

Supplementary Information for:

Relation between ^{207}Pb NMR chemical shift and the morphology and crystal structure for the apatites $\text{Pb}_5(\text{AO}_4)_3\text{Cl}$, vanadinite ($\text{A} = \text{V}$), pyromorphite ($\text{A} = \text{P}$), and mimetite ($\text{A} = \text{As}$)

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July 21, 2020

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Relation of the ^{207}Pb isotropic chemical shift to parameters of the crystal structure

The newly determined value of the isotropic chemical shift for the $4f \text{Pb}^{2+}$ ions in the mimetite structure (which are only coordinated by oxygen) fits well into a previously suggested correlation between δ_{iso} and the shortest Pb—O distance in the coordination sphere, see Fig. S1. Inclusion of the δ_{iso} value for mimetite does not alter slope or intercept of the previously published linear fit (Zeman et al. 2019).

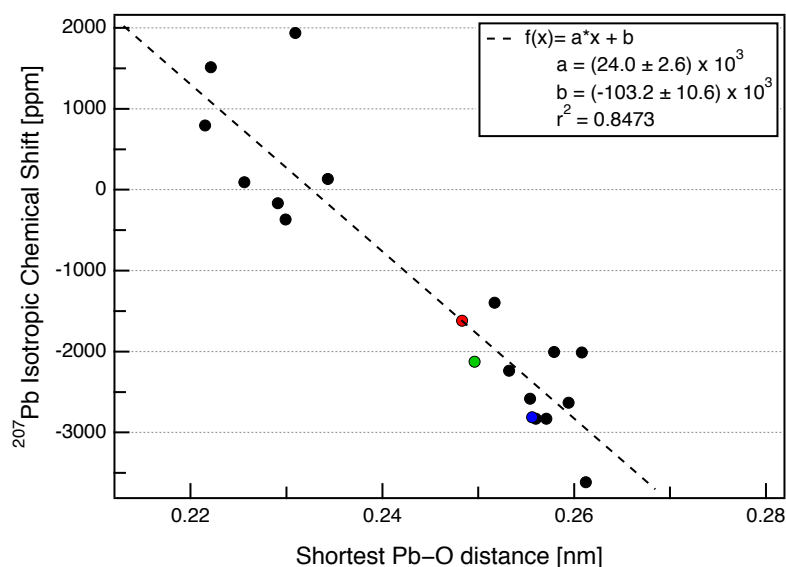


Figure S1. ^{207}Pb NMR isotropic chemical shifts of lead on Wyckoff position $4f$ versus the respective shortest existing Pb—O distance, with the newly determined value for mimetite shown in green. The isotropic shifts of vanadinite (red) and pyromorphite (blue) were already included into the fit, along with the values of 15 other lead-bearing minerals, listed in detail in Zeman et al. 2019.

Determination of the full ^{207}Pb chemical shift tensor from single crystal experiments

The full ^{207}Pb CS tensors, as well as the initially unknown orientation of the rotation axis may be fitted from only one rotation pattern, as detailed in references Zeman et al. 2017, Zeman et al. 2018, and Zeman et al. 2019. The re-determined ^{207}Pb CS tensors for pyromorphite reported here can be considered more precise than those reported in our original publication (Zeman et al. 2017) for three reasons: (i) The current simultaneous fit also includes the previously published rotation pattern (Zeman et al. 2017), leading to overall higher accuracy. (ii) The current fit was performed in the *CRY* frame, i.e. extracting the tensor in the form given in Eq. 3. This has the advantage that constraints due to crystal symmetry can be applied to the CS tensor. Since the ^{207}Pb on Wyckoff position *4f* are positioned on a threefold rotation axis, δ must be uniaxial, i.e. $\delta_{a^*a^*}^{CRY} = \delta_{bb}^{CRY}$, and because this axis is parallel to *c*, $\delta_{a^*c}^{CRY} = \delta_{bc}^{CRY} = 0$, which reduces the number of free fit parameters for the *4f* position. (iii) When the CS tensor is determined in the *CRY* frame, the orientation of all *eigenvectors* in the unit cell is obtained directly by tensor diagonalization. It is customary to report NMR interaction tensors in their principal axes system (*PAS*), where they only have their *eigenvalues* on the main diagonal:

$$\delta^{PAS} = \begin{pmatrix} \delta_{11} & 0 & 0 \\ 0 & \delta_{22} & 0 \\ 0 & 0 & \delta_{33} \end{pmatrix} \quad (\text{S1})$$

