5	437	260	<0.1	330	14	20	9	5
<u>Plateaux</u>																															
15PL02	17	<0.1	<1	14	7.9	<0.05	<0.01	<0.2	<0.5	<1	<0.1	7	<1	416	<20	1.0	230	<1	<0.1	<0.1	853	1.5	<0.5	47	230	<0.1	170	14	<20	7	4
18PL02B	19	<0.1	<1	13	9.5	<0.05	<0.01	<0.2	<0.5	<1	<0.1	8	<1	457	<20	<0.5	270	1	<0.1	0.3	1010	2.2	<0.5	284	370	<0.1	300	15	20	14	4
18PL07	17	<0.1	<1	15	10.3	<0.05	<0.01	<0.2	<0.5	<1	<0.1	9	<1	744	<20	<0.5	230	<1	<0.1	<0.1	856	4.0	<0.5	33	200	<0.1	190	15	30	7	7
18PL25	12	<0.1	<1	31	1.6	<0.05	<0.01	<0.2	<0.5	<1	<0.1	3	<1	66	<20	<0.5	240	<1	<0.1	<0.1	402	1.7	<0.5	34	80	<0.1	10	6	20	2	6
18PL27	13	<0.1	<1	8	9.0	<0.05	<0.01	<0.2	<0.5	<1	<0.1	6	<1	536	<20	<0.5	160	<1	<0.1	<0.1	945	4.7	<0.5	27	160	<0.1	160	12	30	6	6

Table S5. Oxygen and hydrogen isotopic compositions of Imini goethite.

Sample number	H ₂ O (wt%)	δD _{VSMOW} (‰)	δ ¹⁸ O _{VSMOW} (‰)
<u>Far West</u>			
18FAR02	10.48	-167	5.31
18FAR02A	11.03	-170	11.09
<u>Tifersine</u>			
18TIF01	11.02	-172	3.39
18TIF20	11.08	-159	3.07
<u>Plateaux</u>			
15PL02	11.06	-164	4.35
18PL02B	11.35	-156	6.03
18PL07	11.03	-168	3.19
18PL25	10.56	-148	4.98

Table S6. Imini goethite (U-Th)/He data.