For this notation, we have ordered the tensor components according to the convention (Haeberlen 1976):

$$|\delta_{33} - \delta_{iso}| \geq |\delta_{11} - \delta_{iso}| \geq |\delta_{22} - \delta_{iso}| \quad (\text{S2})$$

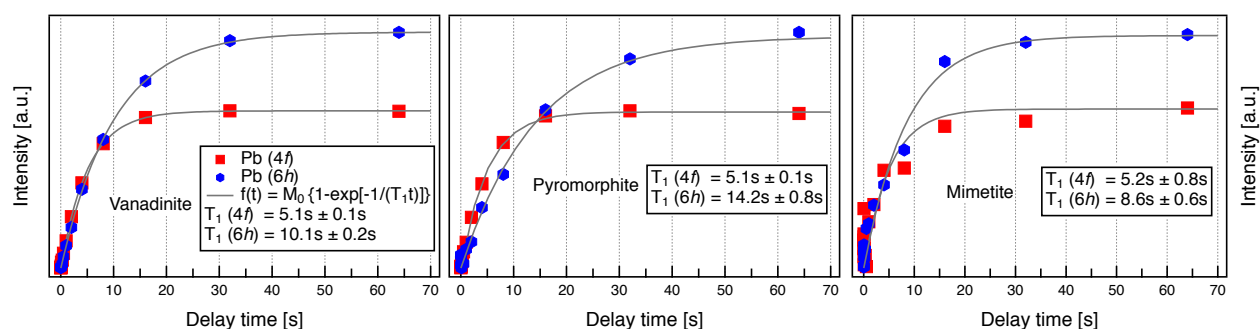
The CS tensor *eigenvalues* and their corresponding *eigenvectors* are listed in Table S1. These values are practically identical with those previously reported (Zeman et al. 2017) for ^{207}Pb at position *6h*, while those for the *4f* position differ by up to 68 ppm. Considering that the *4f* are never resolved in the individual rotation patterns, the accuracy of their tensor determination especially benefits from the simultaneous fit over two rotation patterns presented here.

Table S1. Chemical shift tensor of ^{207}Pb at the position *6h* and *4f* in the pyromorphite structure, as determined from single-crystal NMR experiments including two rotation patterns (one in Fig. 6 and one published in Zeman et al. 2017). The orientation of the corresponding *eigenvectors* are listed in spherical coordinates in the *a*bc* coordinate system and refer to the atoms closest to the origin for each crystallographic orbit. All experimental tensor components have an error of about 0.5%, as determined by the fitting routine.

	^{207}Pb at <i>6h</i>		^{207}Pb at <i>4f</i>	
	<i>Eigenvalues</i>	<i>Eigenvector</i>	<i>Eigenvalues</i>	<i>Eigenvector</i>
δ_{11}^{PAS}	-1772 ppm	90.0°, 106.7°	-2730 ppm	90.0°, 0.0°
δ_{22}^{PAS}	-1822 ppm	0.0°, 0.0°	-2730 ppm	90.0°, 90.0°
δ_{33}^{PAS}	-2917 ppm	90.0°, 16.7°	-2980 ppm	0.0°, 0.0°

T_1 relaxation times of ^{207}Pb

Longitudinal relaxation times were measured using the saturation recovery method, on static single crystals in an arbitrary orientation for vanadinite and pyromorphite, and on a powder sample under 25 kHz MAS for mimetite. The saturation curves (where an accumulated intensity is used for the three $6h$ and two $4f$ lead species) are shown below.



References Cited

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