Sample	⁴ He	± s	We igh t	²³⁸ U	²³² Th	¹⁴⁷ Sm	⁴ He	± s	²³⁸ U	²³² Th	¹⁴⁷ Sm	eU	GHe age	±
name	(ccSTP)	(ccSTP)	(μg)	(ng)	(ng)	(ng)	(nccSTP/g)	(nccSTP/g)	(ppm)	(ppm)	(ppm)	(ppm)	(Ma)	(Ma)
<u>Far West</u>														
18FAR02AA-1	1.16 × 10 ⁻⁹	1.2 × 10 ⁻¹¹	15	0.13	0.014	0.002	77,242	1159	8.6	0.9	0.15	9	72.1	3.6
18FAR02AA-2	1.85 × 10 ⁻⁹	1.9 × 10 ⁻¹¹	26	0.20	0.008	0.001	71,171	1068	7.9	0.3	0.03	8	73.5	3.7
18FAR02AA-3	9.33 × 10 ⁻¹⁰	9.3 × 10 ⁻¹²	13	0.11	0.004	0.001	71,783	1077	8.4	0.3	0.05	8	69.8	3.5
18FAR02AB-1	2.58 × 10 ⁻⁹	2.6 × 10 ⁻¹¹	22	0.23	0.006	0.001	117,195	1758	10.4	0.3	0.04	10	91.9	4.6
18FAR02AB-2	1.93 × 10 ⁻⁹	1.9 × 10 ⁻¹¹	14	0.18	0.005	0.001	138,036	2071	12.8	0.4	0.07	13	88.0	4.4
18FAR02AB-3	1.53 × 10 ⁻⁹	1.5 × 10 ⁻¹¹	11	0.14	0.005	0.002	139,125	2087	12.8	0.4	0.14	13	88.6	4.4
18FAR02AC-1	2.19 × 10 ⁻⁹	2.2 × 10 ⁻¹¹	15	0.19	0.002	0.000	146,249	2194	13.0	0.2	0.03	13	92.1	4.6
18FAR02AC-2	1.39 × 10 ⁻⁹	1.4 × 10 ⁻¹¹	9	0.13	0.002	0.001	154,243	2314	13.9	0.3	0.06	14	90.7	4.5
18FAR02AC-3	1.85 × 10 ⁻⁹	1.8 × 10 ⁻¹¹	13	0.16	0.011	0.001	142,102	2132	12.4	0.8	0.08	13	92.7	4.6
<u>Tifersine</u>														
18TIF01A-1	5.15 × 10 ⁻¹⁰	5.2 × 10 ⁻¹²	9	0.05	0.022	0.003	57,241	859	5.5	2.4	0.31	6	77.6	3.9
18TIF01A-2	8.12 × 10 ⁻¹⁰	8.1 × 10 ⁻¹²	11	0.08	0.014	0.003	73,814	1107	7.3	1.2	0.26	8	80.0	4.0
18TIF01A-3	2.63 × 10 ⁻⁹	2.6 × 10 ⁻¹¹	45	0.25	0.005	0.001	58,542	878	5.5	0.1	0.03	6	87.0	4.4
18TIF01B-2	1.67 × 10 ⁻⁹	1.7 × 10 ⁻¹¹	16	0.16	0.006	0.001	104,327	1565	10.2	0.4	0.06	10	83.3	4.2
18TIF01C-1	1.88 × 10 ⁻⁹	1.9 × 10 ⁻¹¹	21	0.17	0.003	0.002	89,457	1342	8.2	0.1	0.09	8	89.4	4.5
18TIF01C-2	1.67 × 10 ⁻⁹	1.7 × 10 ⁻¹¹	17	0.15	0.008	0.001	98,022	1470	8.9	0.4	0.07	9	89.5	4.5
18TIF01C-3	1.54 × 10 ⁻⁹	1.5 × 10 ⁻¹¹	17	0.14	0.008	0.001	90,334	1355	8.0	0.5	0.07	8	91.4	4.6
<u>Plateaux</u>														
18PL07A-1	4.76 × 10 ⁻⁹	4.8 × 10 ⁻¹¹	39	0.45	0.006	0.002	121,972	1830	11.6	0.2	0.06	12	86.1	4.3
18PL07A-2	8.30 × 10 ⁻⁹	8.3 × 10 ⁻¹¹	71	0.83	0.001	0.002	116,948	1754	11.7	0.0	0.03	12	82.0	4.1
18PL07A-3	8.14 × 10 ⁻⁹	8.1 × 10 ⁻¹¹	69	0.81	0.004	0.002	117,972	1770	11.7	0.1	0.03	12	82.7	4.1
18PL07B-1	3.17 × 10 ⁻⁹	3.2 × 10 ⁻¹¹	31	0.33	0.010	0.001	102,228	1533	10.6	0.3	0.03	11	78.8	3.9
18PL07B-2	2.04 × 10 ⁻⁹	2.0 × 10 ⁻¹¹	18	0.20	0.002	0.001	113,365	1700	11.0	0.1	0.03	11	84.5	4.2
18PL07B-3	1.91 × 10 ⁻⁹	1.9 × 10 ⁻¹¹	16	0.19	0.006	0.001	119,433	1792	11.8	0.4	0.05	12	83.0	4.2
18PL07C-1	2.46 × 10 ⁻⁹	2.5 × 10 ⁻¹¹	25	0.24	0.003	0.001	98,375	1476	9.5	0.1	0.03	10	83.0	4.2
18PL07C-2	3.10 × 10 ⁻⁹	3.1 × 10 ⁻¹¹	31	0.31	0.007	0.001	99,862	1498	9.9	0.2	0.04	10	83.0	4.2
18PL07C-3	2.48 × 10 ⁻⁹	2.5 × 10 ⁻¹¹	24	0.24	0.004	0.001	103,500	1552	10.1	0.2	0.03	10	84.0	4.2
18PL07D-1	4.41 × 10 ⁻⁹	4.4 × 10 ⁻¹¹	41	0.45	0.003	0.001	107,668	1615	10.9	0.1	0.02	11	81.0	4.1
18PL07D-3	5.85 × 10 ⁻⁹	5.9 × 10 ⁻¹¹	57	0.60	0.010	0.002	102,702	1541	10.6	0.2	0.04	11	79.3	4.0
18PL07E-1	1.54 × 10 ⁻⁹	1.5 × 10 ⁻¹¹	15	0.15	0.004	0.001	102,464	1537	9.9	0.3	0.06	10	84.5	4.2
18PL07E-2	3.79 × 10 ⁻⁹	3.8 × 10 ⁻¹¹	36	0.38	0.005	0.002	105,215	1578	10.6	0.1	0.05	11	81.4	4.1
18PL07E-3	2.59 × 10 ⁻⁹	2.6 × 10 ⁻¹¹	25	0.26	0.008	0.001	103,594	1554	10.5	0.3	0.05	11	80.6	4.0
18PL07F-1	3.25 × 10 ⁻⁹	3.2 × 10 ⁻¹¹	31	0.31	0.006	0.002	104,809	1572	10.0	0.2	0.07	10	85.9	4.3

18PL07F-2	1.66×10^{-9}	1.7×10^{-11}	16	0.16	0.001	0.000	103,881	1558	9.9	0.1	0.03	10	86.0	4.3
18PL07F-3	2.01×10^{-9}	2.0×10^{-11}	18	0.20	0.008	0.001	111,496	1672	11.0	0.5	0.06	11	82.4	4.1
<u>Far West</u>														
18FAR02-1	8.87×10^{-10}	8.9×10^{-12}	15	0.11	0.005	0.002	59,111	887	7.6	0.3	0.11	8	63.5	3.2
18FAR02-2	7.54×10^{-10}	7.5×10^{-12}	26	0.10	0.006	0.002	28,999	435	3.9	0.2	0.07	4	60.5	3.0
18FAR02-3	4.73×10^{-10}	4.7×10^{-12}	13	0.06	0.025	0.004	36,377	546	4.9	1.9	0.29	5	55.9	2.8
18FAR02-4	9.87×10^{-9}	9.9×10^{-12}	22	0.12	0.006	0.001	44,849	673	5.5	0.3	0.06	6	66.3	3.3
18FAR02-5	1.46×10^{-9}	1.5×10^{-11}	14	0.19	0.008	0.002	104,466	1567	13.7	0.6	0.14	14	61.2	3.1
<u>Tifersine</u>														
18TIF20-1	1.28×10^{-9}	1.3×10^{-11}	11	0.22	0.010	0.002	116,751	1751	20.5	0.9	0.14	21	46.5	2.3
18TIF20-2	5.17×10^{-9}	5.2×10^{-11}	38	0.80	0.005	0.002	135,938	2039	21.1	0.1	0.06	21	53.1	2.7
18TIF20-3	1.52×10^{-9}	1.5×10^{-11}	12	0.20	0.007	0.002	126,592	1899	16.6	0.6	0.14	17	62.3	3.1
18TIF20-4	1.16×10^{-8}	1.2×10^{-10}	78	1.70	0.014	0.006	148,619	2229	21.8	0.2	0.08	22	56.1	2.8
18TIF20-5	1.57×10^{-9}	1.6×10^{-11}	9	0.21	0.049	0.009	174,474	2617	23.4	5.4	0.98	25	58.2	2.9
<u>Plateaux</u>														
18PL25-1	8.60×10^{-10}	8.6×10^{-12}	37	0.12	0.033	0.003	23,254	349	3.2	0.9	0.08	3	56.1	2.8
18PL25-2	1.19×10^{-9}	1.2×10^{-11}	65	0.14	0.013	0.001	18,337	275	2.2	0.2	0.02	2	67.1	3.4
18PL25-3	4.44×10^{-10}	4.4×10^{-12}	17	0.05	0.019	0.003	26,102	392	3.1	1.1	0.17	3	64.0	3.2
18PL25-5	5.79×10^{-10}	5.8×10^{-12}	46	0.06	0.004	0.001	12,584	189	1.3	0.1	0.02	1	78.2	3.9
<u>Plateaux</u>														
15PL02-1	1.05×10^{-8}	1.1×10^{-10}	200	1.29	0.007	n.a.	52,666	790	6.5	0.0	n.a.	6	66.5	3.3
15PL02-2	5.87×10^{-9}	5.9×10^{-11}	100	0.62	0.008	n.a.	58,665	880	6.2	0.1	n.a.	6	77.5	3.9
15PL02-3	1.64×10^{-8}	1.6×10^{-10}	260	1.90	0.008	n.a.	63,228	948	7.3	0.0	n.a.	7	71.1	3.6
15PL02-4	6.19×10^{-8}	6.3×10^{-10}	782	6.39	0.026	0.03	79,100	1186	8.2	0.0	0.04	8	79.1	4.0
<u>Plateaux</u>														
18PL02B-2	1.09×10^{-8}	1.1×10^{-10}	85	1.10	0.002	0.005	128,669	1930	13.0	0.0	0.06	13	81.2	4.1
18PL02B-3	6.16×10^{-9}	6.2×10^{-11}	57	0.63	0.009	0.003	108,154	1622	11.1	0.2	0.06	11	79.8	4.0
18PL02B-4	4.53×10^{-9}	4.5×10^{-11}	41	0.44	0.069	0.039	110,419	1656	10.7	1.7	0.94	11	81.8	4.1
18PL02B-5	3.55×10^{-9}	3.6×10^{-11}	32	0.36	0.142	0.016	110,999	1665	11.2	4.4	0.50	12	74.6	3.7

n.a. = not available.